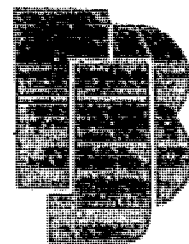


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THE PHYSICO-CHEMICAL PROPERTIES
OF THE LANTHANIDE COMPLEXES
WITH THENOYLTRIFLUOROACETONE

II. Infra-red spectra of the Lanthanide
complexes with TTA in the region
from 1700 to 400 cm^{-1}

S. Lis

WARSZAWA

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INSTITUTE OF NUCLEAR RESEARCH

THE PHYSICO-CHEMICAL PROPERTIES OF THE LANTHANIDE COMPLEXES
WITH THENOYLTRIFLUOROACETONE

III. Infra-red spectra of the lanthanide complexes with TTA
in the region from 1700 to 400 cm^{-1}

WŁASNOŚCI FIZYKO-CHEMICZNE KOMPLEKSÓW LANTANOWCÓW
Z TIENOILOTRÓJFLUOROACETONEM

III. Widma w podczerwieni kompleksów lantanowców z TTA
w obszarze 1700-400 cm^{-1}

ФИЗИКОХИМИЧЕСКИЕ СВОЙСТВА КОМПЛЕКСОВ ЛАНТАНИДОВ
С ТЕНОИЛТРИФТОРАЦЕТОНОМ

III. Инфракрасные спектры комплексов лантанидов с ТТА
в области 1700-400 cm^{-1}

Stanisław Lis

Abstract

The i.r. spectra of the $\text{Ln}(\text{TТА})_3 \cdot n\text{H}_2\text{O}$ complexes and the dehydrated complexes of Nd, Gd and Lu with TТА as well as the $\text{Al}(\text{TТА})_3$ and $\text{Fe}(\text{TТА})_3$ complexes have been studied in the range $1700\text{--}400\text{ cm}^{-1}$. All spectra of the investigated complexes in the range $1700\text{--}700\text{ cm}^{-1}$ are similar. The significant differences between Ln complexes and those of Al, Fe occur in the range $700\text{--}400\text{ cm}^{-1}$. It has been found that the wave number of the band appearing in the Ln complexes in the vicinity of 490 cm^{-1} increases monotonically with the atomic number. The behaviour of the ν_2 and rocking bands of hydrating water molecules has been discussed. The $1600\text{--}1500\text{ cm}^{-1}$ range was analysed in detail and also the majority of the absorption bands in the remaining part of the spectrum has been assigned.

(auth)

Streszczenie

Zbadano widma w podczerwieni kompleksów $\text{Ln}(\text{TТА})_3 \cdot \text{H}_2\text{O}$, odwodnionych kompleksów Nd, Gd i Lu oraz kompleksów $\text{Al}(\text{TТА})_3$ i $\text{Fe}(\text{TТА})_3$ w obszarze $1700\text{--}400\text{ cm}^{-1}$. Widma w podczerwieni wszystkich przebadanych związków są w zakresie $1700\text{--}700\text{ cm}^{-1}$ podobne. Istotne różnice występują między widmami kompleksów Ln oraz Al i Fe w obszarze $700\text{--}400\text{ cm}^{-1}$. Stwierdzono, że liczba falowa występującego w kompleksach lantanowców pasma w pobliżu 490 cm^{-1} wykazuje monotoniczny wzrost ze zmianą liczby atomowej. Przedyskutowano zachowanie się pasma ν_2 i libracyjnego dla wody występującej w kompleksach, przeanalizowano szczegółowo obszar $1600\text{--}1500\text{ cm}^{-1}$ oraz przyporządkowano większość pasm absorpcji w pozostałej części widma.

Резюме

Исследованы ИК-спектры комплексов $\text{Ln}(\text{TТА})_3 \cdot n\text{H}_2\text{O}$, дегидратированных комплексов Nd, Gd и Lu а также комплексов $\text{Al}(\text{TТА})_3$ и $\text{Fe}(\text{TТА})_3$ в области $1700\text{--}400\text{ cm}^{-1}$. Спектры всех изучаемых комплексов в области $1700\text{--}700\text{ cm}^{-1}$ были похожи друг на друга. Значимые различия спектров наблюдались в области $700\text{--}400\text{ cm}^{-1}$. Показано, что положение полосы при около 490 cm^{-1} , выступающей в спектрах комплексов лантанидов, монотонно смещается с увеличением атомного числа элемента, Z. Рассмотрено поведение полос ν_2 и либрационной молекул воды в комплексах. Подробно проанализована область $1600\text{--}1500\text{ cm}^{-1}$. Определено большинство абсорбционных полос в остальной части спектров.

This paper is a continuation of studies concerning the physico-chemical properties of lanthanide complexes with TTA. The preparation of the complexes of the general formula $\text{Ln}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ has been described previously^{1/}. The composition of these compounds, their thermal properties and solubility of the hydrated and dehydrated complexes in inert solvents has also been discussed in detail^{2/}. The infra-red spectra of the $\text{Ln}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ complexes provide new information concerning the structure of these compounds and give a basis for the discussion of the hydrogen bonding in these complexes.

There is a great number of papers on the infra-red spectra of complexes of different metals with different β -diketones, but most of them deal with the compounds with acetylacetonone /AA/. There are, only few references to the i.r. spectra of complexes of metals with TTA. Heltsclaw and Collman^{3/} have determined the spectra of several β -diketones /i.e. TTA/ and their copper compounds in the range 4000-600 cm^{-1} reporting, however, neither the wave numbers nor the recorded spectra. Ferraro and Healy^{4/} have discussed the i.r. spectra of compounds of the type $\text{M}_x(\text{TTA})_y\text{S}_z$, where $\text{M} = \text{Nd}, \text{Th}, \text{UO}_2$ and S is the neutral ligand from the group of organophosphorus compounds /e.g. TBP/. The latter authors claimed that the neutral organophosphorus ligand in the $\text{M}_x(\text{TTA})_y\text{S}_z$ complexes causes the splitting of the carbonyl peak at 1600 cm^{-1} into two peaks, indicating that one of the TTA molecules acts as a monodentate ligand in these complexes. The peak at higher frequency, viz., 1622 cm^{-1} was ascribed to the free ketonic carbonyl function which would mean that one of the TTA molecules is monodentate. However, Li et al.^{5/} have shown that the splitting of the carbonyl band at 1600 cm^{-1} is not a conclusive proof for the presence of a monodentate diketone grouping since even in

some simple $M(\text{TTA})_2$ compounds the band is split. In addition, Lewis et al.^{6/} have shown that one of the criteria for the presence of monodentate β -diketone groupings in platinum complexes is the presence of a band at about 1690 cm^{-1} due to a free ketonic carbonyl function. Baskin and Krishna Prasad^{7/} have reported the spectra of U^{4+} , Th^{4+} , Zr^{4+} , Hf^{4+} , Ce^{4+} complexes with TTA in the range $1800-500 \text{ cm}^{-1}$. The i.r. spectra of the compounds investigated show strong similarities with little variation in the frequencies of their absorption bands. Purushotham et al.^{8/} have discussed the i.r. spectra of the anhydrous complexes of some lanthanides with TTA and tried to assign some of the absorption bands to particular functional groups in the compound molecule. Charles et al.^{9/} have reported the main absorption bands for $\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}$. Ohwada^{10/} has analysed the i.r. spectra of TTA in the range $3120-1105 \text{ cm}^{-1}$ and discussed the i.r. spectra of some of the metal complexes with TTA in the range $1700-1300 \text{ cm}^{-1}$. Noskova et al.^{11,12/} have analysed the spectra of some metal complexes and the spectrum of TTA in the range $3800-230 \text{ cm}^{-1}$ and on the basis of this investigations arrived at the conclusion that there is no distinct delocalization of the π -electrons in all the compounds studied when the substituents /trifluoromethyl and thiophene/ are introduced into the AA molecule.

The i.r. spectra of the hydrated and dehydrated complexes of all lanthanides with TTA have, however, not yet been investigated.

EXPERIMENTAL

The preparation of complexes, the results of elemental analysis and of water titration by the K.Fischer method have been described in the previous paper^{1/}. The i.r. spectra in the range $1700-400 \text{ cm}^{-1}$ were recorded with the UR-10

spectrophotometer working in a two-beam compensated system. In the range 700-400 cm^{-1} a KBr crystal and in the range 1700-700 cm^{-1} a NaCl crystal were used. Depending on the range, KBr or NaCl cuvettes were used. The measured samples were prepared as mulls in nujol or hexachlorobutadiene. The samples of dehydrated complexes have been obtained by heating small amounts of the complexes at 107°C and grinding with nujol or hexachlorobutadiene in a dry glove box. The spectrophotometer performance was controlled by recording the standard spectrum of polistyrene.

RESULTS AND DISCUSSION

The i.r. spectra of the hydrated $\text{Ln}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ complexes of all lanthanides /excluding Pm/ in the range 1700-700 cm^{-1} are very similar to each other. There are, however, substantial differences in the range 700-400 cm^{-1} .

THE RANGE 700-400 cm^{-1} . The i.r. spectra of the TTA and hydrated $\text{Ln}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ complexes obtained under similar conditions have some absorption bands at the same frequencies /Tab.I, Fig.1/. The bands in the vicinity of 460, 520, 563, 580, 605, 643, 683 cm^{-1} occur in the spectra of both TTA and hydrated complexes. The new bands in the hydrated complexes not present in TTA are the 490 and 694 cm^{-1} bands. The 490 cm^{-1} band changes its position when passing from the La complexes /489 cm^{-1} / to the Lu-complexes /503 cm^{-1} /, the 694 cm^{-1} peak maintaining its constant position. In the case of TTA, a distinct shoulder appears at 470 cm^{-1} , absent from the spectra of hydrated complexes. Also a peak at 559 cm^{-1} can be observed, which in the case of hydrated complexes appears at 563 cm^{-1} as a slightly marked shoulder.

The comparison of the spectra in the range 700-400 cm^{-1} of hydrated complexes of different lanthanides leads to the

conclusion that the spectra from La to Tm are identical except for the band near 490 cm^{-1} , which shifts to higher wave numbers with increasing Z. The spectra of Yb and Lu complexes being similar between themselves differ markedly from those of other lanthanides. In the spectra of Yb and Lu complexes there is a weak band at 475 cm^{-1} absent from the spectra of lighter lanthanides, whereas the 694 cm^{-1} band occurring as a clearly visible peak in La-Tm spectra can be seen in Yb and Lu spectra only as a slightly marked shoulder.

As far as the dehydrated complexes are concerned the spectra of the Nd, Gd and Lu complexes only have been recorded /Tab.II, Fig.2/. The spectra of the hydrated and the dehydrated complexes of Nd and Gd differ in two points: the intensity of the band at 460 cm^{-1} is much higher for the dehydrated complexes, whereas the band at 694 cm^{-1} , which exists as a distinct peak in the hydrated complexes, occurs in the dehydrated complexes as a slightly marked shoulder. In the case of the Lu complex the bands, which in the hydrated complex appear at 460 and 475 cm^{-1} , are shifted to 453 and 464 cm^{-1} and their intensity is increased considerably.

In the spectra of the dehydrated Lu complex two bands at 425 and 535 cm^{-1} can be found, which are absent from the spectra of the dehydrated complexes of Nd and Gd.

It follows that two absorption bands are particularly interesting in the range $700-400\text{ cm}^{-1}$: the 459 cm^{-1} (La) - 503 cm^{-1} (Lu) band and the 694 cm^{-1} band. Because the band near 490 cm^{-1} shifts to higher wave numbers with increasing Z and because it does not exist in TTA and in $\text{Al}(\text{TTA})_3$ and $\text{Fe}(\text{TTA})_3$ complexes /Tab.III, Fig.3/, the conclusion can be drawn that this vibration contains, as a component, a stretching vibration of the Ln-O /ligand/ group. The relation between Ln-O vibration frequency and the atomic number of the lanthanides for the investigated complexes is shown

in Fig.4. This band occurs both in the hydrated and dehydrated complexes. For compounds of the type $\text{Ln}(\text{AA})_3$ Misumi and Iwasaki^{13/} report the values 420-432 cm^{-1} /Pr-Er/ as stretching vibration of the Ln-O group, whereas Liang et al^{14/} ascribe the band near 410 cm^{-1} in the $\text{Eu}(\text{AA})_3 \cdot 2\text{H}_2\text{O}$ complex to a complicated mode involving the Eu-O stretch. In another paper Liang et al.^{15/} ascribe the band occurring in the vicinity of 400 cm^{-1} in the complexes $\text{Eu}(\text{TFAA})_4 \cdot \text{DMA}$, $\text{Eu}(\text{BTTA})_4 \cdot \text{DMA}$, $\text{Eu}(\text{RA})_4 \cdot \text{Pip}$ and $\text{Eu}(\text{DBM})\text{Pip}$ to a complicated mode involving the Eu-O stretch. In the case of the $\text{Al}(\text{TTA})_3$ and $\text{Fe}(\text{TTA})_3$ complexes the band at 520 cm^{-1} was ascribed by Noskova^{11/} to the $\nu(\text{M-O})$ and in-plane deformation vibration of the chelate ring.

The 694 cm^{-1} band is present in the hydrated complexes within the series La-Tm. The Yb and Lu complexes which contain one molecule of water have only a slightly marked shoulder in this region. There is no counterpart of this band in the TTA and anhydrous complexes of $\text{Al}(\text{TTA})_3$ and $\text{Fe}(\text{TTA})_3$. It seems therefore that the band at 694 cm^{-1} present in the hydrated complexes containing more than one molecule of water, should be assigned to the Ln-OH₂ rocking mode. The relatively weak intensity of this band seems to confirm the correctness of such an assignment^{16/}. In the hydrated sulphates of lanthanides the Ln-OH₂ rocking vibrations appear near 750 cm^{-1} and their wave numbers increase slightly with Z^{17/}. Assuming therefore, that the strength of hydrogen bonding in these salts does not change with Z, the increase in the wave number of the Ln-OH₂ rocking vibration suggests an increase in the coordination strength of water molecules. The lower value of the Ln-OH₂ rocking vibrations in the discussed lanthanide complexes can be attributed, assuming a similar Ln-OH₂ distance, to weaker hydrogen bonding of water molecules in $\text{Ln}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ complexes^{18,19/} as compared to the hydrated sulphates.

The remaining bands occurring in TTA, and in the hydrated and dehydrated complexes at the same or slightly shifted wave numbers can be ascribed to the vibrations of substituents and chelate ring. The bands 563 and 605 cm^{-1} belong to the out-of-plane and in-plane bending vibrations of C=C in the thiophene ring, respectively^{20-24/}. The band at 580 cm^{-1} can be assigned to the deformation mode of CF_3 group observed in many fluorinated β -diketones^{15,25-27/}. This assignment is supported by the fact that the complexes with AA and thiophene molecule do not absorb in this region. The bands 520 and 683 cm^{-1} are easily interpreted as the in-plane and the 643 cm^{-1} band as the out-of-plane deformation vibrations of the chelate ring^{15,25,28-30/}. Taking into account the fact that most of the vibrations below 700 cm^{-1} are more or less coupled with the M-O stretching mode^{31/}, the bands 643 and 683 cm^{-1} which shift when passing from La to Al and Fe complexes seem to contain as a component the stretching vibration of the Ln-O group.

THE RANGE 1700-700 cm^{-1} . The i.r. spectra of the hydrated lanthanide complexes with TTA are very similar in this range /Tab.IV, Fig.5/. Slight differences occur only in one region: the complexes of La to Eu /inclusive/ have only one absorption band near 1300 cm^{-1} , whereas the complexes of Gd to Lu, besides the 1305-1310 cm^{-1} band analogous to that in the light lanthanides, have a poorly resolved peak at 1295 cm^{-1} . The greatest differences between TTA and hydrated complexes, neglecting the small differences at lower frequencies, exist in the range 1600-1500 cm^{-1} . In this range TTA has two clear absorption bands: the first one, very broad, at 1606 cm^{-1} with a shoulder at 1635 cm^{-1} and the second, poorly shaped at 1525 cm^{-1} . In the case of hydrated and dehydrated lanthanide complexes with TTA there are four distinctly marked absorption bands at 1605-1610, 1585, 1540

and 1515 cm^{-1} . In the case of TTA the very broad band 1606-1635 cm^{-1} is undoubtedly the superposition of the vibrations: $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ of the chelate ring and of the stretching vibration of the thiophene ring. The interpretation of the four absorption bands of the complexes in the range 1600-1500 cm^{-1} can be based on the following premise: all metal complexes with AA have, in principle, two absorption bands in the range 1600-1500 cm^{-1} , the first at higher wave number can be assigned mainly to the $\nu(\text{C}=\text{O})$ vibration and the second at lower wave number can be attributed to the $\nu(\text{C}=\text{C})$ vibration of the chelate ring^{15,29-38/}. The distance between them is 50 cm^{-1} or more. On the other hand, for metal complexes with β -diketones other than AA /e.g. BA, DBM, TTA/ Haltzelaw^{3/} and Subramanian et al.^{39/} have found that in the range 1650-1500 cm^{-1} /besides those two absorption bands namely $\nu(\text{CO})$ and $\nu(\text{CC})/$ some other peaks exist, which should be attributed to vibrations of functional groups such as phenyl, furan and thiophene rings.

It seems therefore to be no doubt that in the complexes with TTA the band with the highest wave number (1605 cm^{-1}) and with the strongest intensity results mainly from the stretching vibration of the $\text{C}=\text{O}$ group of ligand (νCO) similarly to the band at 1540 cm^{-1} which can be derived from $\nu(\text{C}=\text{C})$ of the ligand. The two remaining peaks namely 1585 and 1515 cm^{-1} should be assigned to the stretching vibrations of the aromatic substituent ring^{8,11,21,23,40,41/}. The occurrence in TTA, of only two absorption bands and of four bands in the Ln complexes can be explained most likely by the lower symmetry of the complexes in comparison to that of TTA. The change into lower symmetry removes the degeneration of some vibrations.

There is still one reason to discuss the range near 1600 cm^{-1} more in detail. It is well known that in this range the band resulting from the bending vibrations, ν_2 , of water

molecules should be visible. For a free water molecule the bending vibration, ν_2 , appears at 1596 cm^{-1} . It is a well established fact, however, that hydrogen bonding increases the frequency ν_2 of water molecules, and the stronger the hydrogen bonding, the greater the force constant of the bending vibration, and the more is the band due to this vibration shifted towards higher wave numbers^{42/}. The spectra of the hydrated and dehydrated lanthanide complexes with TTA are, however, almost identical and there are no absorption bands between 1610 and 1700 cm^{-1} . It must be therefore assumed that the rather weak ν_2 H-O-H band undoubtedly is screened by the very strong $\nu(\text{C}\cdots\text{O})$ band.

The above discussion does not explain, however, why the ν_2 H-O-H vibration in the $\text{Ln}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ complexes has such a low frequency. In ice, where the coordination effect is absent and only hydrogen bonding exists, the ν_2 H-O-H band occurs at 1650 cm^{-1} . It seems to be no doubt that the coordination of H_2O molecule to the Ln^{+3} ion decreases the frequency of bending vibrations of water molecules. Therefore the position of the ν_2 H-O-H band in the investigated complexes is defined by two factors: a/ relatively weak hydrogen bonding due to water molecules, which increases the ν_2 H-O-H frequency in comparison to the frequency of free water, and b/ the coordination effect which decreases this frequency.

The remaining absorption bands in the $1500\text{-}700 \text{ cm}^{-1}$ range are very difficult to experimental interpretation. It seems possible, however, to interpret the band at 1465 cm^{-1} as the $\nu_{\text{as}}(\text{C}\cdots\text{O}) + \text{CH}$ bending^{15/}, and the peak at 1413 cm^{-1} as the stretching vibration of the thiophene ring, $\nu_s(\text{C}\cdots\text{C})$. The 1465 cm^{-1} band is shifted slightly to higher wave numbers with increasing Z, its shape also changing slightly. It is very well shaped for Yb and Lu complexes in contrast to other lanthanides. The 1413 cm^{-1} peak preserves its constant position and intensity. Furthermore, the bands 1251 , 1063 and

1037 cm^{-1} can be assigned to the C-H in-plane bending vibrations of thiophene, the 719 cm^{-1} band to the C-H out-of-plane bending vibration, and 360 cm^{-1} to the stretching and bending vibrations of thiophene ring^{20-24/}. Moreover, it seems very likely that the CF_3 group gives absorption bands in the range $1300, 1140$ and 1062 cm^{-1} ^{8, 15,25/}, although the 1300 cm^{-1} band does not originate from CF_3 itself. The remaining bands result from the chelate ring vibrations. The band at 1359 cm^{-1} occurs both in TTA and in the complexes of Al^{3+} , Fe^{3+} and Ln^{3+} at the same wave number, although its intensity in TTA being slightly different from that in the complexes. Richardson^{43/} and some other authors^{10,11,44-47/} assign the band near 1350 cm^{-1} , appearing in the $\text{Ln}(\text{NFAA})_3 \cdot n\text{H}_2\text{O}$ complexes, to the $\nu(\text{C}\cdots\text{C})_{\text{Ch}^+} + (\text{C}-\text{F}_3)$ vibrations. At the same frequency the $\nu(\text{C}\cdots\text{C})$ thiophene vibrations exist, but as being relatively weak are undoubtedly screened. The interpretation of the band near 1300 cm^{-1} is very difficult. In TTA it occurs at 1282 cm^{-1} with a well-marked shoulder at 1305 cm^{-1} . For the $\text{Al}(\text{TTA})_3$ complex this band is shifted to 1323 cm^{-1} , for the $\text{Fe}(\text{TTA})_3$ it is found at 1305 , and for the Ln complexes one broad very intensive peak exists at 1300 cm^{-1} . Bellamy^{48/} and Ohwada^{10/} describe the intensive band near 1300 cm^{-1} , which appears in the metal complexes with TTA, as the enclitic bonding vibration of the $\nu(\text{C}-\text{O}-\text{M})$ type. It is probable that in this region a fairly intensive band from thiophene vibrations $/1292 \text{ cm}^{-1}/$ exists. Liang^{45/} assigns the intensive band at 1290 cm^{-1} , present in the $\text{Eu}(\text{TFAA})_4 \cdot \text{DMA}$ and $\text{Eu}(\text{BTAA})_4 \cdot \text{DMA}$ complexes to the asymmetric vibrations of the CF_3 group. Taking into account that this band is shifted when TTA is attached to the Ln^{+3} ions, and that it shifts to higher frequencies along the La to Lu series, its assignment to the (C-O)-M grouping vibrations mainly with some share of the CF_3 group asymmetric vibrations seems very probable.

The sharp and intensive band at 1202 cm^{-1} occurring in TTA is found at the same frequency in the $\text{Al}(\text{TTA})_3$ and $\text{Fe}(\text{TTA})_3$ complexes. In the Ln complexes it is shifted about 10 cm^{-1} towards the lower wave numbers. Most of the authors are of the opinion that the band near 1190 cm^{-1} occurring in the β -diketone complexes is due to the in-plane bending vibrations of the C-H chelate group. This seems to be supported by the fact that in the cyanoacetyl-acetone and its Na-salt spectrum^{49/}, there is no absorption band in the range $1250\text{--}1050\text{ cm}^{-1}$. For TTA the peak of low intensity at 908 cm^{-1} is characteristic, whereas the Al, Fe and Ln complexes do not absorb in this range. However, for all discussed complexes the sharp and relatively intensive absorption band between 930 and 940 cm^{-1} is very characteristic. The band which appears in this range in the case of enolic forms of AA and HFAA is assigned to the OH out-of-plane bending vibration^{25/}. The band in the range $930\text{--}940\text{ cm}^{-1}$ for metal β -diketones complexes is described as resulting from very complicated vibrations, having the $\nu(\text{C}\cdots\text{O})$ vibration as a component^{29/}. The band occurring at 790 cm^{-1} in the studied complexes, and at somewhat higher wave numbers in the TTA is undoubtedly due to the C-H out-of-plane bending vibrations of the chelate. The very broad band between $2600\text{--}2900\text{ cm}^{-1}$ of a rather low intensity existing in TTA, has no equivalent in the spectra of the complexes. This band is assigned to the stretching vibrations of the OH group taking part in the intramolecular hydrogen bonding.

CONCLUSIONS

From the results described above the following general conclusions can be drawn:

1. The comparison of the i.r. spectra of the complexes of lanthanides with those of Al and Fe leads to the conclusion that they are generally similar in the range 1700-700 cm^{-1} . The significant differences occur, however, in the range 700-400 cm^{-1} , where the deformation mode of the chelate ring and the vibrations in which the M-O bonding participate, are predominant.
2. The change in the i.r. spectra of the $\text{Ln}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ complexes with the lanthanide are small and concern mainly the $\nu(\text{M-O})$ band. The wave number of this band increases linearly with increasing Z although the points for Tm and Yb deviate from the straight line. Provided, the atomic weight is a decisive factor in the $\nu(\text{M-O})$ vibration a decrease in the $\nu(\text{M-O})$ frequency should be expected with increasing A. It should therefore be assumed that the relationship between $\nu(\text{M-O})$ and Z is governed by other factors, the most important being the decrease in the M-O bonding length in the region from La to Lu. Fig.4 shows that the $\nu(\text{M-O})$ wave number changes significantly from La to Ce and from Gd to Tb.
3. The decreasing ionic radius within the lanthanide series causes a change in the hydration degree of the investigated complexes. In the Yb and Lu complexes which have only one water molecule with both O-H groups participating in hydrogen bonding, the 694 cm^{-1} band assigned to the rocking mode is practically invisible. In the La to Tm complexes which have two water molecules, one of the O-H groups seems to participate in only a very weak hydrogen bonding, if at all, so that a significant rocking band results.

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TABLE I. Infra-red absorption bands of the $(TfA)_3Ln \cdot nH_2O$ complexes in the 400 - 700 cm^{-1} region.

TfA	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	R.I.
456 m	456	458	459	459	460	460	462	464	464	464	465	461	460	460	w
470 ch													475	475	w
	489	493	492	494	495	494	496	499	499	500	501	498	500	503	w mainly Ln-O stretch
517 w	519	518	520	520	520	520	520	520	520	520	520	520	520	520	w Ch-ring deformation
559 m	562	565	565	563	563	563	562	562	564	563	562	563	563	565	sh T-ring out-of-plane bend
581 s	580	580	580	582	581	582	582	583	582	583	583	584	586	585	s CF_3 bend
607 m	605	605	605	606	605	605	605	605	605	606	605	606	606	606	m T-ring in-plane bend
641 s	642	641	642	643	642	643	643	643	642	644	643	643	644	644	s Ch-ring deformation
680 s	681	683	683	685	683	683	683	683	683	684	683	683	686	685	s Ch-ring deformation
	694	694	694	695	695	695	695	694	695	695	695	694			m H_2O rocking

R.I. - relative intensity: w - weak; m - medium; s - strong; vs - very strong; sh - shoulder;
T - thiophene;
Ch - chelate.

TABLE II. Infra-red absorption bands of the dehydrated complexes in the 400-700 cm^{-1} region.

Nd	Gd	Lu
		424 w
		453 m
458	461	464 m
492	496	504 m
520	520	521 w
		535 w
563	563	565 sh
582	582	585 s
605	605	606 m
642	642	644 s
683	683	685 s
693 sh	693 sh	

TABLE III. Infra-red absorption bands of the $\text{Al}(\text{TTA})_2$ and $\text{Fe}(\text{TTA})_3$ complexes in the 400-700 cm^{-1} region.

Al	Fe
425 s	
	458 w
460 w	
522 w	
	534 m
543 m	
563 m	565 w
	591 s
605 s	607 sh
	647 s
657 s	
	667 s
693 s	

TABLE IV. Infra-red absorption bands of the PFA and $\text{Ln}(\text{PFA})_3 \cdot x\text{H}_2\text{O}$ complexes in the 700-1700 cm^{-1} region.

PFA	La	Ca	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	R.I.
719 m	720	719	720	719	717	718	716	719	717	718	720	720	718	716	m T C-H out-of-plane bend
750 w	751	751	752	752	751	751	752	750	751	752	752	750	752	751	w
776 w	770	770	770	769	769	769	770	770	770	770	770	770	770	771	w
793 m	790	790	790	788	788	788	789	788	789	789	788	789	789	789	m CH C-H out-of-plane bend
863 w	861	862	863	862	861	862	862	861	861	862	862	860	860	862	m T ring stretch and bend
1008 w	932	933	932	929	932	935	935	939	938	939	936	935	937	937	m complicated mode involving C=O stretch
	1012	1015	1015	1012	1013	1015	1015	1015	1015	1016	1017	1015	1015	1017	w
1037 w	1036	1037	1035	1035	1037	1037	1037	1038	1038	1038	1038	1037	1038	1039	w T C-H in-plane bend
1066 m	1062	1062	1062	1061	1062	1063	1062	1063	1062	1063	1063	1062	1063	1064	m CF_3 stretch
1083 w	1082	1083	1083	1082	1082	1083	1083	1083	1083	1083	1083	1083	1084	1082	w T C-H in-plane bend
1112 m	1135	1140	1140	1140	1140	1140	1139	1140	1138	1140	1140	1140	1140	1140	m CF_3 stretch
1164 s	1190	1190	1190	1192	1192	1190	1193	1192	1190	1192	1192	1190	1192	1190	s CH C-H in-plane bend
1202 s	1231	1232	1231	1230	1231	1232	1233	1234	1232	1233	1231	1233	1233	1234	m
1253 w	1250	1250	1252	1250	1251	1251	1252	1252	1252	1253	1251	1252	1252	1252	m T C-H in-plane bend
1292 m							1295	1292	1290	1295	1295	1295	1296	1295	sh
	1306	1304	1302	1300	1302	1304	1305	1305	1305	1305	1305	1308	1312	1311	vs (C-O)-M stretch and CF_3 stretch
1305 sh															
1356 m	1355	1358	1358	1358	1359	1359	1360	1360	1359	1360	1359	1360	1360	1360	m C=C stretch and CF_3 stretch
1415 s	1413	1413	1414	1410	1412	1412	1413	1413	1412	1413	1412	1415	1415	1413	s T ring stretch
1445 sh	1433	1437	1435	1438	1437	1446	1441	1442	1441	1443	1443	1443	1445	1445	w
							1453	1452	1450	1452	1453	1453			w
	1465	1458	1459	1460	1460	1461	1464	1465	1464	1467	1469	1469	1468	1460	w C=O stretch and C-H bend
1527 w	1515	1515	1510	1513	1514	1514	1515	1515	1515	1512	1515	1517	1515	1515	m T ring stretch
	1550	1542	1543	1542	1543	1543	1545	1543	1543	1545	1545	1543	1545	1545	m mainly C=C stretch
	1590	1589	1590	1595	1595	1597	1599	1599	1597	1600	1606	1609	1600	1600	sh T ring stretch
1609 s															
	1610	1610	1610	1605	1605	1605	1610	1607	1605	1610	1605	1610	1612	1610	vs mainly C=O stretch
1640 sh															

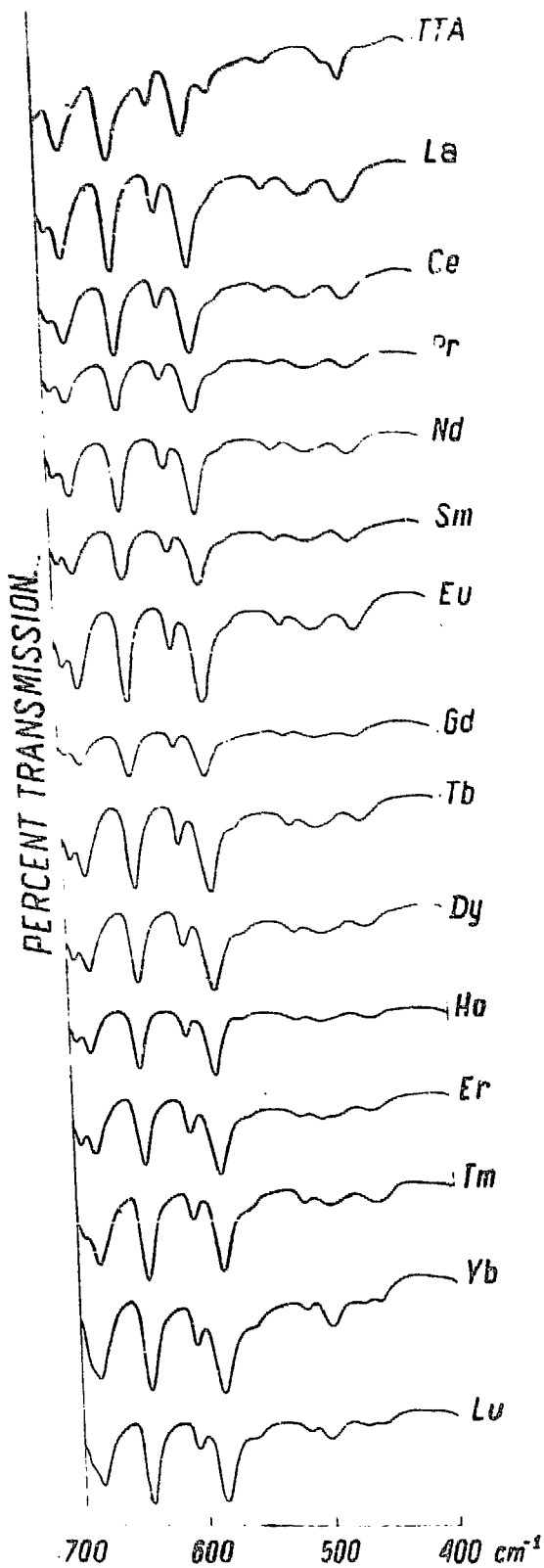
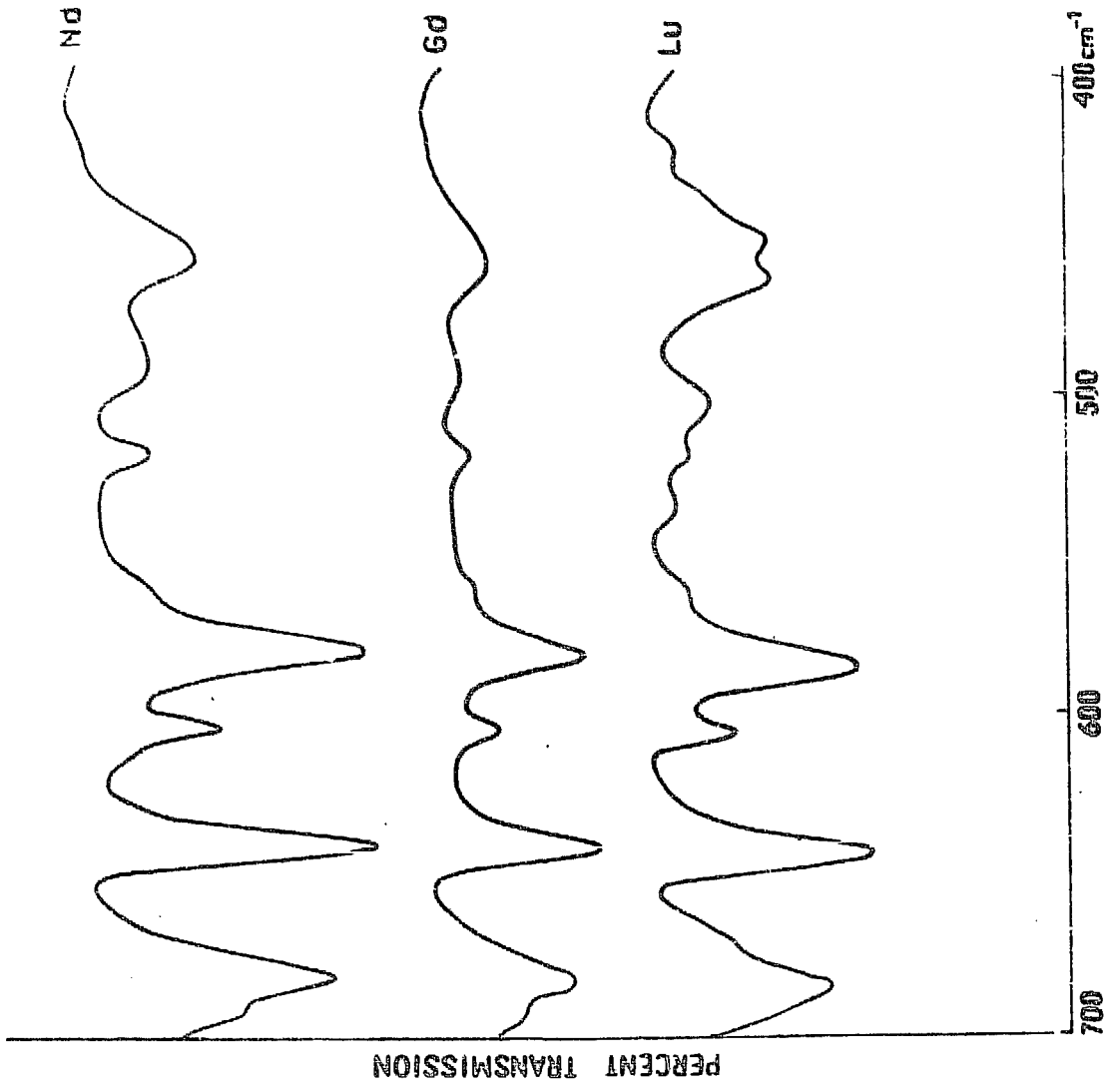


Fig. 1.
 I.R. spectra
 of the TTA and
 $\text{Ln}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$
 complexes in
 the 700-400 cm^{-1}
 region.

FIG. 2.
I.R. spectra
of the de-
hydrated com-
plexes in the
700 - 400 cm^{-1}
region.



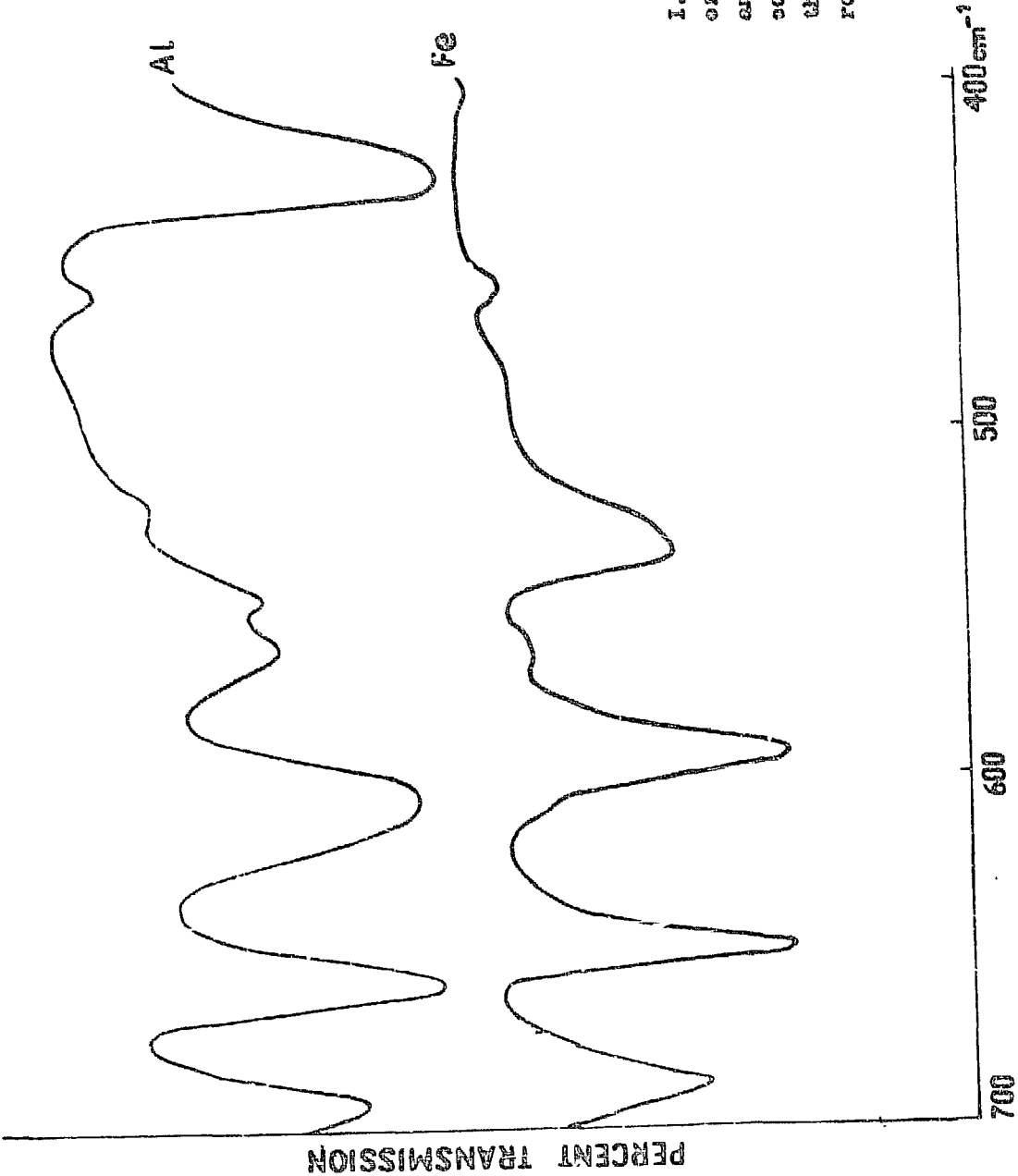


FIG. 3.

I.R. spectra
of the $\text{Al}(\text{TTA})_3$
and $\text{Fe}(\text{TTA})_3$
complexes in
the $700\text{--}400\text{ cm}^{-1}$
region.

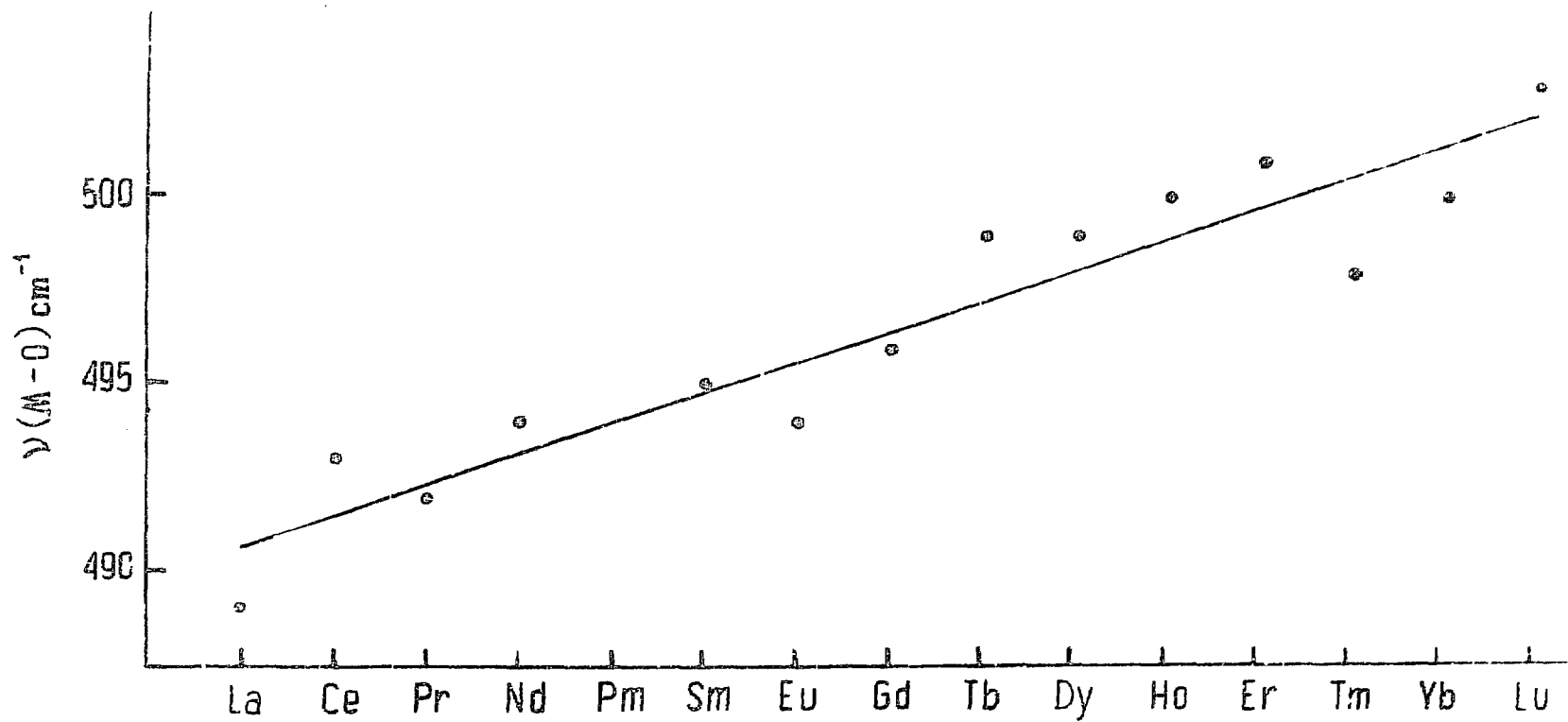


Fig.4. Relation between $\nu(\text{Ln-O})$ and atomic number Z.

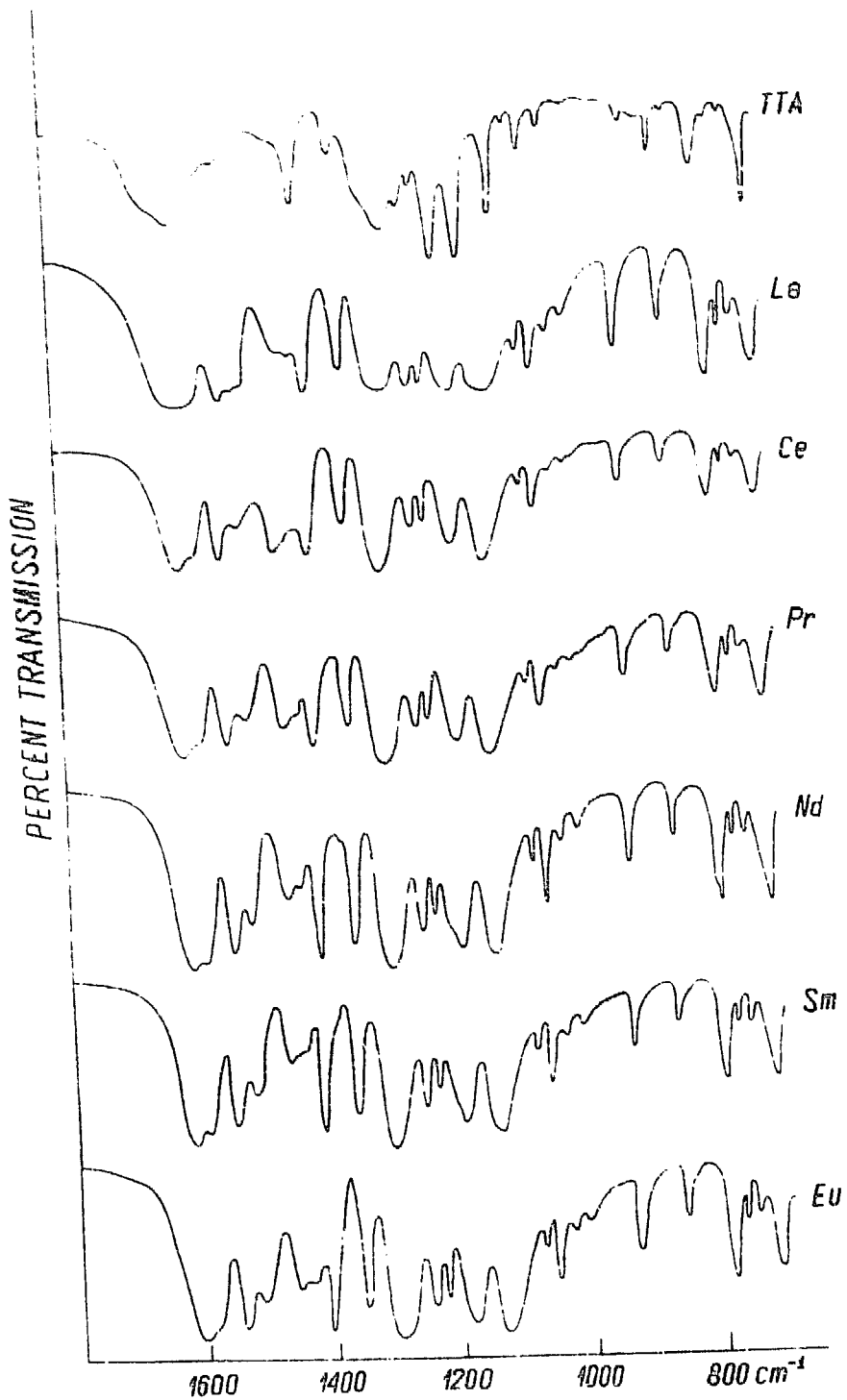


Fig.5. I.R. spectra of the TTA and $\text{La}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ complexes in the 1800-700 cm^{-1} region.

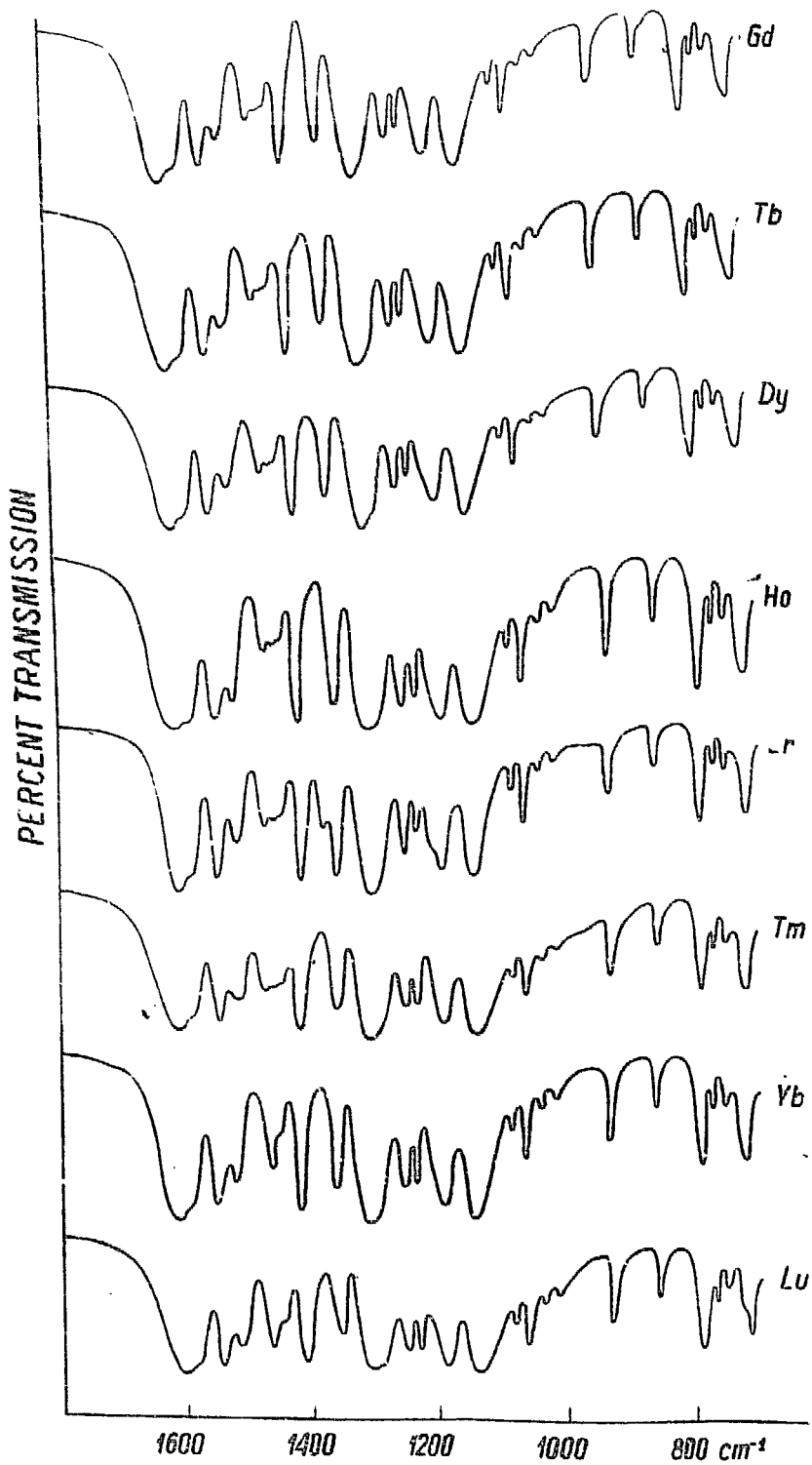


Fig. 6. /continued/

