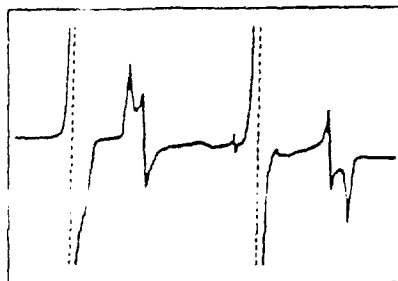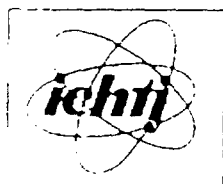Zakopane 31st May - 4th June 1993

ELECTRON SPIN RESONANCE
OF
RADICALS AND METAL COMPLEXES

1st INTERNATIONAL CONFERENCE
OF
THE POLISH ESR GROUP

Organiser :
Institute of Nuclear
Chemistry and Technology
Warsaw, Poland

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Zakopane'93

Welcome to the 1st International Conference of the Polish ESR Group on Electron Spin Resonance of Radicals and Metal Complexes which is being held in Tatra Mountain National Park.

It is our pleasure to announce an additional informal presentation to be given by Prof. Arthur Charlesby on Tuesday evening.

Typescripts of papers for publication in a special edition of "Radiation Physics and Chemistry" should be handed to Hanna Ambroż during the Conference or sent as soon as possible after the Conference to the Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland.

We invite all Polish participants to join the Polish ESR Group. The first meeting of this Group is to be held on Wednesday evening (as stated in the programme).

The Participants exhibiting posters should put them up as soon as possible so that others may read them during conference breaks.

Bar facilities by the fireplace will be available after dinner each evening.

The excursion to Morskie Oko lake. This will take some 2 hours of walking slightly uphill from Łysa Polana. If anyone wants to be driven by Highlander's horse driven wagoon please contact the organisers.

THE POLISH ESR GROUP
1st
INTERNATIONAL
CONFERENCE '93
Zakopane

Organising Committee:
Prof. ANDRZEJ CHMIELEWSKI
Assoc. Prof. B. HANNA AMBROZ
Dr. ZBIGNIEW ZIMEK

Conference

Programme

Sunday, 30th May

12.00 - 1.00 *Registration*

5.00 - 6.00 *Registration*

Monday, 31th May

9.00 - 12.00 *Registration*

1.00 - 2.00 *Lunch*

SESSION 1
Chairman : ANDRZEJ PŁONKA

2.00 - 2.05 ANDRZEJ CHMIELEWSKI
Opening Address

2.05 - 3.00 JAN STANKOWSKI
EPR in Fullerenes

3.00 - 3.15 CESARE OLIVA
Anisotropic Quantum Spin Fluid and Anisotropic
Quantum Spin Glass Formation in La-Cuprate-Based
Catalysts for Phenol Oxidation

3.15 - 3.30 JACEK MICHALIK
Radiation-Induced Silver Agglomeration in A Zeolites.

3.30 - 3.45 ~~ADAM JEZIERSKI~~
EPR Investigations of Iminoxy Free Radicals and
Paramagnetic Metal-Oxime Systems

4.00 - 4.30 *Tea*

4.30 - 5.15 JERZY KROH
Electron Interaction with Stabilizing Matrix.

5.15 - 6.00 STANISŁAW K. HOFFMANN
Electron Spin-Echo Studies of Spin-Spin Relaxation
Processes

6.00 - 7.00 *Dinner*

7.30 - 8.30   *Breakfast*

SESSION 2
Chairman : HARRY KURRECK

9.00 - 9.45   BRUCE C. GILBERT
              EPR Studies of the Generations and Reactions of Free
              Radicals in Chemical and Biochemical Systems
9.45 - 10.00 KRZYSZTOF GWOŹDZIŃSKI
              Structural Changes in Erythrocytes and Their Components
              Induced by Copper and Mercury Ions
10.00 - 10.15 RYSZARD KRZYMINIEWSKI
              Conversion of Free Radicals upon Annealing of
              X-Irradiated Single Crystal of Cholest-4-en-3-one
10.15 - 10.30 ~~B. GONET~~
              Free Radical Properties of the Coffee
10.30 - 10.45 ZBIGNIEW P. ZAGÓRSKI
              Pulse Radiolysis Studies of Short-Lived Species
              in Solid Amino Acids as Precursors of Radicals
              Detected by ESR

11.00 - 11.30 *Coffee*

11.30 - 12.15 MARTYN C. R. SYMONS
              ESR Studies of Radiation Damage to DNA and Proteins
12.15 - 12.30 KNUT HILDEBRAND
              ESR and Pulse Radiolysis Studies on the Free-Radical-
              Induced Oxidation of Phloroglucinol in Aqueous Solution
12.30 - 12.45 ~~OLGA V. MIKHALITSINA~~
              Radiation Stability of Crown Ether-Metal Ions
              Complexes

1.00 - 2.00   *Lunch*

2.00 - 7.00   *Excursion to Morskie Oko Lake*

7.00 - 8.00   *Dinner*

8.00 - 10.00 Prof. CHARLESBY'S Informal Lecture

7.30 - 8.30 *Breakfast*

SESSION 3
Chairman : WOJCIECH FRONCISZ

9.00 - 10.00 HARRY KURRECK
              Mimicking Primary Processes in Photosynthesis-
              Covalently Linked Porphyrin Quinones
10.00 - 10.45 ARTHUR CHARLESBY
              Pulsed NMR Studies; T_2 Relaxation and Physical
              Properties of Macromolecules
10.45 - 11.00 H. K. SHARMA
              EPR Spectra of Polymeric Complexes of Silicon IV
              with Tetrasulphur Tetraimide ($S_4N_4H_4$)

11.00 - 11.30 *Coffee*

11.30 - 1.00 Poster Session I

 1.00 - 2.00 *Lunch*

 2.00 - 6.00 Poster Session II

 6.00 - 7.00 *Dinner*

 7.00 - 9.00 Meeting of the Polish ESR Group

THURSDAY, 3RD JUNE

7.30 - 8.30 *Breakfast*

SESSION 4
Chairman : STANISŁAW K. HOFFMANN

9.00 - 10.00 MARINA BRUSTOLON
             Molecular Dynamics of Radicals in the solid state.
             ESR, ENDOR and Pulsed ESR Studies

10.00 - 11.00   ANDRZEJ PŁONKA
                Dispersive Kinetics of Radiation-Induced Species in
                Condensed Media

11.00 - 11.30   *Coffee*

11.30 - 12.15   WOJCIECH FRONCISZ
                Multiquantum EPR Spectroscopy

 1.00 - 2.00   *Lunch*

 2.00 - 6.00   *Free time*

 6.00 - 9.30   *Conference dinner*
                Speaker: Prof. Bruce Gilbert
                *Performance of local Tatra Mountain Highlander Music
                and Dance Group*

FRIDAY, 4TH JUNE

 7.30 - 8.30   *Breakfast*

 9.00   *Farewell*

Lectures

EPR IN FULLERENES

J. Stankowski

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60-179 Poznań, Smoluchowskiego 17, Poland

So far EPR investigations of carbon have not provided an unambigous answer to the question about the contributions of the localized electron state and the conducting electron state to the experimentally observed value of g - factor. New hopes to solve this problem are related to fullerene, a carbon molecule whose atoms form a two-dimensional system of well defined topology. As follows from EPR studies of liquid C_{60} solution and their frozen glasses as well as of microscopic C_{60} monocrystals and polycrystalline solid solutions Me_xC_{60} (Me = K or Rb), there are two types of paramagnetic centers: anion - radicals, formed by way of attracting subsequent electrons, and cation - radicals which are ionized molecules of C_{60} carbon.

ANISOTROPIC QUANTUM SPIN FLUID AND ANISOTROPIC QUANTUM SPIN GLASS FORMATION IN La-CUPRATE-BASED CATALYSTS FOR PHENOL OXIDATION

Cesare Oliva*, Lucio Forni, Anatoli V.Vishniakov°
Ivan E.Mukovozov° and Giorgio Termignone

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 D.I.Mendeleev Moscow Institute of Chemical Technology
Miusskaja Sq. 9 Moscow, Russia

In a previous work [1] we reported on the study of a set of
La-Eu-cuprates as catalysts for oxidation of phenol with hydrogen
peroxide. A deeper investigation on the changes brought about by the
partial substitution of Eu^{3+} for La^{3+} in $La_{2-x}Eu_xCuO_{4+\delta}$ are here
reported. Furthermore, we aimed to throw some light on the effect on
crystal structure and on electric conductivity of the solid,
accompanying such a substitution.

The experimental EPR spectra of $La_{2-x}Eu_xCuO_{4+\delta}$ have been collected
at different temperatures between 66 up to 360 K. When x = 0 the EPR
pattern is composed of two different lines, only the narrower of
which can be attributed to isolated Cu^{2+} ions in axially symmetric
geometry. The second EPR line, nearly 1000 G broad, is similar to
that observed [2,3] with oxygen-deficient (δ<0) samples. The line
was attributed either to an anisotropic quantum spin fluid (AQSF)
state formed by uncharged S=1/2 "spin solitons" interacting with
S=0, charge e, "holons" at temperature T>T_{SG}, T_{SG} being the critical
temperature for the spin glass formation [2], or to other spin-spin
and spin-lattice correlations [3]. A similar broad band was observed
also with perfectly stoichiometric (δ=0) samples [2] and in that
case it was attributed to propagating S = 1/2 holes or to S = 1 hole
pairs, interacting with the many-body AQSF Cu^{2+} state.
When x > 0 new EPR features are formed at g $\cong$ 3. They can be
attributed to Anisotropic Quantum Spin Glass formation. A very
interesting EPR pattern was recorded in a particular case, composed
by a four-lines pattern affected by a Jahn-Teller effect. The g $\cong$ 3
value of this EPR pattern is typical for AQSG systems [2], while the
spectral shape is coherent with a paramagnetic system involving one
Cu^{2+} nucleus. We suggest that O^- ions, which could form AQSG phases
[2], also interact with a Cu^{2+} ion forming $Cu^{2+}O^-$ hole pairs.

Finally, we tried also to deepen our knowledge of the effect of
catalyst ageing during the oxidation of phenol.

1) L.Forni, C.Oliva, A.V.Vishniakov, A.M.Ezerets, I.E.Mukovozov,
   F.P.Vatti and V.N.Zubkovskaja, *J.Catal.*, submitted.
2) H.Thomann, R.A.Klemm, D.C.Johnston, P.J.Tindall, H.Jin and
   D.P.Goshorn, *Phys.Rev.B*, 38 (1988) 6552.
3) F.Nakamura, K.Yoshida, K.Sugiyama, Y.Maeno and T.Fujita,
   Physica C, 185 (1991) 1103.

Radiation - induced silver agglomeration in A zeolites

J. Michalik[1], T. Wąsowicz[1], J. Sadło[1], A. van der Pol[2] and E. de Boer[2]

[1] Institute of Nuclear Chemistry and Technology, 03-195 Warsaw, Poland
[2] University of Nijmegen, Toernoiveld, 6525 ED Nijmegen, The Netherlands

Zeolites have the propensity to stabilize various transient species. The structure of zeolite A is well suited for stabilizing small silver clusters. Paramagnetic silver clusters of low nuclearity can be characterized by ESR spectroscopy. The magnetic parameters of various Ag atoms and Ag cluster radiation-induced in dehydrated and hydrated $^{109}Ag_n$-NaA zeolites, where n=1 or 6, are compiled in Table1.

Table 1. EPR parameters of silver atoms and clusters in ^{109}Ag-NaA zeolites.

Sample	Site	a_{iso} (MHz)	g_{iso}	H_{pp} (G)
$^{109}Ag_1$-NaA/130°C	Ag^0 (A)	1545	1.993	16.0
	Ag^0 (B)	1582	2.015	17.0
	Ag^0 (C)	1707	2.016	11.5
	Ag^0 (D)	1729	1.989	9.0
	Ag_2^+	828	1.996	6.0
	Ag_3^{2+}	610	1.973	4.0
$^{109}Ag_6$-NaA/130°C	Ag_6^{n+}	207	2.033	25.0
$^{109}Ag_1$-NaA/H_2O	Ag^0 (K)	2039	2.026	6.7
	Ag^0 (L)	1484	2.008	32.0
	Ag^0 (M)	1580	2.012	16.6
	cluster I	394	2.006	7.0
	cluster II	390	1.949	7.0
free atom in gas phase	$^{109}Ag^0$	1979	2.0022	

The formation of small silver clusters in specific sites in irradiated A zeolites depends on the inital content of the Ag^+ cations and amount of water molecules in zeolite cages. In dehydrated Ag_1-NaA zeolites after irradiation and thermal annealing above 200K Ag_2^+ and Ag_3^{2+} clusters are formed. The EPR spectra of $^{109}Ag_2^+$ and $^{109}Ag_3^{2+}$ are highly resolved, exhibiting the features of g and hyperfine anisotropy. From temperature dependent measurements it could be concluded that trimer Ag_3^{2+} is rapidly rotating around its three-fold axis.

Two new silver clusters, denoted I and II were found both in hydrated Ag_1-NaA and Ag_6-NaA zeolite. From the analysis of the well resolved EPR spectra it was inferred that I and II are also trimers but their isotropic hyperfine splitting constants amount to only circa 400MHz, whereas Ag_3^{2+} in dehydrated Ag_1-NaA has A_{iso}= 600 MHz. This difference was attributed to interaction of the trimers I and II with the ions in zeolite lattice and water molecules.

The ESEEM experiments indicate that Ag_3^{2+} and trimers I and II interacts indeed with Al nuclei of zeolite lattice and with D_2O molecules. In hydrated Ag-NaA zeolites the interaction of both trimers with D_2O molecules is strong, which leads to a splitting of the ^2D peak in frequency domain ESEEM spectra.

EPR INVESTIGATIONS OF IMINOXY FREE RADICALS
AND PARAMAGNETIC METAL-OXIME SYSTEMS

Piotr J. Chmielewski, Jacek Sienkiewicz, Zdzisław Siatecki
and Adam Jezierski

*Institute of Chemistry, Wrocław University,
Wrocław, Poland*

Iminoxy free radicals are σ-radicals containing a $>C=N \overset{\displaystyle \cdot O}{\nearrow}$ group. Interaction between the unpaired electron and ^{14}N nucleus in this type of radical is characterized by an unusually large constant $A_{iso}(^{14}N) \sim 30$ G. Iminoxy radicals can be obtained (i) by oxidation of parent oximes, nitroso and isonitroso compounds in solution[1];
(ii) by γ-irradiation of oximes in the solid state (a simple method of obtaining anisotropic EPR parameters for iminoxy radicals) [2];
(iii) by reacting photolytically generated radicals with aryl nitriloxide [3];
(iv) by reacting NO_2 with β-diketones [4].
In our investigation we used the first and second methods. Ketone monooxime and α-diketone dioxime were used. Typical EPR anisotropic parameters for free radical derivatives from di-2-pyridyl ketone oxime are $A_x=21.9$, $A_y=24.2$, $A_z=41.7$, (in 10^{-4} cm^{-1} units), $g_x=2.0093$, $g_y=2.0058$ and $g_z=2.0025$.

Transition metal complexes with α-diketone dioximes were obtained and γ-irradiated. EPR spectra of this type of compounds show the differing extent of delocalization of density of unpaired electron on metal. We observed two situations:
(i) an EPR spectrum similar to the γ-irradiated oxime (no interaction with metal);
(ii) redox reaction on the metal center; in this case the superhyperfine interaction with ^{14}N nuclei from ligands is observed (e.g. for Ni(α-furildioxime)$_2$ complex).

EPR spectra were analysed using originally written program on an IBM-PC microcomputer.

Solvent effect was investigated for the iminoxyls on the basis of hyperfine and superhyperfine constant analysis. In simple iminoxy radicals, changes of $A_{iso}(^{14}N)$ value is typical [1] reflecting the linear dependence of the value on solvent polarity parameter. For iminoxyls containing a diethyl phosphonate group, $A_{iso}(^{14}N)$ practically does not dependent on solvent polarity but (for isomer Z) $A_{iso}(^{31}P)$ values strongly increase with increasing of solvent polarity [2,5]. For iminoxyls containing pyridyl group the opposite directions in changes of $A_{iso}(^{14}N,=N-O\cdot)$ and $A_{iso}(^{14}N,py)$ were observed.

[1] A. Jezierski, *Magn. Reson. Chem.*, 27, 130 (1989)
[2] P. J. Chmielewski, A. Jezierski, Z. Siatecki, *J. Chem. Soc. Perkin Trans.* 2, 1421 (1992)
[3] A. Alberti, G. F. Pedulli, *Gazz. Chim. Ital.*, 118, 131 (1988)
[4] N. D. Yordanov, V. Iliev, D. Shopov, A. Jezierski, B. Jezowska-Trzebiatowska, *Inorg. Chim. Acta*, 60, 9 (1982)
[5] Z. Siatecki, P. J. Chmielewski, A. Jezierski, *Magn. Reson. Chem.*, 30, 163 (1992)

Jerzy Kroh

ELECTRON INTERACTION WITH STABILIZING MATRIX

ABSTRACT

Two models of electron localization are presented.

The first one is based on the statistical approach to electron

structure and properties. The distribution of preexisting traps is

computer simulated by molecular dynamic calculations.

The behaviour of electron is defined by path integrals method.

The results are compared with experimental data for molten

LiBr + KBr system.

The second model is based on electron vibron coupling. The model

agrees well with experiment for electrons solvated in water,

alcohols ammonia, amines ethers and alkanes. Deuteration effects

of intramolecular vibrational modes measured by Raman spectroscopy

are discussed for methanol glass at 77 K.

ELECTRON SPIN-ECHO STUDIES OF SPIN-SPIN RELAXATION PROCESSES

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A brief outline of the relaxation processes leading to the spin echo amplitude decay will be presented and discussed. Especially a role of the dipole-dipole interaction between electron and surrounding nuclei of a matrix will be described as an important mechanism for solids with a low concentration of the paramagnetic centers. The problem of the phase relaxation and phase memory time T_M will be shown for radical SeO_3^- center in $(NH_4)_3H(SeO_4)_2$ and Cu(II) ions in triglicine selenate crystals. The results of temperature T_M measurements for these crystals are shown in the figures below.

$(NH_4)_3H(SeO_4)_2$

TGSe:Cu(II)
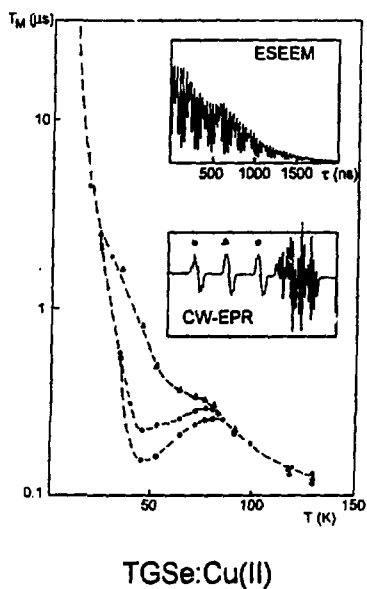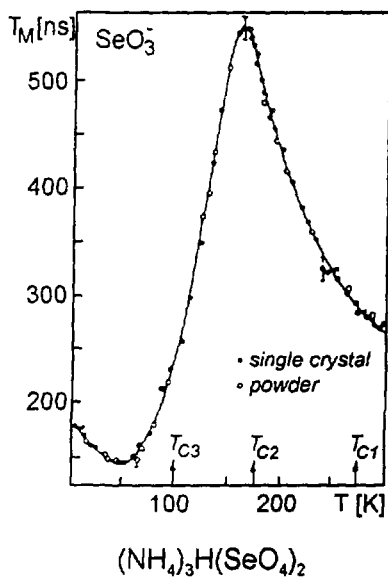
ESR STUDIES OF THE GENERATIONS AND REACTIONS OF FREE RADICALS IN CHEMICAL AND BIOCHEMICAL SYSTEMS

B C GILBERT

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Our understanding of the properties of free radicals and the ways in which they are formed has rapidly increased, to match the tremendously enhanced interest in their use in synthesis and their possible involvement in biological, industrial and environmental processes. On the basis of foundations laid largely by Gomberg, Waters, Hey, Kharasch and others, spectroscopic techniques (especially pulse radiolysis) have provided crucial structural, kinetic, and mechanistic details about radical-containing systems; this knowledge largely now underpins our attempts to find evidence for and identify the crucial roles of free radicals present in biological systems, where the problems of direct detection and complete characterization pose a formidable challenge.

The main emphasis of this lecture will be on the ways in which ESR spectroscopy, in conjunction with ancillary techniques involving radiolysis, photolysis, flow-systems and trapping, can provide vital evidence for radical formation and behaviour in chemical models for biological systems.

The type of approaches discussed will involve **flow-systems** (to provide direct evidence for radicals formed *in situ* as well as to study reaction kinetics), the use of **spin-trapping** approaches (to convert short-lived, transient radicals into longer-lived nitroxides which can be studied at leisure), and the use of **spin-labels** (for example to act as **spin scavengers** and hence to report on the sites of radical generation).

These approaches will be illustrated via their application to a series of problems of biological relevance, including: formation of radicals in metal-oxygen, metal-peroxide reactions, including the effect of ligands as potential inhibitors and accelerators; the reaction of oxygen-centred radicals with carbohydrates and the occurrence of fragmentation (including acid- and base- catalysed reactions); the reaction of oxygen-centred radicals with nucleic acids, with examples of strand-breakage following internal hydrogen and/or electron-transfer; radical-induced fragmentation reactions of cystine, methionine and other sulphur-containing compounds; spin-trapping and spin-labelling studies of radical damage to proteins.

Structural changes in erythrocytes and their components induced by copper and mercury ions.

K. Gwoździński

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The action of copper and mercury ions on human erythrocyte components has been studied using spin labeling method. Copper and mercury are strong toxic metals which cause the destruction of erythrocytes. Both heavy metals induce hemolysis of human red blood cells. The decrease of membrane fluidity was observed at different depths within the lipid bilayer indicated using two spin labeled fatty acids (methyl 5-doxylpalmitate and methyl 12-doxylstearate). Copper oxidize thiol groups of proteins to corresponding dithiols. On the other hand the mercury formes -S-Hg-S- bridges between two neigbouring thiol groups. Using 4-maleimido-2,2,6,6-tetramethyl-piperidine-1-oxyl the increase of mobilization of cytoplasmatic peptides or/and proteins was found after copper and mercury treatment. Both heavy metals decreased internal viscosity of red blood cells. The effect of copper and mercury ions on isolated membrane and hemoglobin was also studied. Both heavy metals induced changes in the protein conformation or disposition of spin labeled fragments of proteins in the membrane. Copper and mercury induced conformational changfes in hemoglobin but the effects of copper ions were more significant than of mercury. We suggest that the action of oxygen radicals species generated by heavy metals in the cells damage is less important than it is assumed. The major cause of cell injury are the alterations in protein structure.

CONVERSION OF FREE RADICALS UPON ANNEALING OF

X-IRRADIATED SINGLE CRYSTAL OF CHOLEST-4-EN-3-ONE.

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[a] Institute of Physics, A.Mickiewicz University,
   Pl-61-614, Poznań, Poland.
[b] Department of Biophysics, University of Rochester,
   Rochester, NY 14642, USA.

Single crystals of the steroid cholest-4-en-3-one were irradiated at 68 K and studied at 68 K and 300 K using X-band ESR and ENDOR. At 68 K, two A and B types of radicals were detected. The A type radical was identified as the one formed by attachment of an electron to the O_3 oxygen atom. The B type was probably formed on the aliphatic part of the molecule. Upon heating in the temperatures ranging from 90-100 K both types of radicals undergo a conversion which is evidenced by their ESR and ENDOR spectra at room temperature being completely different from those taken at 68 K. The radical A converts into neutral one and becomes like a radical formed in single crystal of cholest-4-en-3-one. Explanation of the radical B conversion would need more research. From ESR and ENDOR data collected for three planes of single crystal rotation, four proton hyperfine coupling tensors of the low temperature radical A were obtained.

Free radical properties of the coffee

B.Gonet, Pomeranian Medical Academy, Szczecin

Commonly used condiment – the coffee has in the last time been the object of interest as far as free radicals are concerned. The coffee gives free radical electron paramagnetic resonance (EPR) signals in roasted beans or powder form. EPR spectra were registered (Radiopan SE/X 2544 spectrometer) from ten sorts of coffee available on our market. All the signals display the same shape and localization (ΔB_{pp} = 0.9 mT, g = 2.003); they differ, however, with regard to intensity of the signal. Figure 1 provides an example by presenting EPR signals from four sorts of coffee.
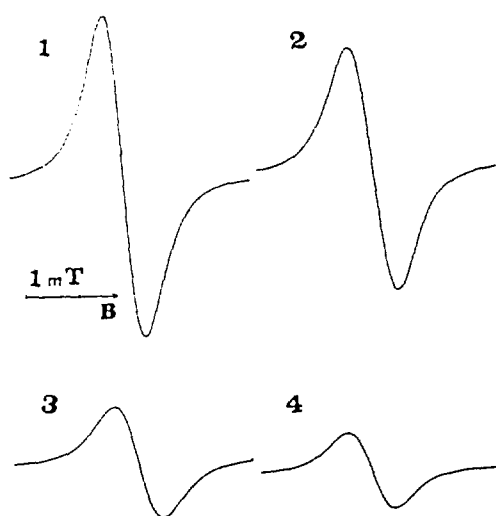

Fig.1
EPR signals from four sorts of coffee: Beyers,di Napoli (1), Heavenly, deca-ffeinated (2), Jacobs, Kronung (3), Nescafe',Colombia Blend (4).

The highest concentration of free radicals was shown by the coffee (1), but the lowest one by Jacobs (2) and Nescafe'(4). High level of free radicals is detected in caffeine-free coffee (2); hence, the source of EPR signal from coffee is not caffeine. Concentration of free radicals in the coffee is of the order of 10^{17}/gram , which exceeds by three orders the quantity of free radicals content in vivo in the tissues of living organisms. The source of EPR signal from the coffee is not known exactly; it is supposed that EPR signal may stem from peroxidizing lipids contained in the oil of coffee seeds. The significance of coffee roasting and grinding procedure should not be here underestimated. Are free radicals, stable, lodging the coffee harmful to the organism? This problem has not as yet been solved.

PULSE RADIOLYSIS STUDIES OF SHORT-LIVED SPECIES IN SOLID AMINO ACIDS AS PRECURSORS OF RADICALS DETECTED BY ESR

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Free radicals of life time sufficiently long for detection by ESR have usually a history of transformation, from primary forms to a final species. It seems interesting to follow this history by different methods, suitable for the detection of the same species. The most obvious choice is spectrophotometry, because free radicals are known to absorb in UV and/or visible ranges, very often with high values of molar extinction coefficient (ε). The idea of comparison of spectrophotometric and ESR measurements was earlier applied to frozen aqueous glasses but interpretation of the results was complicated by intensive absorption of trapped electron occuring usually as primary effect and by composed changes in matrices following thawing. Much better understanding was possible due to studies of inorganic single crystals which do not exhibit any changes of the matrices over a great range of temperature (e.g. the matrices of potassium perchlorate or periodate). Our investigation concentrates on polycrystalline amino acids. The pulse radiolysis method with Čerenkow light detection [2] has opened a new possibility to study optical absorption of polycrystalline or amorphous samples, even of low transparency. Electronic spectra of species of life time below microseconds can be recorded. Electron pulse irradiated α L-alanine exhibits short lived spectrum with the λ maximum at 460 nm [1], and the final stable spectrum, obtained by reflection spectrophotometry (Kubelka function) with λ maximum at 345 nm. The stable species is tentatively identified as a free radical detected by ESR, as it has the same stability. The short lived species is assumed to be an intermediate of the process of deamination, being the precursor of the stable radical. Some other amino acids of similar optical spectra are examined.

[1] Z.P.Zagórski and Z.Tomasiński, J.Radioanal.Nucl.Chem.,Letters 146, 197 (1990)
[2] Z.P.Zagórski, Radiat.Phys.Chem. 39, 11 (1992)

ESR STUDIES OF RADIATION DAMAGE TO DNA AND PROTEINS

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Exposure of biopolymers to ionising radiation in dilute aqueous solution results in damage to water and the resulting radicals attack the solute molecules in various ways. This form of damage is usually described as "indirect". However, in cellular systems 'direct' damage is more frequent, especially to nuclear DNA, where the concentration of water may be quite low. In this review, I will be primarily concerned with direct damage.

The initial chemical consequence of direct damage is electron-ejection followed by electron-capture. ESR studies have established that electron-loss is fixed in the purine bases (mainly as $G^{\cdot+}$) whilst electron-capture occurs mainly at the pyrimidine bases ($C^{\cdot+}$ and $T^{\cdot+}$). Almost certainly, these centres are stabilised by proton-loss and proton-gain.

These results indicate that even though electron-loss must occur initially from all regions of the DNA, including the phosphate and sugar units, it moves rapidly into the stacked base system. Similarly, the ejected electrons fail to react with phosphate, also electron-capture has been observed for sugar-phosphate derivatives. Also, the electron hole and electron-gain centres are well separated, since radical-pairs (triplet-states) have never been detected by esr spectroscopy.

In our view, a similar situation arises for direct damage to proteins. Electron-loss must initially be mainly from the amide back-bone and the esr results suggest that this is rapidly trapped by loss of an N-H proton to give amido radicals. However, electrons are not trapped by the protein back-bone, unless there are no electron-affinic groups present.

In many cases, the results establish that these electrons move through large distances before being specifically trapped at unique sites. Examples of this long-range migration will be discussed.

ESR and pulse radiolysis studies on the free-radical-induced oxidation of phloroglucinol in aqueous solution.

K. Hildenbrand, D. Wang, I. György, M.N. Schuchmann and C. von Sonntag

Max-Planck-Institut für Strahlenchemie, Stiftstr. 34,

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Phenols play a major role as antioxidants both in nature as well as in industrial application. A large variety is found in plants. Some of them are phloroglucinol derivatives. The free-radical key reactions of these antioxidants have been studied by using the parent compound as a model.

Phloroglucinol **1a** and its monoanion **1b** have phenolic structures while the 3,5-dihydroxy-2,5-cyclohexadienone structure **2c** dominates in the dianion.[1,2]

Scheme 1
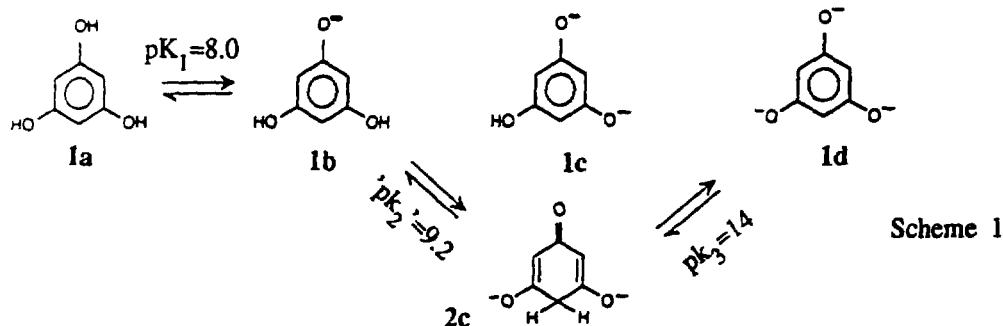
Reaction of phloroglucinol with oxidizing radicals ($\cdot$OH, $\cdot N_3$, $\cdot Br_2^-$) was studied in acidic and alkaline solutions by pulse radiolysis with optical detection as well as by ESR using a flow system and irradiating *in situ* either with an electron beam or with UV light. The results are summarized in Scheme 2. At pH > 6.5 the presence of the 2,5-cyclohexadienone type radical anion **4b** was established which slowly equilibrates with the mono- and dianion **3b** and **3c** of the phloroglucinol radical **3a**.

Scheme 2
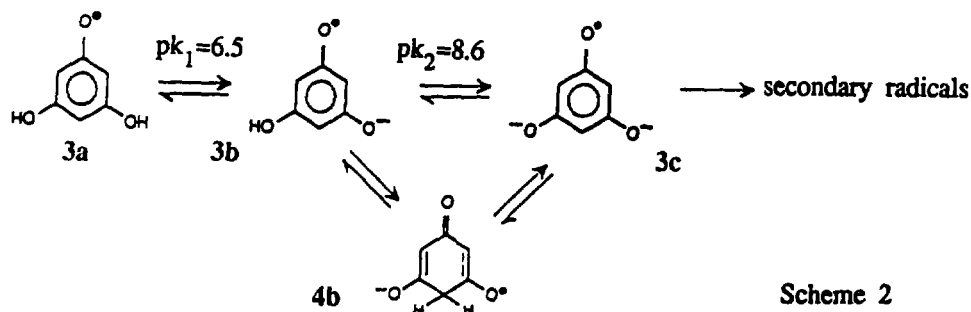
1) D. Wang, K. Hildenbrand, J. Leitich, H.-P. Schuchmann, C. von Sonntag, Z. Naturforsch., 1993, in press

2) M. Lohrie, W. Knoche, J. Am. Chem. Soc., 1993, **115**, 919–924

Radiation Stability Of Crown Ether - Metal Ions Complexes

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The radiation stability of cyclic compounds is known to determine by ring tension. The value of ring tension causes by a number of reasons such as changing of valence angles, bond length etc. The dependence of the radiochemical yield of radicals on the ring size of cyclic polyethers, cyclic alkans and crown ethers is corroborated by experimental data. Also the ring tension may be changed by the ligand - dentant interaction energy, that is ion-dipole interaction between the cation and the negatively charged oxygen atoms of the polyether ring. The energy of this interaction is characterized by the stability constant between metal ions and crown ethers. The radiation chemical yields of radicals G_R in crown ether complexes being quantitative characteristic of ring cleavage are given in Table

N	Compound	$G_R, \dfrac{rad}{100ev}$	$\log K_{complexes}$ [1]
1	18C6	5.7±1.1	
2	18C6 BeCl$_2$	5.6±0.8	
3	18C6 MgCl$_2$	7.9±1.1	2.5±0.2
4	18C6 CaCl$_2$	8.3±0.7	3.7±0.2
5	18C6 SrCl$_2$	9.3±0.3	5.0±0.1
6	18C6 BaCl$_2$	10.1±0.5	6.0±0.1

According to these data, extension G_R occurs when the stability constant complex (or ring tension) increases. The values G_R for the compounds 1 and 2 are the same that is evidence of the effective transfer of excitation energy from dentant to ligand.

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Mimicking Primary Processes in Photosynthesis – Covalently Linked Porphyrin Quinones

H. Kurreck, H. Dieks, J. v. Gersdorff, J. Gätschmann, J. Sobek, K. Möbius, J. Schlüpmann, H. Levanon, K. Hasharoni.

Abstract: Porphyrin Quinones, covalently linked via different aliphatic bridges, have been synthesized and studied in their (porphyrin) cationic and (semiquinone) anionic radical states by EPR, ENDOR and TRIPLE Resonance techniques. Electron transfer (ET) from the porphyrin donor to the quinone acceptor could be observed by time-resolved Picosecond Fluorescence Spectroscopy (singlet ET) and by time-resolved EPR spectroscopy (triplet ET) in isotropic fluid solution and in anisotropic media (liquid crystals). Unexpected results of photoexcitation of porphyrin quinones in reversed micelles will be discussed. Replacing the quinone acceptor by the flavin system, not only interesting ET reactions from the photoexcited porphyrin donor to the flavin acceptor are operative, but, in addition, energy transfer from the photoexcited flavin donor to porphyrin moiety could be measured by optical spectroscopy.

PULSED NMR STUDIES; T_2 RELAXATION AND PHYSICAL PROPERTIES OF MACROMOLECULES

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ESR and NMR techniques have acquired an outstanding position in the analysis of chemical reactions and modification in the chemical structure of both low and high molecular weight materials. It is surprising that the use of pulsed NMR has not been more fully utilised in the determination of morphology and mobility of high molecular systems such as polymers and biopolymers where molecular arrangement may play as crucial role in important physical properties as does the detailed chemical arrangement of their small constituent units.

The spin lattice relaxation T_2 follows a simple expotential decrease with time and its rate provides information on average molecular weight and any changes due to radiation or other processes; it can also analyse the motion of molecules at various temperatures in the partially crystalline, glassy or flexible states as well as on the influence of solvents or other additives.

This simple, non-destructive and almost immediate technique applies to fairly low molecular weight macromolecular systems. When these are partially crosslinked a two fold structure emerges in the T_2 relaxation curve, with an additional more rapid component due to a different pattern of molecular motion in the crosslinked fraction. The double expotential decay then provides a direct method of assessing the network fraction or gel, far quicker than the more usual solubility technique. Furthermore it provides a measurement on the average molecular weight M_c between successive crosslinks, a quantity which may determine the elastic properties of the composite network, its swellability etc. Comparison between samples with various additives can then serve to determine how far these modify the structure of the high molecular weight polymer e.g. by oxidation at higher temperatures or on standing.

For higher molecular weight macromolecules this twin structure comprising network and non-network components may also be observed even when no permanent network is present (e.g. the sample is completely soluble). This apparent intrusion of a temporary network is ascribed to the presence of entanglements between separate long

chains; these entanglements form and reform at a rate which depends on temperature and thereby determine such properties as creep in a material under stress. The density and average lifetime of these entanglements can be deduced from the T_2 measurements, thereby offering a rapid and quantitative method of assessing the major factor (such as creep) involved in the rheology of polymers, so widely used for their valuable mechanical properties.

By a series of T_2 measurements of a series of identical samples, modified to known extents by radiation etc., the information provided by standard T_2 measurements can provide a most valuable technique both for understanding the fundamental cause of many of these most important physical properties, but also a simple rapid and non-destructive method of assessment for industrial manufacture and control.

Another extension is towards the behaviour of biological systems. So far attention has been largely focussed on the detailed chemical changes produced by radiation and additives etc. Is it possible that the observed changes in biological behaviour are due at least in part to the modified morphological structure, arrangement and mobility of these very high molecular systems. For example could the great sensitivity of DNA to radiation be simply due to the radom crosslinking of the two macromelecules in the helix, preventing their separation for purposes of duplication and therefore effective biological death. Another possibility is simple main chain scission. Both these patterns have been studied in great detail for simpler polymeric macromolecules and should be readily detected by pulsed NMR T_2 methods. These have already shown very simply the role of certain additives in diverting the radiation-induced reaction. Could we hope to see this promising and simple technique of research investigated further in these far more complex but important biological systems?

EPR SPECTRA OF POLYMERIC COMPLEXES OF SILICON (IV) WITH TEPRASULPHUR TETRAIMIDE ($S_4N_4H_4$).

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Polymeric complexes of Si (IV) with $S_4N_4H_4$ were
prepared under varying conditions of Pressure and
Temperature. Polymeric Complexes have the molecular
formulae; $P_1 = (S_4N_4H_4 \; SiCl_4)_3$, $P_2 = (S_4N_4H_2 \; SiCl_2)_{11}$.
The various parameters g_{11}, $g_{\perp}$, χ_A, μ_{eff} and A_H have
been computed for polymers P_1 & P_2 to establish the
structure and nature of both complexes. P_1 has free
electron and g = 2.001 with vanishing of spin orbital
coupling while P_2 has unpaired electron with slight
spin orbital coupling. P_1 is a coordinated trimer
having S - N $\rightarrow$ Si $\leftarrow$ N - S linkage while in P_2 there
is hyperfine splitting of unpaired electrons of two
antipodal N atoms between, S - N - Si - N - S covalent
linkage. P_2 is a polymeric complex having covalently
linked Si (IV) with antipodal N atoms of $S_4N_4H_2$ units.

Molecular Dynamics of Radicals in the solid state.
ESR, ENDOR and Pulsed ESR Studies

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The study of molecular motions in solids is of paramount importance for many fields, as for example photochemistry in solids, supramolecular chemistry, characterization of glassy materials.
In this contribution we will give some examples of the use of cw ESR (lineshapes), pulsed ESR (relaxation times) and ENDOR (enhancements and linewidths) for gathering information on intra- and intermolecular motions in solids.
Examples will be given on the determination of the dynamical properties of methyl and methylene rotations in radicals in single crystals and powders [1], and on studies on intra- and intermolecular motions of long chain radicals in urea inclusion compounds [2].

[1] M. Brustolon and U. Segre: "Advanced EPR. Applications in Biology and Biochemistry", A.J. Hoff editor, Chapter 16, 1989, Elsevier, Amsterdam.

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DISPERSIVE KINETICS OF RADIATION-INDUCED SPECIES
IN CONDENSED MEDIA

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Distribution in reactivity of radiation produced species in condensed media becomes evident in kinetics only when not preserved during the reaction course. This happens when the rate of reaction exceeds those of internal rearrangements restoring the distribution of reactant reactivity in the system. As the representation examples one can take the fast reactions of radiation induced intermediates in liquids followed at subpicosecond time scales or reactions of the same intermediates followed at much longer time scales in low temperature solids and find similar reaction patterns following from reaction modelling in statically disordered systems [1]. The effects of matrix dynamics are rationalized in terms of the renewal theory [2]. When the rates of relaxations exceed markedly those of reactions the classical patterns of reaction kinetics are valid for disordered systems. These findings will be shown to give the proper description of reaction dynamics in the glass transition region which is of fundamental interest in current studies on radiation effects in glass forming systems, especially in melts and concentrated solutions of polymers.

References:

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2. A. Plonka, "Developments in Dispersive Kinetics", Prog. Reaction Kinetics (1991) **16**, 157-333.

MULTIQUANTUM EPR SPECTROSCOPY

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Multiple frequency irradiation of the spin system under magnetic resonance conditions leads to multiquantum transitions. In most experiments bichromatic irradiation has been used and various effects due to multiquantum processes have been observed.

The longitudinal detection of the magnetization vector enables an observation of transitions involving an even number of quanta (1,2).

For the transverse components of the magnetization vector the intermodulation sidebands appear due to processes engaging an odd number of photons. The corresponding EPR absorption and dispersion spectra exhibit new lines (3,4). Their position and intensity depend on the incident microwave power, frequencies and relaxation times of the investigated spin system.

The phenomena of multiquantum transitions can be described by the proper set of Bloch equations (5). Applying numerical procedure to solve this set of differential equations the behavior of the intermodulation sidebands can be studied.

It has been experimentally shown that multiquantum EPR spectroscopy can be used to determine longitudinal relaxation times, to perform ELDOR and ENDOR experiments(6-8).

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6. H. S. Mchaourab and J. S. Hyde, J. Chem. Phys. **98**, 1768 (1993)

7. H. S. Mchaourab, T. C. Christidis, W. Froncisz, P. B. Sczaniecki and J. S. Hyde, J. Magn. Reson. **92**, 429 (1991)

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Posters

SYNTHESIS OF Rb_3C_{60} INVESTIGATED BY EPR METHOD

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Recently, L.Kevan has presented a completely new method of preparation the rubidium doped superconducting fullerenes. This new approach involves alkai metal-azides RbN_3 as the source of alkai metal and heating the azide-C_{60} mixture for only about 5 minutes at high temperature. The obtained superconductor has been characterized using EPR and magnetically modulated microwave absorption (MMMA).

During one day following doping process both the EPR and MMMA signals are found to be dramatically time dependent. The time dependences of MMMA and EPR intensities are probably due to the diffusion and redistribution of rubidium within the grains of a policrystalline fullerene sample.

To explain the observed phenomenon We have proposed simple model of reaction based on diffusion theory in solids and the Avrami equations. More, using our model we have calculated the Josephson penetration depth of intergrain Josephson junctions occuring in the granular fullerene superconductor. The parameters estimated according our "diffusion model" are in good agreement with the parameters known earlier from literature.

EPR OF FULLERENE C_{60} AND FULLERITES Me_xC_{60}

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EPR studies of fullerene C_{60} and superconducting fullerites Me_xC_{60} (Me = K, Rb) have been performed for temperature ranging from 4 to 300 K.

1. "Pure" fullerene C_{60} :

Fullerene C_{60} samples are characterized by a very weak EPR spectrum of g_+ = 2.0025 and linewidth $2\Delta B_{l\epsilon}$ = 2 Gs at room temperature (RT). It is related to the $(\dot{C}_{60})^+$ holes in defected structure. Apart from this line for some samples of "pure" fullerene C_{60} we have observed the line with g_- between 2.0006 and 2.0012 what was ascribed to the negative ion $(\dot{C}_{60})^-$ [1,2]. In both cases the observed EPR line is narrow and does not change with temperature, which means that the hole and the electron are delocalized on all carbon atoms of fullerene ball and EPR line is dynamically averaged on this ball.

2. Fullerites Me_xC_{60} :

For Me=K a strong two component EPR spectrum was recorded. The narrow line (N) was of width $2\Delta B_{l\epsilon}$ = 2 Gs while the wide (W) linewidth was $2\Delta B_{l\epsilon}^W$ = 14 Gs at RT. For Me=Rb only one wide EPR line characterized by g^{Rb} = 2.0012 is observed. Narrow lines for K_xC_{60} we ascribed to paramagnetic centers of $(\dot{C}_{60})^+$ or $(\dot{C}_{60})^-$ radical - ions (like in "pure" C_{60}) and a wide lines for both K_xC_{60} and Rb_xC_{60} one can attributed to the $(\dot{C}_{60})^{-y}$ radical-ion (y valence) strongly bounded in the $[Me_x(\dot{C}_{60})^{-y}]$ complex (c). The g^c factor and the linewidth $2\Delta B_{l\epsilon}^c$ ascribed to it are strongly dependent both on temperature and composition.

3. Concentrations of spins :

The concentration of spins determined at RT from the wide line of EPR spectrum for different Me_xC_{60} samples oscillates about the number of fullerene balls implied by the stoichiometry of the compounds.

4. Metallic behaviour :

For sample K_xC_{60} with x << 1 we have found characteristic for metals Dyson's shape of EPR signal. Asymmetry of this signal appear about 40 K and increase with lowering temperature.

5. Superconductivity :

Magnetic modulated microwave absorption (MMMA) measurements have been applied to determine T_c for all Me_xC_{60} samples.

1 S. G. Kukolich, D. R. Huffman, Chem.Phys.Lett. 182 (1991) 263
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EFFECT OF GALLOTANNINS ON DPPH RADICAL

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Gallotannins are widely distributed throughout the plant kingdom and were applied for centuries in manufacturing of leather and in the folks medicine. Recently, polyphenols were used also as corrosion inhibitors. The scavenging action on the peroxy radicals and on the DPPH radical of some flavonoids, catechins, gallotannins and α-tocopherol was reported [1].We examined the scavenging effect of several plant extracts of gallotanins on DPPH radical. The composition and the structure of extracts were determined by ^{13}C NMR and FAB mass spectrometry.

Fig.1 The spectrum of DPPH in DMSO (a) and in the presence of gallotannin (pharmaceutical) after (b) 5 min. (c) 13 min.
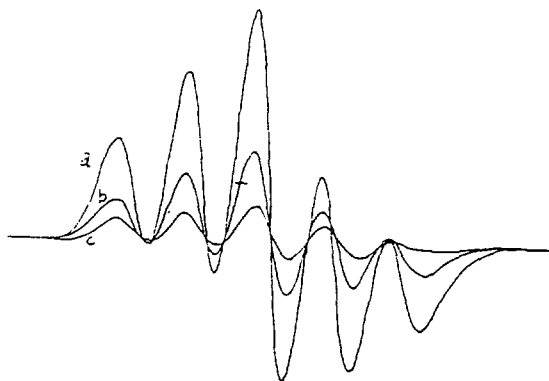
Fig.2 The structure of gallotannine (pentagalloiloglucose)
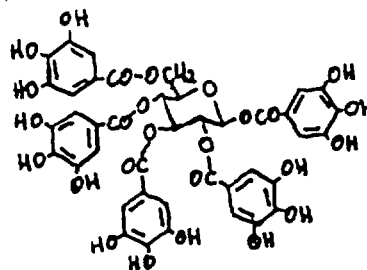
The results indicate that the increase of molecular weight of tanins with the accompanying increase of the number of phenolic hydroxyl groups resulted in an increase of the scavenging effect.

[1] T. Hatano *et.al*, Chem. Pharm. Bull.,37, 2016 (1989)

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NITROXIDE RADICAL AS A PROBE FOR HYDROGEN BOUNDING IN CHLORO- AND FLUOROANILINES

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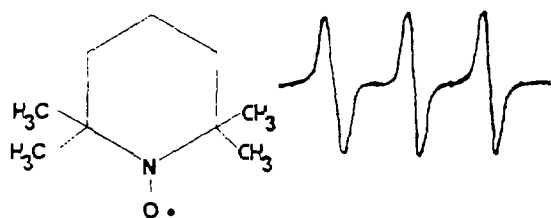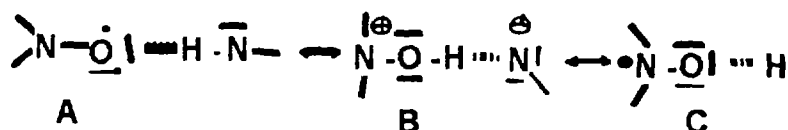The 2,2,6,6 - tetrametylopiperidine radical (TMPN) is a stable radical. It exhibits an electron donor properties and forms hydrogen bond complexes with alcohols [1,2] and amines [3]. The structure of the radical and ESR

Fig. 1

spectrum in CCl_4 solution are shown in Fig.1. The hydrogen bonds are formed through the oxygen atom of the nitroxide group and the contributions of mesomeric structures B and C explain an increase of the spin-spin coupling constant A. The dependence of A [mT] on the concentration of aniline and its monochloro derivatives is illustrated in Fig.2.
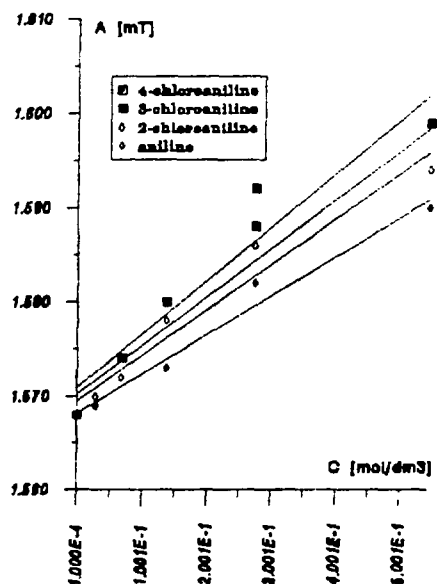
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Fig. 2

ENDOR study of free radicals in X-irradiated glutarimide

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Glutarimide single crystals grown from H_2O and D_2O solutions were X irradiated. ESR and ENDOR measurements were carried out on a Bruker instrument. ENDOR from room temperature irradiated samples were obtained at two temperatures, 295 and 120 K. Some experiments with irradiation and measurements at 4.2 K were made.

The data from the room temperature irradiated crystal indicate the presence of a radical species with two quite anisotropic and two nearly isotropic hydrogens. The couplings of the nearly isotropic hydrogens changed significantly and reversibly with temperature in the ENDOR measurements between 295 and 120 K. The ESR spectra also changed. A provisional interpretation of the data suggests that a ring opening has occurred after irradiation at room temperature resulting in a R - CH_2 - $\overset{\cdot}{C}H_2$ fragment, exhibiting some motion at 295 but not at 120 K. Irradiation at low temperature does not produce imidyl radicals in contrast to the case of succinimide [1].

[1] A. Lund, P.O. Samskog, L. Eberson and S. Lunell
J. Phys. Chem. 86, 2459 (1982)

Free radicals of isatoic anhydride and its derivatives as studied by in situ electrochemical-ESR-technique

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Isatoic anhydride undergoes electrochemical reduction in DMSO to form radicals which were studied by in situ spectroelectrochemical techniques and are not described in the literature before.

The following derivatives were used in this study:

$$R_1 = H, CH_3; \quad X = O, S; \quad R_2 = H, Cl, NO_2$$
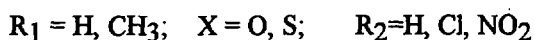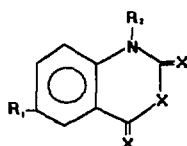
The in situ electrochemical measurements were made in a quartz flat cell and a rectangular microwave cavity. To have a better control of the potential at the platinum mesh electrode we applied two counter electrodes. One counter electrode was situated above and the other below the working electrode [1].

The radical anions formed by reduction were investigated by electrochemical and spectroscopical methods. Half-life of the radicals were estimated. The shortest half-life was 140 ms, the longest about 100 s. Hyperfine coupling constants were determined by simulating the experimental spectra.

A tentative assignment of the hyperfine coupling constants were done on the basis of Hückel calculations.

Trithioisatoic anhydride gives two reduction waves and two well distinguished radicals. These two radicals are due to tautomeric forms of the compound. Furthermore it is assumed that reduction converts one tautomeric form to the other. This can be verified by in situ EC-UV-spectroscopy and calculating the cyclic voltammograms .

Comparison of the half-life estimated by ESR-spectroscopy with half-life obtained by cyclic voltammetric measurements at different sweep rates indicates that there is no simple one electron mechanism. but a more complicated mechanism which is now under study.

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AN ESR STUDY OF SULFUR-CONTAINING AMINO ACIDS IN AQUEOUS FROZEN SOLUTION.

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The reaction pathway of the OH radical induced oxidation of some sulfur- containing aminoacids in acidified aqueous frozen solution have been investigated by radiation chemical methods with Electron Spin Resonance detection.

The radicals produced by reactions of hydroxyl radicals with a number of sulfur-containing amino acids (homomethionine, methionine, S-methylcysteine, s-carboxymethylcysteine, S-carboxyethylcysteine and 2,2'-thiodiethanoic acid) in frozen acid aqueous matrix have been identified by ESR spectroscopy over the range 77-200K.

Irradiation were performed with Co-60 gamma source with doses 1-3 kGy. ESR spectra were obtained using Bruker ESP-300 spectrometer with a variable temperature cavity. .

For all compounds studied the $\alpha-$(alkylthio)-alkyl radicals are the only radical species present over the temperature range 120-160K.

In the temperature below 180 K two different type of behaviour have been observed.

For methionine, homomethionine and S-methylcysteine, we have observed dimeric sulfur-centred radical cations over the temperature range 180-200K. For other amino acids we have not observed dimer arising.

ESR study radiation induced radicals in solid peptides .

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ESR studies on irradiated peptides in the crystalline state can provide important information about the mechanisms of radiation-induced radical processes in proteins.

Among the biologically available amino acid residues mathionine is particulary susceptible to oxidation because of possessing of an easily oxidizable sulfur moiety.

Moreover,in the past few years a growing interest in redox processes in biological systems has stimulated several investigations of methionine containing peptides.

The gamma irradiated at 77K of polycrystalline methionine containing peptides: Ala-Met, Val-Met and Met-Ala, Met-Val were ivestigated by Electron Spin Resonsnce spectroscopy.

The radicals produced by the irradiation, their relative amounts and stability were studied as a function of temperature over the range 77- 298 K.

Anion radicals formed by addition of electron to the carbonyl group of the peptide bond are major component observed at 77K in all peptides. For peptides Ala-Met and Val-Met the radical anions decay to produce deamination radicals on warming to 120-230 K.

On futher warming to 293 K decarboxylation radicals (for Ala-Met and Met-Val) and H-abstracion radicals at the α-carbon of the C-terminal amino acid residue (for Val-Met and Met-Ala) were detected.

The experimental ESR spectra were simulated by the ESR simulation program provided by NIEHS LMB National Institutes of Health, USA.

INFLUENCE OF Mn(II) AND CH_4 ON THE EVOLUTION OF LIGHT INDUCED RADICALS IN CHLOROPLASTS

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The photochemical activity of chloroplasts isolated from leaves of PHASEOLUS VULGARIS, TRITICUM VULGARE, SCINDAPSUS AURENS was studied by EPR spectroscopy. The evolution of free radicals (FR) and of the Mn containing complexes reveals new aspects of the TB-type of carbon assimilation. The plants were grown in CH_4 atmosphere, in a dietary medium containing various (0.0125%-0.5%) concentration of Mn(II) ions. The EPR spectra, fig.1a and 1.c, of a standard sample consisting of chloroplasts isolated from leaves grown in air, reveal the presence of two types of FR: (i) the light induced one, fig.1e, with $g_1=2.004$ and $\Delta H_1=0.9$ mT, related to the primary photochemical act; (ii) the dark stable one, fig.1a, 1e, with $g_2=2.006$ and $\Delta H_2=4.2$ mT
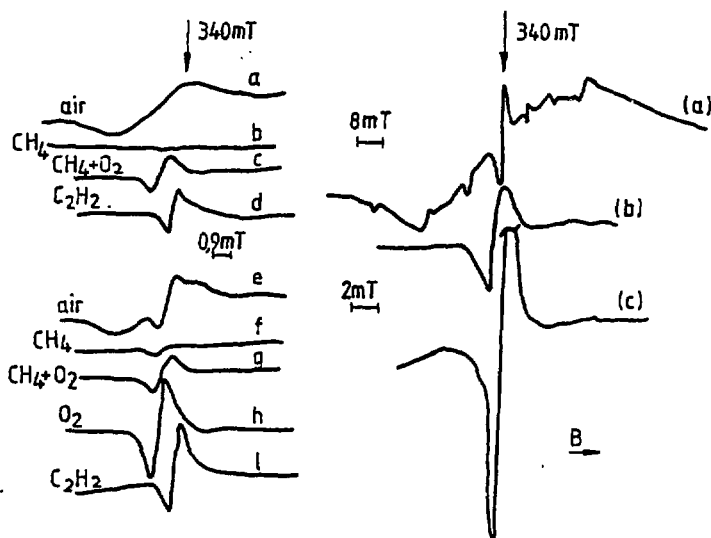

Fig.1 Free radical spectra of chloroplasts in several environment

Fig.2 Spectra of Mn(II) in chloroplasts(a) and of free radicals in dark (b) and upon illumination (c)

The signal (2) is gradually broadened from $\Delta H_2=3.7$ mT for the plants stored in CH_4 for 1-4 days, to $\Delta H_2=5.0$ mT for a storage of 90 days, finally, remaining visible in the spectrum only the signal (1) with $g_1=2.004$ and $\Delta H_1=0.71$ mT, fig.1b and 1f. The exposure to O_2 (20%-100%) results in the generation of light stable FR, fig.1c and 1g with $g_3=2.005$ and $\Delta H_3=0.72-1$ mT, attributed to the oxidized chlorophyll. In solution with 0.1% Mn the plants have different evolutions in CH_4 and in air, respectively, those ones stored in CH_4 being viable even after 21 days, whereas those ones stored in air reveal the necrosis after 5 days, fig.1d, 1h anhd 1i, respectively. More kinds of paramagnetic species were identified: the hydrated Mn(II) with g=2.00 and $A_0=10$ mT, the clustered Mn ($\Delta H=60$ mT) as well as the photosensible free radicals with g=2.005 and $\Delta H=1$ mT. The viable leaves exhibit an enhanced photosensibility, fig.2b,c the effect of necrosis being related to both the process of Mn association and the reduced photosensibility of the FR. The contents of Mn(II) lower than 0.1% are the most suitable for substitution, in vivo, of Mg(II) by Mn(II) in the porphyrinic centre of chlorophyll, resulting in the Mn-substituted pheophytin, which can induced an outstanding photoactivity

BIOSYNTESIS OF CHLOROPHILL-LIKE Cu(II)-PHEOPHYTIN

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The biosynthesis of chlorophill-like Cu(II)-pheophytin was realized in plants (PHASEOLUS VULGARIS) grown in dietary media containing Cu(II) ions in concentration ranging from 0.0125% to 0.05%.The Cu(II) in excess affects the leaf integrity, resulting in the blue-green coloured domains which are gradually extended (3-5 days) on the full outline of the leaves. EPR investigation of these types of choloroplasts shows that for concentrations of 0.0125% and 0.05% Cu(II) ions, the spectra are typical for axially coordinated complexes, fig. 1a,d,e, with $g_{\parallel}=2.24$, $g_{\perp}=2.05$, $A_{\parallel}=18.5mT$, $A_{\perp}=(2.8)mT$. The ligand superhyperfine structure, $a_{\parallel}=1.41mT$, due to the interaction of the unpaired electron with the nitrogen atoms of the porphyrin ring of pheophytin suggests that takes place the synthesis, *in vivo*, of chlorophyll-like Cu(II)-pheophytin. For concentration of 0.5% Cu(II), the spectra consists in a single broad line, $\Delta B=25mT$, with $g_{\parallel}=2.26$ and $g_{\perp}=2.08$, without hyperfine splittings, which is typical for clustered ions.
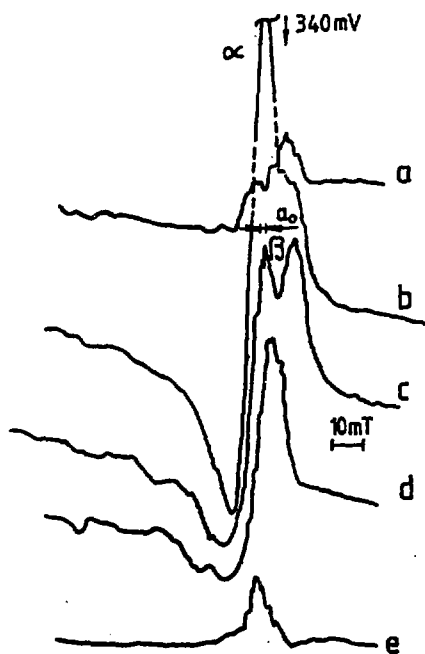
Fig.1 EPR spectra of chlorophyll-like Cu(II)-pheophytin (a,d,e) and of Cu(II)-containing chloroplasts(b,c).

The obtained results suggest the Cu(II) ions accumulated on the border part of the leaves as immobilized species, possibly as chlorophyll-like Cu(II)-pheophytin, achieving the first step of necrosis. Upon increasing the content of Cu(II), the clustered species are distributed in the whole leaf, resulting in the dipolar broadening of the EPR line. Contrary to the results obtained for Mn(II)-phophytin, the absence of the photosensible free radicals in chloroplasts containing Cu(II)-pheophytin indicate the alteration of the pigment/lipoprotein aggregates.

The chlorophyll-like Cu-pheophytin obtained by syntesis *in vitro* exhibits a spectrum consisting in :the signal (α) with $g_0=2.045$ and $\Delta B=7mT$, fig.1b, without hyperfine structure;the signal (ß) which is remarkably similar, fig.1c, to that one synthesized *in vivo* with the parameters: $g_{\parallel}=2.18$, $g_{\perp}=2.05$, $A_{\parallel}=19mT$, $A_{\perp}=(3)mT$ and $a_{\parallel}=1.48mT$. The first one (α) rapidly decreases upon admission of O_2 molecules, certifying the antiferromagnetic coupling of two-closely neighboring Cu(II) atoms *via* a pair of oxygen atoms, resulting in the formation of dimeric species of chlorophyll-like Cu(II)-pheophytin.

INFLUENCE OF HYDRATION OF SELECTED GADOLINIUM β-DIKETONATES ON THEIR EPR SPECTRA

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The complexes of β-diketones are the most widely studied coordination compounds of lanthanides and have been used in many applications in chemistry and physics.

The gadolinium chelates with: acetylacetone - $Gd(acac)_3 \cdot 3H_2O$, thenoyltriflouro-acetone - $Gd(TTA)_3 \cdot 2H_2O$, and benzoylacetone - $Gd(BAC)_3 \cdot 2H_2O$, have been chosen for EPR study (X and Q bands). The EPR spectra of these β-diketonates were obtained in the form of badly separated signals and thus were difficult to interpret. In order to improve the spectra resolution a computer analysis was made using the RKU program based on Fourier transform. This analysis permitted a considerable increase in resolution of the spectra and revealing their fine structure. The EPR spectra after the computer treatment were compared with the literature data, mainly those of Gd^{+3} in glasses [1].

Preliminary analysis of the data obtained leads to the conclusion that Gd^{+3} ion in the trihydrated $Gd(acac)_3 \cdot 3H_2O$ complex is exposed to a strong crystal field of a symmetry approximate to the rhombic one. The value of the parameter, $\lambda = E/D$, obtained is about 0.25. In the case of $Gd(acac)_3 \cdot 3H_2O$ the number of lines and positions of some components in the EPR spectra is different from those obtained for dihydrated complexes.

The differences in the line positions are minimal and result from insignificant changes of the crystal field in the dihydrated complexes (i.e. $Gd(TTA)_3 \cdot 2H_2O$ and $Gd(BAC)_3 \cdot 2H_2O$) This proves a change in the coordination number of Gd^{+3} and thus in the crystal field at the Gd^{+3} position as well. The estimated value of $\lambda = E/D$ in this case is equal to about 0.13.

The results obtained in this work show, for the first time, the potential use of the computer analysis in increasing the resolution of the EPR spectra making it possible to analyse the fine structure of Gd^{+3} ion in condensed phase (as pure compounds).

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STUDIES ON THE DETECTON OF RADIATION TREATED FOODSTUFFS BY THE EPR SPECTROSCOPY.

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Standard method of dose estimation in irradiated poultry has been worked out. The powdered defatted tightbone is used for the epr measurements and three to fifefold reirradiation with a dose of 1 kGy is applied for the dose extrapolation by jackknifing technique. The method allows to distinguish between the low dose and medium dose (6-7 kGy) radiation processings as well as to point at the overdosage (10 kGy) of the poultry.

In fishbones and scales of sweet-water and Baltic see fishes like carp (Cyprinus carpio), wels (Silurus glanis), trout (Salmo), pile (Esox lusius) and cod (Gadus morrhua) the detection of dose level below 1 kGy has been confirmed by the epr examination of deffated samples. The normalised epr signal intensities depend on the strain of the fish.

A long lived multicomponent epr signal has been found in seeds taken from pressed figs exposed to radiation. The stability of the epr signal in this fruit is comparable to that observed by us in dates (J. Sci. Food Agric. 58, 407-415, 1992, Appl. Radiat. Isot. 44, No . 1/2 432-427 ,1993).

Relatively stable epr signals have been found in dehydrated macaroni as available in the market after its exposure to ionising radiation. The decay of radiation induced epr signals was studied in time. The signals were detected after 9 month of storage in air at room temperature.

The influence of epr spectrometer settings (microwave power and modulation amplitude) on the detectability of celluloze radicals in seeds and nuts has been studied in colaboration with dr Raffi group, CEN Cadarache. It has been confirmed that there is a region of spectrometer settings suitable for the detection of satellite lines of the epr celluloze radical (triplet) in seeds. No chance of the detection appears outside this region.

THE EPR DETECTABILITY LEVELS IN MOLLUSC'S SHELLS EXPOSED TO THE ACTION OF IONIZING RADIATION

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The exposure of mineralized tissues to ionizing radiation results in the production of paramagnetic species that can be detected by epr spectroscopy. The epr radical signals from cartilaginous phase of the tissue decay within few days in reaction with diffusing oxygen, while the remaining signal derived from crystalline matrix of calcareous phase is extremely stable and survives in the tissue for may years. The lowest detectability level (0.2 Gy) of the stable epr signal assigned usually to CO_3^{-3} or CO_2^{-1} radical ions - substitutional dopants in crystalline hydroxyapatite lattice - has been found in human teeth enamel characterised by the highest level of crystallinity among biological materials.

In general, the exoskeletal structure of lower animals have an architecture similar to mammalian or avian bones in that they posses an organic matrix around which crystalline calcium carbonate with verying amount of calcium phosphates and magnesium carbonate are deposited. However, in shells of molluscs more than 20 different minerals, both amorphous and crystalline were found. Nevertheless, the exoskeleton of numerous crustacea and the skeleton of bone fishes have a mineral content that is predominantly calcium phosphate, much like mammalian bone. Therefore, the dose sensitivity and stability of radiation induced epr signals in crystalline matrices of all these animals could be often comparable.

Among several scores of samples the best results have been obtained with terrestrial grove snail shells, with ocean pearl oyster shell and with shells of fresh water molluscs (Viviparus contectus, Dreissena polymorpha and Anodonta anatina). In cited examples the detectability level was between 1 and 5 Gy. It has to be noted that in some other shells radiation induced epr signals were not observed.

It is believed that by the epr examination of terrestrial and aquatic animals collected in the vicinity of nuclear accidents or highly radioactive nuclear deposits in oceans the estimation of cumulated dose of radiation will be possible.

EPR STUDIES ON THE GENERATION OF SUPEROXIDE AND HYDROXYL RADICALS BY HUMAN NEUTROPHILS

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Stimulation of polymorphonuclear leucocytes results in the generation of oxygen-centered radicals (respiratory burst). Spin trapping techniques employing 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) are being applied to investigate the production of free radicals. DMPO reacts with O_2^- to form 5,5-dimethyl-2-hydroperoxy-1-pyrroline-N-oxide (DMPO-OOH) and with OH⁺ to form 5,5-dimethyl-2-hydroxy-1-pyrroline-N-oxide (DMPO-OH). Neutrophils stimulated with opsonized zymosan in the presence of DMPO, dimethylsulfoxide, and diethylenetriaminepentaecetic acid showed increased concentrations of hydroxyl adducts (DMPO-OH) only in the first ten minutes after stimulation. The concentration of the superoxide adduct (DMPO-OOH) decreases in the first five minutes. Thereafter a large increase with a maximum at about 30 minutes is observed. In patients with pancreatitis superoxide production is markedly increased whereas an increase of hydroxyl adducts could hardly be detected. No spin trap adducts were seen with unstimulated neutrophils. Reasons for the lack of the increased hydroxyl adduct production in prancreatitis and at the peak of superoxide production are discussed.

EPR OF A NITROXIDE ADSORBED ON SiO_2 AND La_2O_3

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Adsorption of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) on SiO_2 and La_2O_3 has been studied by EPR. Linear dependence of the individual linewidth $\Delta H_{1/2}$ on the surface radical concentration C was obtained $\Delta H_{1/2}=\Delta H_0+a\cdot C$, where $a=2\cdot10^{-17}$ $G\cdot m^2$ and $\Delta H_0=18.4$ G for La_2O_3 and $a=3.5\cdot10^{-17} G\cdot m^2$, $\Delta H_0=11.7$ G for SiO_2. The comparison of the concentrational behaviors of the linewidths of TEMPO on SiO_2 and La_2O_3 indicates that spectra of TEMPO on La_2O_3 exhibit unresolved hyperfine splitting from coordinatively unsaturated La^{3+} ($I=7/2$) ions on the surface of La_2O_3. It was concluded that upon adsorption radicals coordinate to La^{3+} with the creation of surface complexes. It was obtained that on the reduced at 873 K La_2O_3 in the contrary to the oxidative La_2O_3 there are centers interacting with TEMPO and leading to the loss of their paramagnetic properties. The concentration of these centers is ~ $3\cdot10^{17}$ m^{-2}. The adsorption of O_2 at 300 K restores the initial concentration of the adsorbed radicals. For the studied oxides of SiO_2, $\alpha-Al_2O_3$, CaO, MgO analogous effects were obtained only for CaO, MgO. It was concluded that the transition of TEMPO from paramagnetic to diamagnetic state is caused by the interaction of TEMPO with the donor center on the basic catalysts surface. The adsorption of O_2 leads to the weakening of donor properties with the following return of electron from TEMPO to the oxide.

1. V.V.Chasov, V.A.Shvets, *Zh.Fiz.Khim.*, **65**, 2449 (1991).

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The aim of this study is the determination of the component lines in the e.p.r. spectra of coals: a) macerals of low carbon content (3 samples), and b) coal of middle carbon content, all its macerals and products of their extraction with pyridine (24 samples). The e.p.r. measurements were carried out in X band at high (20 dB) (at room and liquid nitrogen temperature) and low (1 dB) attenuation of microwave power and in Q band. The e.p.r. spectra of macerals of middle carbon content and their extraction residues consist of: a) a Gaussian and two Lorentzian lines for exinites and vitrinites, b) two Lorentzian lines for inertinites. The e.p.r. spectra of extraction products are single lines. In macerals and in residues of their extraction four populations of paramagnetic centres are present which give rise to e.p.r. lines of following widths:
A. 0.87 - 0.94 mT, (0.72 - 0.76 mT), Gaussian
B. 0.37 - 0.55 mT, (0.36 - 0.47 mT), Lorentzian
C. 0.19 - 0.29 mT, (0.20 - 0.22 mT), Lorentzian
D. 0.08 - 0.12 mT, (0.07 - 0.11 mT), Lorentzian.
(In parantheses the line widths for the extraction residues are given).
Narrow lines (D) are observed in the e.p.r. spectra of all macerals, the broad signal (A,B) occur only in the e.p.r. spectra of exinites and vitrinites, whereas the narrow lines (C) occur only for inertinites.
The e.p.r. spectra of studied coals and extraction residues consist of four components.
The spectra of low carbon content macerals are sums of two Gaussian lines (0.81 - 0.89 mT) and one Lorentzian line (0.42 - 0.54 mT).
The Gaussian lines are saturated at relatively low microwave power. The width of e.p.r. lines measured at room temperature and at liquid nitrogen temperature is the same. When measured in Q band the line width is greater then in X band [1].
On the basis of experimental data presented above following conclusions may be drawn:
1. Coal and its macerals give rise to multicomponent EPR spectra. The number of component lines depends upon the kind of maceral and upon the carbon content of the sample.
2. Following assignments of the e.p.r. lines cannot be assumed as correct: a) assignment of narrow and brod lines to the molecular and macromolecular phase of coal [2], because paramagnetic centres giving rise to broad and narrow lines occur in both parts of coal substance, and b) assignment to individual macerals [3, 4], because the paramagnetic centres giving rise to narrow lines occur not only in inertinites, but also in other macerals.
3. Unpaired electrons in structures consisting of few aromatic rings are responsible for wide Gaussian lines. The saturation behaviour of these lines is similar to that of lines from such structures [5]. These lines do not occur in macerals of low carbon content.
5. Spin-spin relaxation of unpaired electrons determines the width of studied e.p.r. lines, because the line width does not depend on temperature.
6. The g-factors within populations of paramagnetic centres are different, because the line width is increasing with increasing microwave frequency.

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ANTIFERROMAGNETIC RESONANCE

in $(K_{1-x}Na_x)MnF_3$ and $(K_{1-x}Li_x)MnF_3$

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The X-band antiferromagnetic resonance spectrum of $KMnF_3$ with impurities Na^+ and Li^+ was studied at temperatures from 40K to T_N. The single crystals of mixed perovskite compounds were grown by the Bridgman method. $KMnF_3$ is characterized by a strong exchange interaction and small anisotropy; it is therefore an attractive material for the study of AFMR.

The field for antiferromagnetic resonance as a function of temperature and an angle is shown. From a comparison of the results of AFMR measurements and the known distortions in the crystal structure it is concluded that a correlation between the structural and magnetic phase transitions appears for the mixed systems.

A SINGLE CRYSTAL EPR STUDY OF BIS (N - BENZYLPYRIDOXAL -DIMINATO) COPPER (II).

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Single crystals of the copper salt were studied by EPR in three perpedicular planes at 300 K and 9.4 GHz. Only one exchange – narrowed line was observed for the two magnetically inequivalent copper ions in the monoclinic symmetry lattice with space group $P2_4/a$ and elementary cell parameters a = 9.561(9), b = 16.605(8), c = 17.561(2) A and β = 104(1)° .The EPR linewidth remained Lorentzian for all orientations considered. The components of the g tensor were found to be g_{xx} = 2.0439, g_{yy} = 2.0649, g_{zz} = 2.2595. The linewidth anizotropy was analyzed in terms of dipole – dipole interactions, magnetic ineqivalency of molecules and the hyperfine interactions.

Paramagnetic silver adducts with various adsorbates in zeolite A

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The intermediate paramagnetic species formed in gamma irradiated Ag-NaA zeolites with adsorbed ammonia and methanol molecules have been studied by ESR spectroscopy.

In zeolites with adsorbed methanol hydroxyalkyl silver radicals $Ag \cdot CH_2OH^+$ have been studied. These adducts for silver loadings greater than one Ag^+ per unit cell are formed directly after irradiation at 77 K. For lower Ag^+ content they appear on annealing above 140 K. It is postulated that the Ag^+ location in the zeolite lattice plays a crucial role in the process, and two different mechanisms of $Ag \cdot CH_2OH^+$ formation are discussed depending on Ag^+ location inside or outside a ß cage.

For zeolites with adsorbed ammonia with silver loadings of about one Ag^+ per unit cell the ESR quartet with *hfs* of 145 G was observed. Trimeric silver cluster and silver-ammonia adduct $Ag \cdot NH_3$ with an unpaired electron residing as well on silver as nitrogen nuclei are discussed as a possible carrier of that spectrum. For silver loadings of about six Ag^+ per unit cell an isotropic septet with *hfs* of 69 G was recorded on annealing at 190 K. This spectrum, never reported earlier, was ascribed to a binuclear silver complex with two magnetically nonequivalent Ag nuclei coordinated by NH_3 ligands.

THE ESR SPECTRA OF MAGNETICALLY ORDERED Ti(III) IONS IN THE TITANIUM- CONTAINING CATALYSTS.

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In the ESR of catalytic systems $TiCl_4$ + $Al(i-C_4H_9)_3$ in toluene solution at exess of aluminium organical compound, the signals with rhomboidal anisotropy of g- factor were detected. These signals we attituded to magnetically ordered $[Ti_2^{6+}]_n$ associates. By ESR methode the disordering effect of these associates was detected during an interaction with piperylene, which is accompaning by change of the spectrum anisotropy from rhomboidal to axial.

For equimolar ratioes of Ti/Al, the nonalkylated dimeric Ti_2^{7+} complexes were detected, with common unpaired electron, delocalized on two titanium ions.

For soluted $TiCl_3$ the ESR spectra of magnetically ordered Ti(III) ions are exchangely bonded between themselves.

THE ESR-SPECTROELECTROCHEMICAL DETECTION OF ORGANOMETALLIC W(+1) COMPLEX COMPOUNDS

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Continuing our study of tungsten(0) organometallic complexes[1] we have prepared new compounds of formula: $trans-W(CO)_4(cycloolefine)_2$. The electrooxidation of these complexes, is chemically totally irreversible under voltammetric conditions at room temperatures (Fig. 1). However, using the low temperature voltammetry, at platinum planar electrode, we have proved the reversible one-electron oxidation. Finally, the $[W(CO)_4(cycloolefine)_2]^+$ unstable species has been generated (at $(-60^\circ C)$ — $(-80^\circ C)$ range) by micro-bulk electrolysis and in situ detected by ESR at $-196^\circ C$ (Fig. 2) using spectroelectrochemical cryostat constructed by us.

600 700 800 900 1000 1100 1200 1300
E/mV vs Ag/AgCl

2600 2800 3000 3200 3400 3600
H/G
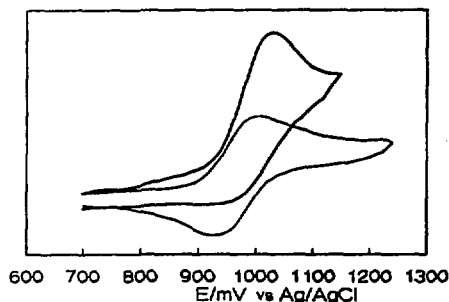
Fig. 1. Cyclic voltammograms of $trans-W(CO)_4(cycloheptene)_2$ at $18^\circ C$, V=0.1 V/s, bold line, $-43^\circ C$, V=0.4 V/s, thin line.
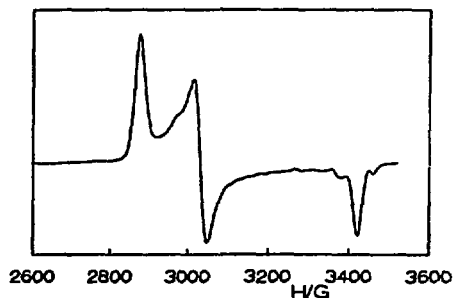
Fig. 2. ESR spectrum obtained at $-196^\circ C$ after electrolysis (at E_a=1.4V at $-60^\circ C$) of starting $trans-W(CO)_4(cycloheptene)_2$ complex in CH_2Cl_2 containing 0.1 M TBAP.

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EPR STUDIES OF COPPER(II) COMPLEXES IMMOBILIZED TO COORDINATING ACRYLIC POLYMERS

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The coordination properties of metal-polymer complexes have widespread implications for catalytic processes, as well as for hydrometallurgy. These processes have led us to systematic EPR studies of Cu(II) complexes with several polymeric ligands [1,2].

EPR spectra were used to indicate and characterize complex formation between Cu(II) and different chelating groups (L) attached to acrylic resins crosslinked by divynylbenzene. Coordination behaviour of the functionalized polymers toward Cu(II) ions was analyzed on the basis of the variation in EPR parameters and ^{14}N superhyperfine structure of EPR spectra depending on a) molar Cu(II):L ratio; b) coordinating properties of the particular groups L affected by pH of the solution. Property a) was controlled by pH, Cu(II) concentrations, metal-binding functional groups in L, and by degree of crosslinking in the polymeric matrix. The changes in Cu(II):L ratio were achieved by complexation of Cu(II) ions in the presence of Zn(II) ions. The Zn(II) ions were predicted to prevent the broadening of EPR lines due to Cu(II)-Cu(II) interactions.

<u>Results</u>: The nature of the parameters above appears to produce the following structural configurations: 1) For CuL and CuL_2 complex, where L=amidoxime, the donor atom set can equal 2N2O or 4N, depending on conditions a) and b) above. 2) for CuL at high pH, where L=oligoamines, the maximum number of N atoms provided by L is involved in equatorial coordination. 3) For CuL_2 complex, where L=hydroxamic acid, four O atoms are set around Cu(II) in a square-planar configuration.

A temperature effect on EPR parameters of Cu(II) complexes immobilized to polymeric ligands was found over the range 295-77 K for Cu(II)-amidoxime polymers in a swollen state.

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EPR STUDIES OF TEMPERATURE AND PRESSURE EFFECTS IN EXCHANGE COUPLING IN Cu(1-phen-3,5-dmpz)$_2$Cl$_2$ SINGLE CRYSTALS

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X-band EPR temperature and pressure (up to 450 MPa) measurements of the dichlorobis(1-phenyl-3,5-dimethylpyrazole) copper (II) crystal shown that exchange coupling between Cu(II) ions is very weak with $|J|$=0.00386 cm^{-1} at room temperature. This coupling is temperature independent but decreases under pressure. Moreover, when pressure is applied to the crystal, the J-value becomes temperature dependent and decreases on cooling. It is shown in Fig. 1. Also the g_z-factor and the linewidth value are affected by temperature and pressure. These effects are discussed and explained as a results of a decrease of the tilt angle between pyrazole ring and Cu(II) coordination plane under pressure and a shortening of the Cu-N bond on cooling. Exchange coupling is suggested to be ferromagnetic at normal conditions with antiferromagnetic contribution appearing under pressure.
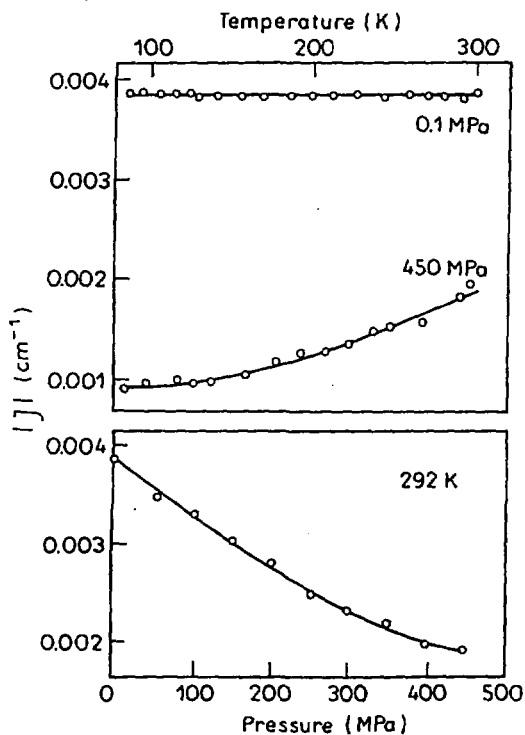
A SUPPRESION OF THE EXCHANGE INTERACTION BY THE VIBRONIC COUPLING IN $[CuX_6]^{2+}$ OCTAHEDRA ?

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A very interesting interrelation between vibronic coupling and a weak exchange interaction between copper(II) ions we have found in $(NH_4)_2Cu(BeF_4)_2 \cdot 6(H_2O)$ and $Cu(4\text{-picNO})_6 \cdot (ClO_4)_2$ crystals. $[Cu(H_2O)_6]^{2+}$ octahedra are elongated along local z-axes and indicated a small orthorhombic distortion. The g-factors at 290 K are $g_z=2.0402$, $g_y=2.163$, $g_x=2.064$ for $(NH_4)_2Cu(BeF_4)_2 \cdot 6(H_2O)$ and $g_z=2.329$, $g_y=2.127$ and $g_x=2.069$ for $Cu(4\text{-picNO})_6 \cdot (ClO_4)_2$ The g-factors are temperature dependent in the both crystals but the principal axes directions are not affected by temperature and the trace of g^2-tensors are unchanged. The g(T) dependences were measured along principal x, y, z axes and are shown in Fig 1. Exchange coupling integrals, obtained by fitting the two-component spectra with theoretical spectrum, are unexpectedly small - $|J|=0$ for the first compound and $|J|=0.00065(8)$ cm^{-1} for the second one. This J-values are temperature independent in the temperature range 77-300K. Our results suggest that when the vibronic coupling operates in crystal the exchange coupling is very weak and temperature independent what is in contradiction with theory.
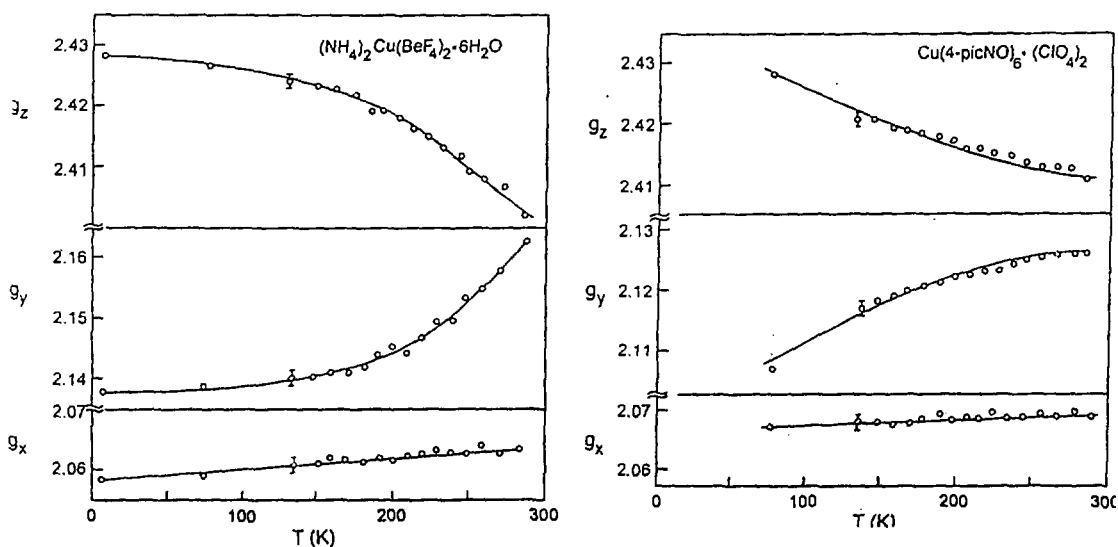
# ELECTRON SPIN ECHO ENVELOPE MODULATIONS OF SeO_3^- RADICALS IN $(NH_4)_3H(SeO_4)_2$ CRYSTALS

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Electron spin echo measurements were performed on SeO_3^- radicals ($S=1/2$) produced by X-ray irradiation in $(NH_4)_3H(SeO_4)_2$ single crystals. The two-pulse experiments were carried out on a BRUKER ESP 380E FT/CW EPR spectrometer with OXFORD CF935 flow helium cryostat. The length of pulse was fixed to 16 ns with started interpulse interval $\tau=144$ ns. The amplitude of pulses was adjusted to obtain the maximal echo amplitude. Measurements were performed with magnetic field direction close to the perpendicular orientation of radical g-tensor with magnetic field value fixed to 343 mT i.e. at central EPR line position. The 16 ns pulse with spectral width 2.23 mT allows to irradiate the whole central line. A monoexponential spin echo amplitude decay $V(t)=\exp(-2\tau/T_M)$ was observed in the temperature range 4.2 - 300 K with the phase memory time T_M value depending on temperature. The decay was modulated by at least three frequencies. A detailed analysis of ESEEM was performed at 121 K where the modulation pattern was most pronounced. In this temperature $T_M=350$ ns. The echo decay function was substracted to get the pure modulation pattern V_m. The Fourier transformation of V_m leads to the ENDOR-like spectrum. The line at 14.6 MHz and phase-reversed line at 29.2 MHz are fundamental and first harmonic proton frequencies, respectively. The similar but worse resolved doublet is clearly seen at low frequencies and can be identified as nitrogen ^{14}N frequencies with 1.05 MHz as the fundamental frequency. A detailed analysis of the modulation pattern and FT-spectrum was performed using $B_0=343$ mT, $T_M=350$ ns, $\omega_{proton}=14.6$ MHz $\omega_{nitrogen}=1.05$ MHz and neglecting nitrogen quadrupole interaction. The modulations are due to protons and nitrogens of the nearest NH_4 groups. The best fit was obtained, however, when only 8 protons and 2 nitrogens of the two nearest NH_4 groups located at distances 0.369 and 0.376 nm were taken with isotropic hyperfine interaction equal to $A^H_{iso}=0.9$ MHz for all protons and $A^N_{iso}=1.7$ MHz for all nitrogens.
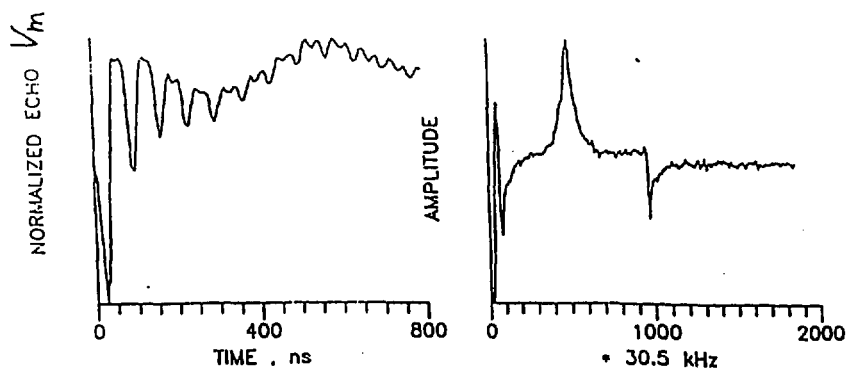
EPR OF SeO_3^- AND CrO_4^{3-} CENTERS IN $(NH_4)_3H(SeO_4)_2$ CRYSTALS

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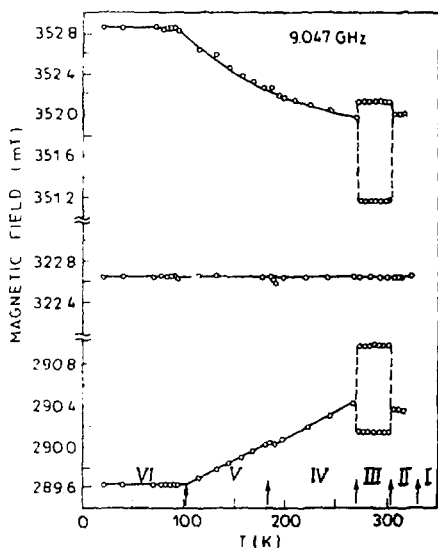Smoluchowskiego 17/19, PL-60179 Poznań, Poland

Paramagnetic centers SeO_3^- and CrO_4^{3-} were produced in single crystals of $(NH_4)_3H(SeO_4)_2$ by X-ray irradiation and then used as monitors of local molecular changes in the crystal phase transitions. The SeO_3^- radicals are unstable and vanish after few days. They vanish, moreover, rapidly with increasing temperature above 300 K. For this reason EPR spectra of SeO_3^- were used in studies of $(NH_4)_3H(SeO_4)_2$ crystal at low temperatures. Selenate ions are connected through the hydrogen bond into dimers $O_3Se-O-H...O-SeO_3$ and X-irradiation results in a breaking of the bridged Se-O bond thus in a destroying the dimer structure. The unpaired electron of SeO_3^- center is located primarily on a 3d orbital of Se atom and the center is sensitive to the environment what is observed by the hyperfine EPR structure of the ^{77}Se isotope. The following effects were observed:

- jump-like phase transitions at T=304 and T=275 K,
- continuous increase in the hyperfine splitting in the temperature range from 275 to 101 K,
- a new phase transition has been discovered at T=101 K.

These effects can be recognized in Figure 1.

CrO_4^{3-} radicals are produced by X-rays in $(NH_4)_3H(SeO_4)_2$ crystals doped with $(NH_4)_2CrO_4$. The unpaired electron of CrO_4^{3-} center is located in 3d-orbital of the Cr^{5+} ion. This paramagnetic center was used for monitoring by EPR the high temperature superionic phase transition of the crystal. We found it to be less sensitive to the structural changes.

INTERDIMER AND INTRADIMER EXCHANGE STUDIES BY EPR IN $Co(en)_3CuCl_5 * H_2O$
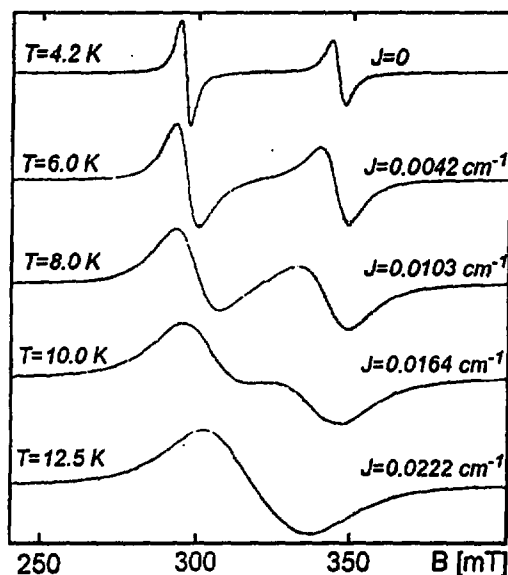
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The orthorhombic crystal structure consists of antiferromagnetically coupled bis(μ-chloro)-bridged dimers $[Cu_2Cl_8]^{4+}$ surrounded by diamagnetic $[Co(en)_3]^{3+}$ complexes, uncoordinated Cl⁻ and H_2O. Intradimer exchange coupling results in a singlet-triplet splitting $2J_0=-14.6$ cm⁻¹ which is temperature independent down to helium temperature [1]. EPR spectra indicate no zero-field splitting at room temperature and only two resonance lines from magnetically inequivalent dimers are resolved allowing to determine interdimer exchange integral $|J'|=0.0072$ cm⁻¹ at 292 K. The J'-value strongly decreases on cooling and under pressure [2]. Below 13 K the lines split into doublets (Fig.1) which can be identified as the fine structure lines from S=1. It is a result of a thermal depopulation of the excited tripled state leading to a continuous "magnetic dilution" of the spin system. It reduces an effective interdimer coupling and stabilize the S=1 state.

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ELECTRON SPIN ECHO MEASUREMENTS OF SPIN-LATTICE AND SPIN-SPIN RELAXATION OF SeO_3^- RADICAL IN $(NH_4)_3H(SeO_4)_2$ SINGLE CRYSTAL

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ESE measurements were performed on a pulse BRUKER ESP 380E FT/CW spectrometer in the temperature range 4.2 - 300 K. Electron spin echo decay shows modulations (ESEEM) due to a weak dipolar coupling of the SeO_3^- unpaired electron (S=1/2) to the protons and nitrogens of the neighbouring NH_4-groups. The modulations are shown in the insert of the left figure. Spin lattice relaxation time T_1 measured by the inversion-recovery method decreases on warming as a result of a direct relaxation process $(T_1^{-1} = a_1 T)$ below 30 K and Orbach-Aminov process above 30 K $(T_1^{-1} = a_2 cosech (\Delta/kT))$. The phase memory time T_M was determined from spin-echo amplitude decay in two-pulse experiments. The T_M-value varies from 178 ns to 596 ns depending on temperature (see right figure). Above 150 K T_M reflects T_1 temperature behavior, whereas below 150 K T_M is determined by SeO_3^- radical dynamics.
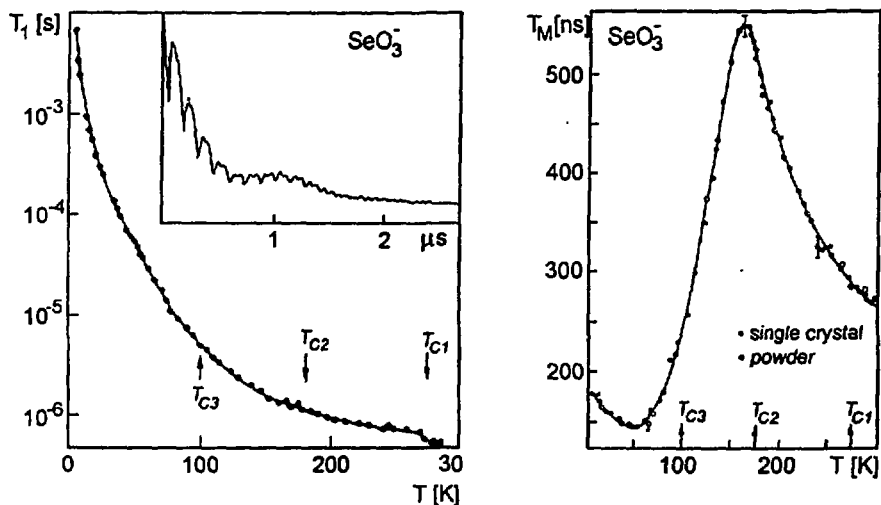
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INFLUENCE OF HYDROSTATIC PRESSURE ON THE PHASE TRANSITION IN $Ni(NH_3)_6I_2$ - EPR STUDIES

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Electron paramagnetic resonance techniques have been used to determine the phase transition temperature in $Ni(NH_3)_6I_2$ as a function of hydrostatic pressure. Measurements of the EPR lineshape versus temperature in the vicinity of the structural phase transition at 20 K were carried out using the new high pressure and low temperature system constructed at the Institute of Molecular Physics. The phase transition temperature T_c were determined from the sudden changes in width and amplitude of the EPR line.

Hydrostatic pressure shifts T_c to higher temperatures with a value of the pressure coeffcient $dT_c/dp=(11\pm2)$ K/GPa. The similar value of dT_c/dp was obtained by means of inelastic neutron scattering studies [1]. This result is discussed in connection with the Clapeyron-Clausius equation and explained on the rigid sphere model [2,3]. It was assumed that hydrostatic pressure changes the lattice constants and effective ionic radii in proportion to the presuure. The repulsion between I ions and rotating NH_3 groups is considered, too. Calculations of the dependence T_c as a function of lattice constant and pressure for the family of compounds $Me(NH_3)_6I_2$, where Me is a divalent metal ion, give satisfactory agreement with the experimental data.

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INTERACTION OF VANADIUM PENTOXIDE WITH H-ZSM-5
ZEOLITE INVESTIGATED BY EPR

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EPR spectroscopie has been used to study the interaction of vanadium pentoxide (2,5% and 5% wt.) with the H-ZSM-5 zeolite at various temperature(100-1100°C) in air, followed by evacuation of samples at 20°C. It appears that a part of the vanadyl ions resulted upon reduction of V_2O_5 oxide, moves predominantly into the zeolite cationic sites with several distorted octahedral symmetry, where as the other part remains on the surface of the zeolite crystals [1].

The degree of distortion of located complexes depends on the composition of the mixture and different treatment conditions (temperature and duration of treatment).

For H-ZSM-5/V_2O_5 calcined at 350-600°C a supplementary splitting in EPR spectrum has been found. The interaction of unpaired electron of vanadium ions with aluminium nuclei at the framework is not excluded [2].

Calcination of mixture at temperatures higher than 800°C determined a continuous decrease in EPR signal intensity, caused by the break-down of the framework structure. This conclusion is supported by our X-ray study.

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THE INFLUENCE OF SURFACE REACTIONS ON ORIGINAL ESR SIGNALS OF POWDERED SAMPLES Zn_3P_2.

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Zn_3P_2 is a promissing material as a new photovoltaic material. Its energy gap is 1.4 eV, near the optimum value for solar cells.

Preliminary investigations of Zn_3P_2 single crystals suggested two models of surface reactions [1]. On the other hand the original paramagnetic signals were observed in powdered samples [2]. As if the influence of surface reactions of air, water + air, annealing with phosphorus and heating at $500^{o}C$ under vacuum on the original ESR signals has been discussed.

Results: the original signals were very sensitive to these reactants and they depended on the type of samples (high or low resistivity). Generally, the presence of H_2O and evaporation at high temperature amplified the original signals. Annealing with phosphorus canceled the paramagnetic effects.

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EPR STUDIES OF REDUCED Zn-CHLORINS AND THEIR ISOTOPE SUBSTITUTED ANALOGS

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Contemporary investigations of complex biological processes show a tendency to the valid explanation of their mechanisms by using relatively simple model systems. Metallochlorins, because of their molecular structure similar to chlorophyll molecules, can be used as model systems in studies of photosynthesis. Radical ions are of particalar interest because of their role as intermediate products in reduction-oxidation processes. Results of redox transformation investigations can be also useful for understanding the drift mobility mechanism of electrons in biological systems.

This paper reports transformations of Zn-chlorin molecules into their mono-π-anions during contact of the metallochlorin solutions with Na and K metals. The studies were done for Zn- complexes of chlorins (ZnC), octaethylchlorins (ZnOEC) and their deuter and ^{15}N substituted derivatives. EPR and quantum chemical methods have been used to investigate the electronic structure of radical anions of the mentioned above complexes. Partially resolved hyperfine structure in EPR spectra of π-radical anions have been observed. Low symmetry of the chlorin molecules leads to a relatively large number of different groups of paramagnetic centres and the spectra become rather complex. Additional difficulties in analysis of the spectra are connected with the alternating linewidth that leads to a slight asymmetry of the EPR lines. Parameters of the EPR spectra were obtained by using optimization procedures in the Fourier domain. Spin density calculations were done by using the INDO method. The density of the unpaired electron was found to be distributed predominantly along the 18-membered conjugation pathway. The values of the spin densities close to zero at outermost carbon atoms of the hydrogenated rings are reflected at the pyrrole rings placed opposite the hydrogenated ones. Proton and nitrogen hyperfine splittings, calculated on the basis of the spin density distribution, were compared with those derived from the experimental spectra. A good correlation between experimental and theoretical data was obtained.

ELECTRON SPIN RESONANCE OF RADICALS AND METAL COMPLEXES

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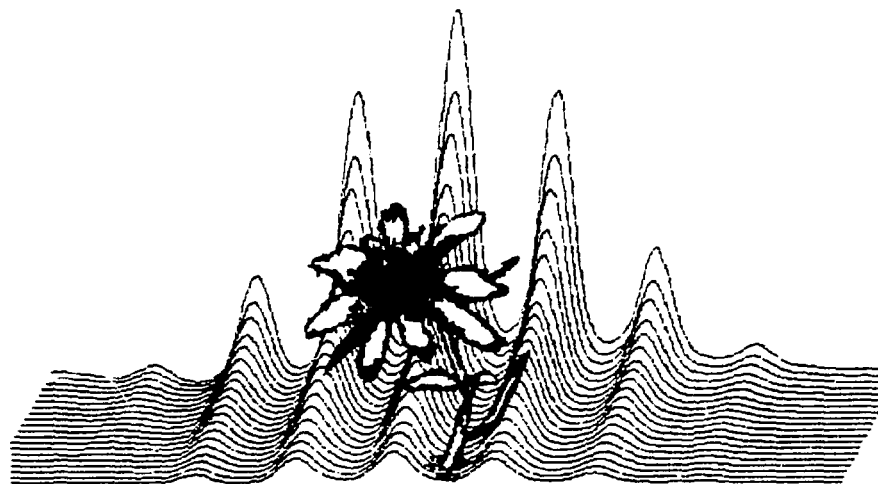Dorodna 16
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