firms the presence of REE in the surface layer of modified sample. After the oxidation process in the both cases (initial and alloyed with REE material), the lower level of spectra of oxidized samples was observed. This result is connected with scale presence at the surface.

In conclusions: oxide scales formed on DPE treated samples are more fine-grained, compact and adheres better that those formed on the untreated ones, structure of grains observed at the oxide layer in the case of initial and modified materials was determined as the spinel type, chromium concentration is highest in the upper part of the scale, what confirms the theory of chromium diffusion from the bulk to the surface of material during oxidation process of chromium alloys.

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# STRUCTURAL STUDIES IN Li(I) ION COORDINATION CHEMISTRY

**Wojciech Starosta, Janusz Leciejewicz**

Coordination chemistry of the lithium(I) ion is an interesting field of research activity since its complexes, apart from their biological significance, can be potential precursors in a search for new coordination polymers (metal-organic frameworks – MOF) with many important practical applications. One can expect that the Li(I) ion which exhibits coordination numbers from 4 to 6 will form with multidentate ligands coordination polymers with a diverse range of topologies and conformations. Such multidentate ligands are represented, among others, by azine carboxylic acids which, besides potentially bidentate carboxylic groups, use hetero-ring nitrogen atoms to chelate metal ions.

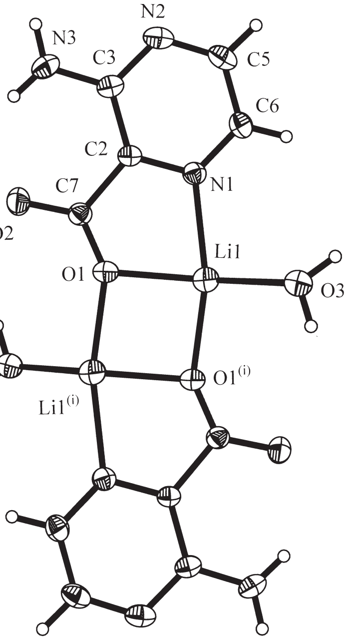

Fig.1. Structural unit of lithium aminopyrazinate with atom labels. Displacement ellipsoids are drawn at 50% probability level.

Polymeric structures with a large number of molecular pattern types have been so far reported for alkaline earths, 3-d transition metal, lanthanides, thorium and uranium complexes with pyridine, pyrazine, pyridazine and pyrimidine carboxylate ligands. On the other hand, only limited information is available on crystal structures of lithium(I) ion compounds so that a systematic study has been undertaken to determine crystal structures of its complexes with the above ligands.

### Part 01. *catena*-Poly[[bis(μ-3-aminopyrazine-2-carboxylato)-$\kappa^{3}N^{1},O{:}N^{1},O$)-dilithium]-di-μ-aqua]

The structure of a lithium(I) complex with 3-aminopyrazine-2-carboxylate and water ligands is composed of centrosymmetric dinuclear units, in which each of two Li(I) ions is chelated by a ligand *via* a N,O bonding group. Its O atom acts as bidentate and bridges the other Li(I) ion (Fig.1). The dinuclear unit is nearly planar with r.m.s. of 0.0125(2) Å. The Li(I) ion is also coordinated by two water O atoms, which bridge dinuclear units into molecular columns along two bridging path-

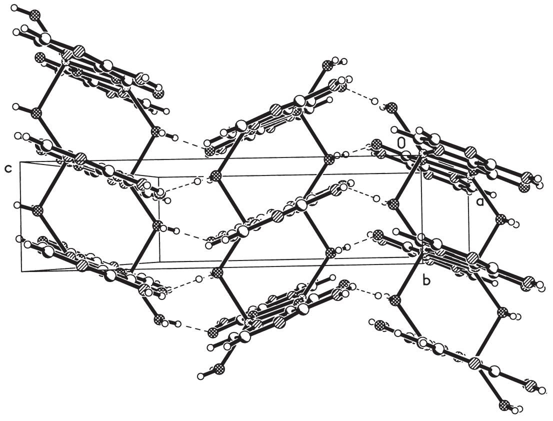

Fig.2. Packing of molecular columns in the structure of lithium aminopyrazinate.

ways propagating in the *b*-axis direction (Fig.2). The coordination geometry of the Li(I) ion is trigonal bipyramidal, with equatorial plane formed by O1, O3, O3$^{(ii)}$ and with N1 and O1$^{(i)}$ at the axial positions. The Li-O and Li-N bond distances and bond angles are typical of Li(I) complexes with carboxylate ligands. The columns are linked by a network of hydrogen bonds, in which water O atoms are donors and non-bonded carboxylate O atoms in adjacent columns act as acceptors. A weak hydrogen bond links an amino N atom with a hetero-ring N atom in an adjacent column. An intramolecular hydrogen bond, which operates between the amino N atom and the non-bonding carboxylate O2 atom is also observed [1].

**Part 02. Bis[[6-carboxypyridazine-3-carboxylato-$\kappa^2N^2,O^3$lithium]-$\mu$-pentahydrogen-dioxygen(1+)]**

The structure of a lithium(I) complex with pyridazine-3,6-dicarboxylate and water ligands is composed of monomers in which a Li(I) ion located in a centre of symmetry is coordinated by two N,O bonding groups donated by two symmetry related ligand molecules and by two symmetry related aqua O atoms in axial positions (Fig.3). The coordination is slightly distorted octahedral. The ligand molecules and a Li(I) ion are coplanar with r.m.s. of 0.0047(2) Å. The second carboxylic group of each ligand remains protonated and makes an angle of 5.9(1)$^o$ with the pyridazine plane. Bond lengths and angles within the ligand ring are close to those reported earlier for both structures of the parent acid. A proton in a special position located between coordinated water molecules is clearly observed on Fourier maps. It maintains the charge balance within monomers and bridges them by short symmetric hydrogen bonds of 2.518(3) Å ($d_{O6\text{-}H63}$ = 1.26 Å, $d_{H63\text{-}O6(i)}$ = 1.26 Å) with O6-H63-O6$^{(i)}$ angle of 180$^o$ to form catenated ribbons (Fig.4). The latter are held together *via* hydrogen bonds with distances in the range from 2.525(2) Å to 2.996(2) Å in which water and protonated carboxylate O atoms act as donors and carboxylate O atoms and hetero-N atoms in adjacent ribbons are as acceptors [2].

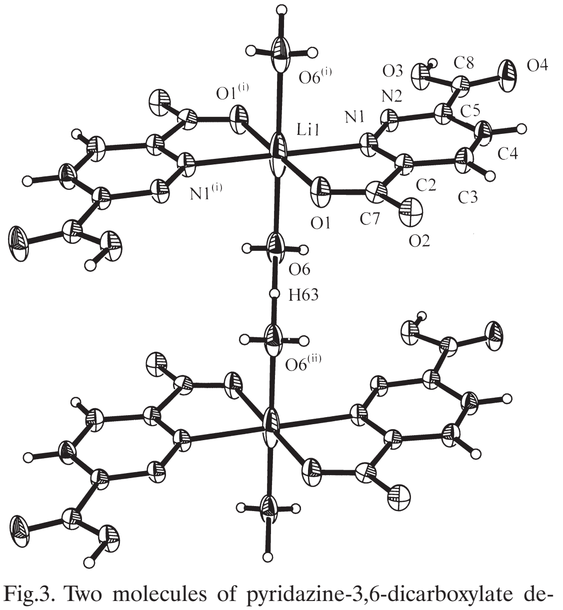

Fig.3. Two molecules of pyridazine-3,6-dicarboxylate dehydrate linked by a symmetrical hydrogen bond with atom labelling scheme and 50% probability displacement ellipsoids.

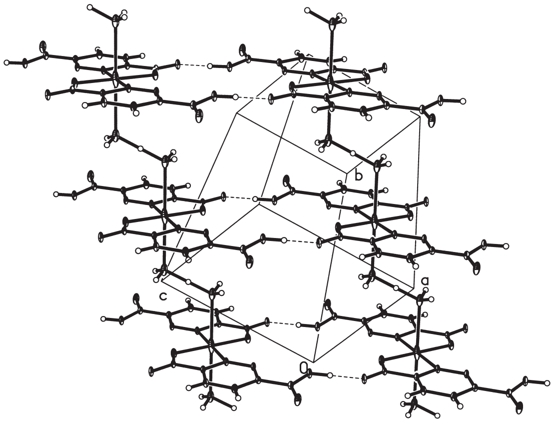

Fig.4. Molecular chains in the structure of pyridazine-3,6-dicarboxylate dehydrate.

**Part 03.** ***catena*-Poly[[bis(($\mu_2$-aqua)(2,6-dicarboxypyrazine-3,5-dicarboxylato-N,O,O')-Lithium(I)] [triaqua-lithium(I)]]**

The asymmetric unit cell of the title compound contains two symmetry independent Li1 and Li2 atoms positioned on a mirror plane with y = 3/4. Pyrazine-ring N1 and N2 atoms and coordinated water O5, O7, O8 atoms are also positioned on this plane (Fig.5). The Li1 ion is chelated by the N1, O4, O4$^{(i)}$ ligand bonding moiety with typical Li-N and Li-O bond distances of 1.126(4) Å and 2.120(2) Å, respectively and two bridging aqua O7 and O8 atoms ($d_{Li1\text{-}O7}$ = 2.069(5) Å, $d_{Li1\text{-}O8}$ = 1.994(4) Å). The O4 and O4$^{(i)}$ atoms are at opposite apices of a distorted trigonal bipyramid; its equatorial plane is composed of coplanar Li1 ion, hetero-ring N1 atom and the bridging O7 and O8 atoms. Pyrazine-ring atoms are coplanar (r.m.s. 0.0009(1) Å); their plane makes an angle of 90$^o$ with the

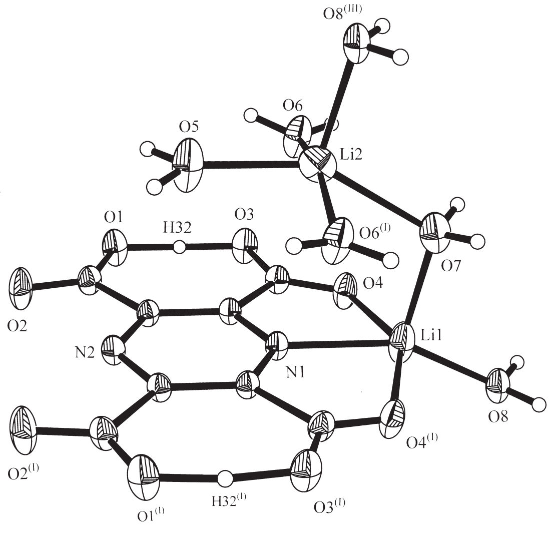

Fig.5. A structural unit of lithium pyrazine tetracarboxylate with atom labels and 50% probability displacement ellipsoids.

equatorial plane. Carboxylic groups C6/O1/O2 and C5/O1/O2 make angles with pyrazine ring of 1.45(13)° and 4.69(14)°, respectively. Bond distances and bond angles within the ligand molecule do not differ from those observed in other complexes with the title ligand. A proton situated between carboxylate O3 and O1 atoms, clearly visible on the Fourier map, forms an intra-molecular hydrogen bond of 2.389(3) Å and O3-H-O1 angle of 173°. The charge of the ligand is thus (2-). Since it is compensated by (1+) charge of the Li1 ion, the resulting anion has a charge of (1-). On the other hand, the Li2 ion as coordinated only by aqua O atoms, retains its charge of (1+). Thus, the ribbon is built of $[Li(C_8H_2N_2O_8)(H_2O)_2]^{1-}$ anions and $[Li(H_2O)_4]^{1+}$ cations bridged by aqua O7 and O8 atoms belonging to coordination spheres of both Li ions (Fig.6). The bridging pathway propagates on the mirror plane with Li1-O7-Li2 angle of 111.30(16)° and Li1-O8-Li2$^{(iii)}$ angle of 104.02(19)°. The coordination environment of the Li2 ion is composed of five aqua O atoms, two of them O7 and O8 are bridging it with the Li1 ions. The Li2 ion, O5, O7 and O8 atoms are coplanar and form an equatorial plane of a distorted trigonal bipyramid with O6 and O6$^{(i)}$ atoms at opposite apices. Li-O bond distances within this coordination polyhedron are in the range from 1.940(1) Å to 2.071(4) Å, the Li2-O7 bridging bond distance amounts to 2.383(5) Å. Coordinated water O atoms are as donors in hydrogen bonds to carboxylate O atoms in adjacent ribbons which act as acceptors [3].

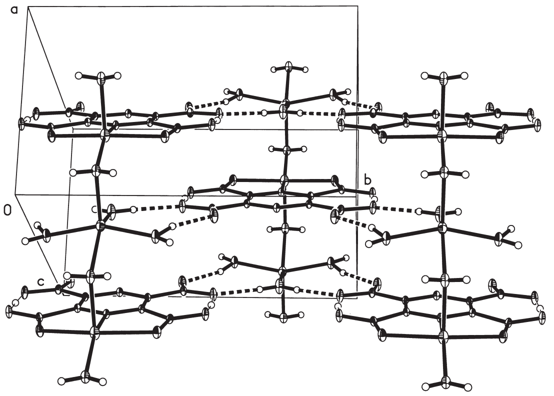

Fig.6. A packing diagram of the lithium pyrazine tetracarboxylate structure.

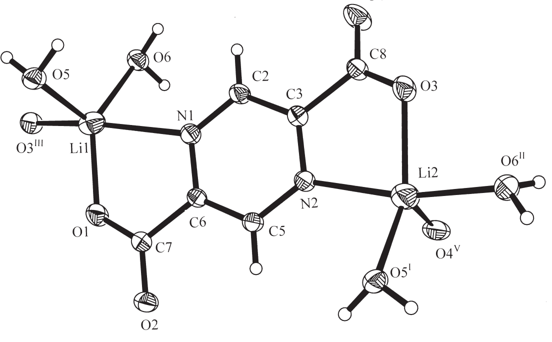

Fig.7. A structural unit of lithium pyrazine-2,5-dicarboxylate with atom labelling scheme and 50% probability displacement ellipsoids.

### Part 04. Poly[di-μ-aqua-$\mu_4$-(pyrazine-2,5-dicarboxylato)-dilithium(I)]

The asymmetric unit cell of the title compound contains a ligand dianion, two symmetry independent Li1 and Li2 ions and two symmetry independent water O5 and O6 atoms (Fig.7). The ligand molecule bridges Li1 and Li2 ions using both its *N,O*-chelating sites; the carboxylate O2 atom remains coordination inactive. The O3 atom, which acts as bidentate bridges the Li2 ion to the adjacent Li1$^{(ii)}$ ion and with the coordinated water O6 atom gives rise to a molecular chain in which metal ions are bridged by the ligand on one side and two O atoms on the other. Water O5 atoms link the chains into molecular layers (Fig.8). The latter, bridged by carboxylate O4 atoms, which link the ligands with Li2$^{(iv)}$ in adjacent layers give rise to a three-dimensional framework. The coordination environment of the Li ion is composed of N1, O5, O3$^{(iii)}$ atoms; they form together with the metal ion an equatorial plane (r.m.s. of 0.0021(1) Å) of a distorted trigonal bipyramid; the O1 and O6 atoms are at its opposite apices. The Li2 ion together with coordinated O3, O4$^{(v)}$ and O5$^{(i)}$ forms an equatorial plane (r.m.s. of 0.0307(1) Å) of a distorted trigonal bipyramid, N2 and O6$^{(ii)}$ are at its apices. The observed Li-O bond distances fall in the range from 1.598(3) Å to 2.131(3) Å observed also in other Li complexes with pyrazine carboxylate and water ligands. The O4-Li2$^{(iv)}$ bond distance is 2.332(4) Å; the Li1-N1 and Li2-N2 bond lengths are 2.360(3) Å and 2.129(3) Å, respectively. The pyrazine ring is planar with r.m.s of 0.0094(1) Å, the carboxylate C7/O1/O2 and C8/O3/O4 groups make with it dihedral angles of 0.55(20)° and 18.68(17)°, respectively. Bond distances and bond angles within the pyrazine ring match those observed in the structure of the parent acid. Hydrogen bond network is composed of coordinated water molecules which are as donors and carboxylate O atoms which act as acceptors [4].

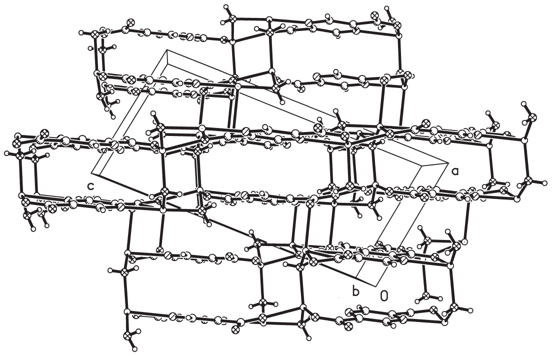

Fig.8. A fragment of a molecular layer.

### Part 05. *trans*-[diaqua-(pyridazine-3-carboxylato-*N,O*)]lithium(I)

The crystal structure of the title compound contains discrete mononuclear molecules in which each Li(I) ion is chelated by one pyridazine-3-carboxylate ligand molecule *via* its N,O bonding group and two water molecules arranged in *trans* mode (Fig.9). The relevant Li-O and Li-N bond distances are close to those reported for other Li(I) complexes with diazine carboxylate ligands. The coordination geometry of the metal ion is distorted tetrahedral. The pyridazine ring is planar. The carboxylate group C7/O1/O2 makes with it a dihedral angle of 2.9(1)°. The planes Li/N2/O1 and Li/O3/O4 make a dihedral angle of 97(2)° each to the other.

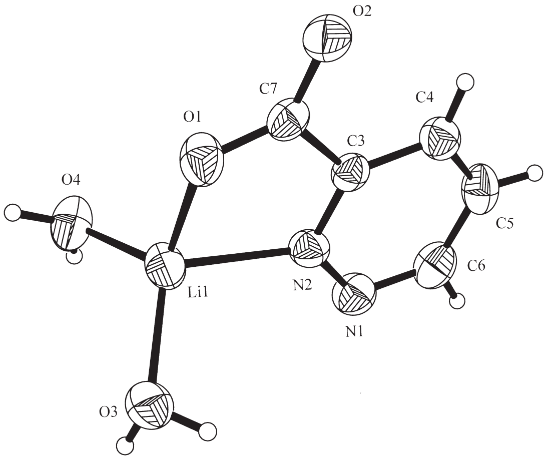

Fig.9. A molecule of lithium pyridazine-3-carboxylate dihydrate with atom labelling scheme and 50% probability displacement ellipsoids.

A network of hydrogen bonds in which water O atoms act as donors and carboxylate O atoms as acceptors is responsible for the cohesion of the crystal (Fig.10).

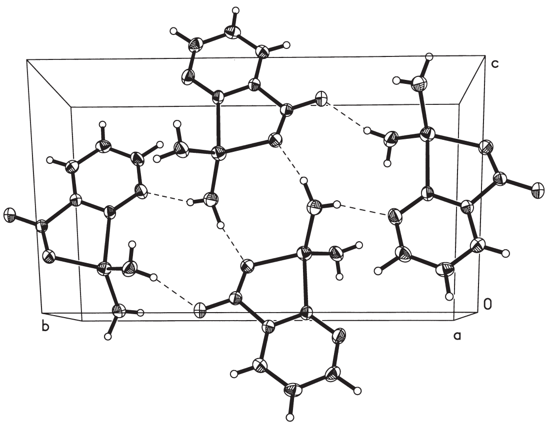

Fig.10. A packing diagram of the lithium pyridazine-3-carboxylate structure.

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# NEUTRON ACTIVATION AND PETROGRAPHIC ANALYSIS OF OCHRE IN SELECTED 15TH-18TH CENTURIES ICONS FROM SOUTH-EASTERN POLAND

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Iron oxide natural pigments of various compositions are the most commonly used pigments on icons from Byzantine, post-Byzantine, Russian and Ukraine Orthodox painting workshops. The purpose of the work was to analyse ochre and other iron oxide pigments from icons of 15th-18th centuries, collected at the Orthodox Art Department at the Castle Museum in Łańcut.

The samples were analysed by neutron activation analysis (NAA) and by thin cross-section petrography; scanning electron microscopy (SEM) was also used to confirm obtained data [1-4]. The main aim was to underline the mineralogical and chemical differences of studied pigments and establish connection between local ochre sources. The clustering analysis using STATISTICA (StatSoft) program was carried out to identify the similarity degree of analysed objects.

The samples for analysis were collected from eleven icons dated 15th-18th centuries. For comparison purpose, 12 inorganic commercially available pigments (George Kremer) and 6 samples of Carpathian ochre collected from exposure located in Czerwonki Hermanowskie near Tyczyn were also used. Tables 1 and 2 include description of the collected samples.

The examples of the cross-sections of samples collected from the marked regions of icon *Pantocrator and the Virgin Panagia* are presented in Fig.1.

The element characterization of studied earth pigments was carried out by instrumental neutron activation analysis (INAA). The twenty eight elements were selected for multi-parameter statistical analysis aimed at idntifying the degree of similarity of the analysed samples. The STATISTICA 8 (StaSoft) program was carried out to identify the similarity degree of analysed objects and principal components analysis. The statistical analysis was performed for standarized and logarithmic variables. Results of this analysis are presented in Fig.2, which clearly show division into groups closely related to origin of the tested samples.