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Synthesis and infrared and Mössbauer studies of Eu(III) complexes with cyanoxime anions

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Abstract

A series of europium(III) complexes with cyanoxime ligands were prepared. The IR spectroscopic data revealed that the ambidentate ligands were coordinated to the central europium(III) atom in either a tridentate or a bidentate manner. The Mössbauer isomer shift (*IS*) values showed a correlation with the quadrupole splitting (*QS*) values in all complexes. A plot of the *IS* values versus the *QS* values showed that with increasing electron density of the Eu(III) nucleus the symmetry of the electronic shell around the Eu(III) atom decreases.

Introduction

The coordination chemistry of cyanoximes, which have the general formula HONC(CN)–R has developed during the past decade. In alkaline solution, these ligands are deprotonated to yield yellow anions.

$$\mathrm{HONC(CN)-R+OH^-} \longrightarrow \mathrm{ONC(CN)-R^- + H_2O} \quad (1)$$

The colour originates from the electron transition from the ground state to a low-lying excited state of the nitroso group, similarly as in the NO_2^- anion [1]. The negative charge in the deprotonated cyanoximes is delocalized as shown for a typical example in Fig. 1. The X-ray single-crystal data indicate that the deprotonated ligands have a planar structure in some of their alkali metal salts and their 3d metal complexes [2–5].

Cyanoximes are ambidentate ligands. They can coordinate via the N [6] or O [7] atom of the NO group, and can form bridges [8] or five-membered chelate rings [5, 9] through the N atom of the NO group and the O or S atom of the amide or thioamide groups.

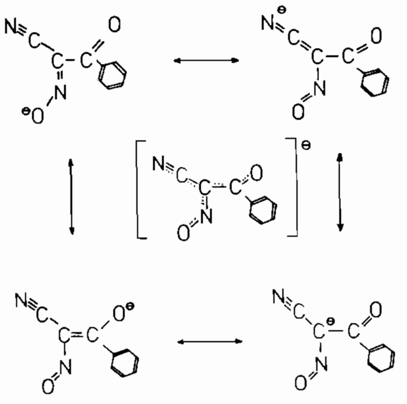

Fig. 1. Negative charge delocalization and different mesomeric structures of BCO^-.

The ligands and their metal complexes have been shown to have biological activity and anti-microbial properties [10–12].

Very little is known on the complexes of $ONC(CN)_2^-$ with rare-earth elements [7, 13].

Our present aim was to derive structural conclusions from IR and Mössbauer studies on a series of systematically selected Eu(III) complexes.

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Experimental

Preparation of europium(III)–cyanoxime complexes

The ligands used in the present work, together with the relevant abbreviations, are depicted in Fig. 2. The silver salts of these cyanoximes were obtained according to eqns. (2) and (3).

$$ML + AgNO_3 \xrightarrow{H_2O} AgL + MNO_3 \qquad (2)$$

$$KH(ACO)_2 + AgNO_3 \xrightarrow{H_2O} Ag(ACO) + KNO_3 + H(ACO) \qquad (3)$$

where ML = K(CCO) [2], Cs(ECO) [14] or Cs(DCO) [15], and H(ACO) is the free aminocyanoxime $HONC(CN)C(O)NH_2$, which does not form a silver salt under these conditions.

The precipitates formed were filtered off, washed in turn with acetone and diethyl ether and dried. The silver salts are yellow, yellow–orange or rose (AgBCO) and are insoluble in water. With the exception of Ag(DCO) and Ag(PCO), they are stable in light.

In the second step, the Eu(III) complexes were prepared according to eqn. (4)

$$EuCl_3 \cdot 6H_2O + 3AgL \xrightarrow{H_2O} EuL_3 \cdot xH_2O + 3AgCl \qquad (4)$$

To 20 cm^3 0.001 M $EuCl_3 \cdot 6H_2O$ solution, three molar equivalents of solid AgL were added. After 15 min, the AgCl formed was filtered off and washed with 5 cm^3 distilled water. The yellow filtrates were kept over concentrated sulfuric acid in a vacuum desiccator. Yellow oil products were obtained, which were triturated with diethyl ether to give solid powders. The powders were washed with diethyl ether, and dried in air. The yields were 90–95%. The exchange reaction between $EuCl_3$ and Ag(PCO) cannot be used to prepare the PCO complex, because both AgCl and the complex are insoluble in water. In this case, $EuCl_3 \cdot 6H_2O$ and Na(PCO) solutions were mixed in a 1:3 molar ratio. The product precipitated from the mixture immediately (yield 62%).

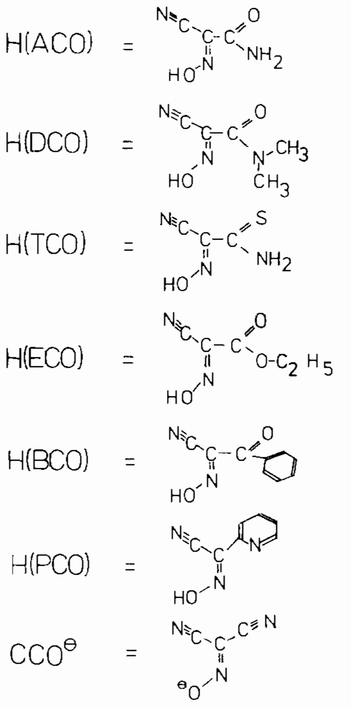

Fig. 2. Structures and abbreviations of ligands studied.

Attempts to prepare complexes of $ONC(CN)_2$ were unsuccessful. This ligand usually undergoes monodentate coordination through the O atom with rare-earth elements. However, this takes place only in the presence of strong σ-donors such as DMSO, triphenylphosphine oxide or HMPA [7, 13].

The reactions between aqueous solutions of EuL_3 and an ethanolic solution of 2,2′-dipyridyl in a molar ratio of 1:1 do not result in the formation of products, except for the system involving PCO^-, which forms a complex with the composition $Eu(PCO)_2(OH) \cdot dipy \cdot H_2O$.

The carbon, hydrogen and nitrogen contents of the complexes were determined by standard analytical procedures. The Eu(III) content in each system was determined by two independent methods (complexometric titration and thermogravimetry). The analytical data and colours of the complexes are presented in Table 1. The good agreement between the measured and calculated values proved the stoichiometric composition of the complexes.

Measurements

The Mössbauer spectra were recorded at room temperature and at liquid nitrogen temperature by using a $^{151}Eu(^{151}Sm)F_3$ source of 3×10^9 Bq activity. The isomer shift (*IS*) values are referred to EuF_3.

In the Mössbauer transition of ^{151}Eu which emits 21.53 keV γ-rays, the nuclear magnetic dipole transition is $\frac{7}{2}+ \rightarrow \frac{5}{2}+$. This implies an eight-line quadrupole pattern. Europium(III), with a $4f^6$ configuration, has a ground state of $^7F_0$, which has a total angular moment of zero. Therefore, any quadrupole splitting (*QS*) in Eu(III) complexes is presumed to arise only from the lattice or coordination sphere contributions to the electric field gradient or from their polarization effect on the core electrons. These contributions are usually small, resulting only in broadening of the resonance lines, as shown by the Γ (half-width) values (see Table 3), which were resolved by a computer program to obtain the *QS*

Table 1. Analytical data on europium(III) complexes

		Molecular weight/ Eu atom		Eu (%)		C (%)		N (%)		H (%)	
		calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
$Eu(ACO)_3 \cdot 2H_2O$	bright yellow	424	428	29.00	28.78	20.6	21.2	24.1	24.8	1.90	2.00
$Eu(ACO)_2(OH) \cdot 2H_2O$	cream-yellow	429	437	35.42	35.08	16.7	16.8	19.5	19.0	2.09	1.46
$Eu_2(DCO)_5(OH) \cdot 4H_2O$	green-yellow	1095	1105	27.80	27.52	27.4	28.3	19.2	19.8	3.57	3.36
$Eu(BCO)_2(OH) \cdot 2H_2O$	orange	523	517	29.36	29.00	41.2	41.3	10.6	10.2	2.29	2.66
$Eu_2(PCO)_5(OH) \cdot H_2O$	cream-white	1051	1053	28.43	28.86	39.3	39.2	19.7	18.9	2.15	2.58
$Eu(ECO)_3 \cdot 2H_2O$	brown-yellow	578	577	26.29	26.35			14.5	13.7		
$Eu(PCO)_2(OH) \cdot (dipy) \cdot H_2O$	cream	635	628	23.92	24.19	45.3	45.1	17.6	18.1	2.99	2.48

In the presence of europium(III) the conventional elemental analytical methods for C and N determination showed a ±1% error.

values reflecting the changes in the symmetry of the near surroundings of the central Eu(III) atom.

The IR spectra were recorded on a Carl Zeiss (Jena) UR20 spectrometer in KBr pellets and Nujol mulls.

X-ray powder diffraction data were collected on a DRON-3 (USSR) diffractometer with filtered Cu Kα radiation.

Results and discussion

The analytical data reported in Table 1 clearly demonstrate that in reaction (4) Eu(III) cyanoxime complexes of stoichiometric composition were formed. Due to the hydrolysis of Eu(III) in aqueous solution, all the complexes except $Eu(ACO)_3 \cdot 2H_2O$ and $Eu(ECO)_3 \cdot 2H_2O$ contain one coordinated hydroxy ion. The proposed preparation mode can be used in general to prepare this type of complex. These compounds cannot be recrystallized from any solvent without decomposition. The X-ray powder diffraction data indicated that all of the complexes studied are X-ray amorphous, not exhibiting long-range order, but having short-range order in the solid state of approximately 20–30 Å.

The IR data are also consistent with the formation of well-defined polymeric compounds. The IR spectra are poorly resolved, with broad peaks. The features of the spectra recorded in KBr pellets and in Nujol mull are the same. The characteristic IR absorptions of the complexes and the corresponding free ligands in the region 4000–400 cm^{-1} are presented in Table 2. The assignments of the vibration frequencies of the –CNO group in the ligands were based on the isotope splitting effect of ^{15}N-enriched samples.

The IR spectra reveal the higher value of $\nu(C\equiv N)$ and the lower value of $\nu(NO)$ in the ACO complex as compared with those of the free anion in its Rb^+ salt, reflecting the coordination of ACO to Eu(III) via the nitrile nitrogen and the NO oxygen (Table 2). The increase in $\nu(C\equiv N)$ and decrease in $\nu(N=O)$ due to metal ion coordination indicate that the delocalized negative charge is situated in the complex on the $N–O^-$ oxygen (first structure in Fig. 1). The $\nu(C=O)$ vibrations appeared at the same frequencies in the spectrum of the complex as in that of the free ligand, indicating that the amide group is not coordinated to Eu(III). The same coordination mode is suggested by the IR spectrum of $Eu(ACO)_2(OH)$.

Analogous coordination behaviour is observed in the complex $Eu_2(DCO)_5(OH) \cdot H_2O$. A strong increase in $\nu(C\equiv N)$ and a decrease in $\nu(NO)$ indicate the participation of the CN and NO groups in the coordination to Eu(III). The vibrations $\nu(C=O)$ (amide-I) appear at the same frequency in the IR

Table 2. IR spectroscopic data on Eu(III) complexes

Complexes	Important bands (cm^{-1}) and their assignments			
	Range 2800–3600 (cm^{-1})	ν(C≡N)	ν(C=O)	ν(NO), (ν(CNO))
Rb(ACO)	3370, sharp 3270, broad ν_{as}NH 3220, broad ν_sNH	2223 sh	1685 sh 1610 (ρ NH$_2$)	1290 1180
$Eu(ACO)_3 \cdot 2H_2O$	3220, broad ν_sNH	2240	1680 1610 (ρ NH$_2$)	1265 1170
$Eu(ACO)_2(OH) \cdot 2H_2O$	3100–3700, very broad νOH+NH	2250	1680 1600	1260 1180
Cs(DCO)	2930 ν_{as}CH 2870 ν_{as}CH	2185	1620 1600 (νC=N) amide	1290
$Eu_2(DCO)_5(OH) \cdot 4H_2O$	2960 ν_{as}CH 2830 ν_sCH 3050–3700 broad ν_H	2225	1630	1255
Cs(ECO)	2980 ν_{as}CH 2830 ν_sCH	2200	1680	1280 (1140)
$Eu(ECO)_3 \cdot 2H_2O$	2990 ν_{as}CH 2850 ν_sCH 3200–3600, broad νOH	2235	1675	1240 (1130)
H(BCO)	3020 ν(C–H) arom.	2190	1650	1055
Cs(BCO)	3080 ν(C–H) arom.	2200	1640	1295 (1190)
$Eu(BCO)_2(OH) \cdot H_2O$	3070 νCH arom. 3100–3650, broad νOH	2230	1610	1280 1185
Na(PCO)	3050 νCH arom.	2208	1590 ν(C=N)(Py)	1205
$Eu_2(PCO)_5(OH) \cdot H_2O$	3300–3600; broad νOH	2240	1610 ν(C=N)(Py)	1180

spectra of Cs(DCO) and the corresponding Eu compound. The oxygen atom in $-C(O)N(CH_3)_2$ does not appear to be coordinated to Eu(III) (Table 2).

The cyanoxime anion ECO$^-$, containing an ethyl ether group, is shown by the IR data to be coordinated to the central Eu(III) in same way as the anions ACO$^-$ and DCO$^-$.

The IR spectrum of the benzoyl cyanoxime anion BCO$^-$ in its complex $Eu(BCO)_2(OH) \cdot 2H_2O$ indicates coordination of both nitrile and carbonyl groups to Eu(III). The ν(C=O) vibration frequency in the spectrum of the complex is 40 cm^{-1} lower than in that of HBCO and Cs(BCO) (Table 2). The nitroso group is also shown to be coordinated by Eu(III), which means that BCO is a tridentate ligand, forming a bridge in the complex.

The IR data on the 2-pyridylcyanoxime (PCO$^-$) complex demonstrate also a tridentate coordination mode. The valence vibration of the nitrile group is 32 cm^{-1} higher in the complex than in the sodium salt of the non-coordinated anion. The 20 cm^{-1} increase in the CN vibration mode of the pyridyl ring in the complex indicates the participation of the latter donor centre as well in the coordination to the Eu(III) (Table 2). The 25 cm^{-1} decrease in the NO frequency as a result of complex formation indicates the coordination of the NO oxygen in the complex. This conclusion is in accordance with Köhler's theory [16]. Accordingly, the last two anions participate in tridentate coordination to europium(III).

The experimentally determined Mössbauer parameters (*IS* and *QS*) of the complexes are presented in Table 3 and the spectrum of $Eu_2(DCO)_5OH \cdot 4H_2O$ in Fig. 3.

The Mössbauer spectra revealed the presence of only one type of chemical state of Eu(III) in all the

Table 3. Mössbauer parameters of Eu(III) complexes

Compounds	Isomer shift (mm s^{-1})	Line width (mm s^{-1})	Quadrupole splitting (mm s^{-1})
$Eu(ACO)_3 \cdot 2H_2O$	0.27	2.89	0.55
$Eu(ACO)_2OH \cdot 2H_2O$	0.40	2.75	0.76
$Eu(ECO)_3 \cdot 2H_2O$	0.29	2.75	0.55
$Eu_2(DCO)_5OH \cdot 4H_2O$	0.36	2.56	0.73
$Eu(BCO)_2OH \cdot H_2O$	0.41	2.68	0.63
$Eu_2(PCO)_5OH \cdot H_2O$	0.51	2.66	0.65
$Eu(PCO)_2OH \cdot dipy \cdot H_2O$	0.49	2.68	0.84

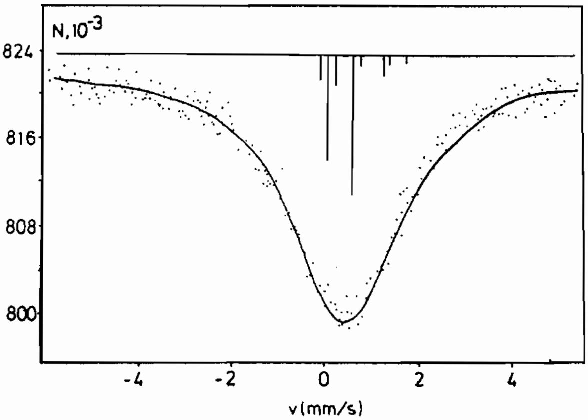

Fig. 3. Mössbauer spectrum of $Eu_2(DCO)_5OH \cdot 4H_2O$ at room temperature.

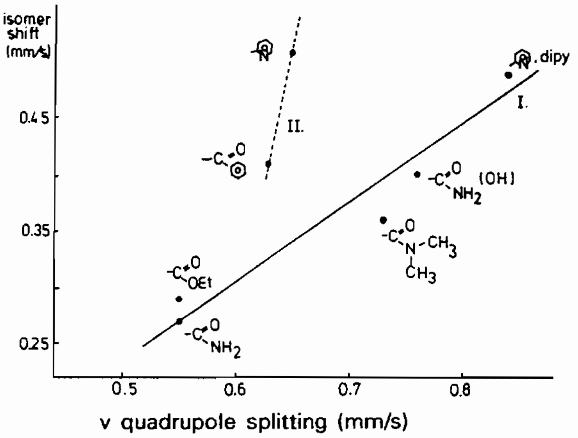

Fig. 4. Plots of *IS* values vs. *QS* values for Eu(III) cyanoxime complexes. Line I: bidentate anions. Line II: tridentate anions.

complexes, indicating that even the dimeric complexes contain Eu(III) atoms in identical or closely analogous surroundings.

The coordination number of Eu(III) influences the symmetry of its coordination sphere, which may be reflected by the Mössbauer *QS* values. It can be seen in Table 3 that most of the *QS* values lie in a narrow velocity range (0.55–0.84 mm s^{-1}), indicating a relatively small variation of the electric field gradient around the Eu(III) nucleus in all complexes. These data permit the supposition of similar (or the same) coordination numbers.

The *IS* values of the mixed ligand complexes containing both cyanoxime and OH^- ligands are considerably higher than that of parent cyanoxime complexes. This demonstrates a higher s electron density at the ^{151}Eu nucleus in the mixed complexes, which may be due to the increasing 6s orbital population and the increasing covalency. The *QS* values of the hydroxy mixed ligand complexes show a higher electric field gradient on the Eu(III) nucleus, and thus a lower symmetry of the electronic shell and consequently of the coordination sphere around the Eu(III). The complexes containing cyanoximes with bulky substituents, i.e. benzoyl (BCO) or pyridyl groups (PCO), have higher *IS* and smaller *QS* values than the other complexes. These ligands are coordinated to Eu(III) in a tridentate manner, which increases the covalency of the coordinate bonds.

A plot of the *IS* values versus the *QS* values (Fig. 4) shows that with increasing *IS* the *QS* values increase. Thus, an increased electron density on the Eu nucleus (probably due to the increased covalency of the coordinate bond) is accompanied by a decreased symmetry of the electronic shell around the Eu atom (probably due to the decreased symmetry of the coordination sphere). The *IS* versus *QS* plot also shows the effects of the bidentate (line I) and tridentate (line II) binding mode.

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