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Complexes of Lanthanoid Salts with Macrocyclic Ligands. Part 19. Sandwich Complexes Between Lanthanide(III) Ions and 15-Crown-5 Ether: Luminescence and Structural Data

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Abstract

The reaction of the lighter lanthanide perchlorates and hexafluorophosphates with 15-crown-5 ether gives sandwich complexes formulated as $LnX_3(C_{10}H_{20}O_5)_2$. Crystalline material was obtained for $Nd(ClO_4)_3(C_{10}H_{20}O_5)_2$ (1), $Eu(ClO_4)_3(C_{10}H_{20}O_5)_2$ (2), and $La(PF_6)_3(C_{10}H_{20}O_5)_2$ (3).

The luminescence spectrum of a powdered sample of (2) was recorded at 77 K under high resolution. The $^5D_0 \rightarrow {}^7F_0$ transition is extremely weak and comprises four distinct components at 578.05 nm (Site I), 579.33/579.41 nm (Site II), and 579.73 nm (Site III). Selective excitations produce spectra which strongly suggest the presence of an inversion centre at the europium ion in Site I; the coordination polyhedron of this site is close to a pentagonal antiprism. A comparison between crystallographic and luminescence data demonstrate the fluxional behaviour of the complex, four configurations of which are frozen at low temperature and give rise to different luminescence spectra.

Complexes (1) and (2) are isomorphous and form tetragonal crystals with an I-centered lattice; (2) belongs to Laue group $4/m$, $a = 10.492(3)$, $c = 14.917(8)$ Å, and $Z = 2$. (3) forms cubic crystals with an F-centered lattice, $a = 30.50(3)$ Å and $Z = 32$. Both structures appear to be highly disordered.

Introduction

The synthesis of a whole series of cyclic polyethers by Pedersen in 1967 [2] opened a new and promising field in coordination chemistry. Indeed, the 'crown' ethers were shown to be good complexing agents exhibiting selective metal binding properties for alkali metal ions [3]. These studies were soon extended to the lanthanoid ions which form moderately stable complexes with crown ethers and podands [1]. Possible practical applications of these complexes include the elaboration of liquid-liquid extraction processes for the separation of the rare earth ions, the stabilization of unusual oxidation states and their use as spectroscopic probes.

Various metal:ligand ratios have been observed and crystal structures have been reported for 1:1 [1, 4], 4:3 [1, 4], and 2:1 [5] complexes. The 1:2 complex $Sm(ClO_4)_3(C_{10}H_{20}O_5)_2 \cdot 5H_2O$ has also been investigated but turned out to be a 1:1 complex containing a $[Sm(C_{10}H_{20}O_5)(H_2O)_4]^{3+}$ cation and an uncomplexed 15-crown-5 ether held in the lattice by hydrogen bonding [6]. We have therefore tried to determine the structure of genuine sandwich 1:2 complexes both by spectroscopic measurements and by crystallography. The results we obtained for 15-crown-5 complexes are presented and discussed in this communication.

Experimental

The perchlorate complexes $Ln(ClO_4)_3(C_{10}H_{20}O_5)_2$ were synthesized according to the previously described procedure [7]. Their purity was checked by infrared spectrometry and elemental analyses. Monocrystals of the neodymium and europium complexes were grown in acetonitrile. The hygroscopic crystals were mounted in Lindeman tubes and were somewhat sensitive to X-rays. Unit cell parameters were determined and data were collected with a Syntex $P2_1$ diffractometer. The crystals of (1) gave poor diffraction patterns and decom-

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†Systematic name: 1,4,7,10,13-pentaoxacyclopentadecane.

#For Part 18, see [1].

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posed rapidly; they are tetragonal with approximate cell dimensions a = 10.54, c = 14.96 Å, Z = 2; no data could be collected. The crystals of (**2**) are also tetragonal a = 10.492(3), c = 14.917(8) Å, U = 1642(1) Å^3, D_M = 1.81, D_c = 1.80 g cm^{-3}, Z = 2 at 293 K. Both (**1**) and (**2**) are frequently twinned, no doubt due to the close correspondence of $\sqrt{2}a$ and c. Of 854 reflections collected for (2), 719 were considered observed ($I/\sigma(I) \geqslant 3.0$). Systematic absences $h + k + l \neq 2n$ indicate a body-centered lattice with Laue group $4/m$ and possible space groups are $I4$, $I\bar{4}$, or $I4/m$. Patterson methods strongly suggested a solution in $I\bar{4}$ or $I4/m$ with one europium ion at a special position 2(a) (0,0,0) and a chlorine atom in 2(b) (0, 0, ½). A trial solution in the centrosymmetric space group $I4/m$ was found and insertion of a further chlorine atom and various other peaks from successive difference Fourier syntheses as oxygen and carbon atoms (in fractional occupancy) eventually gave R_F = 0.065, but no recognisable structure. The distance between neighbouring Eu-atoms is 10.5 Å. If the heavy atom position is correct then the point group symmetry of that site is C_{4h}, which cannot be rationalised without disorder. The presence of an inversion centre is however consistent with the luminescence measurements (q.v.). Trial solutions were attempted in the other possible space groups without success.

To prepare the hexafluorophosphate complex $La(PF_6)_3(C_{10}H_{20}O_5)_2$, an excess of lanthanum carbonate was added to freshly prepared aqueous hexafluorophosphoric acid until the solution was neutral. This was filtered, carefully concentrated at 30 °C and a large excess of ligand added. The resulting pasty material was stirred with ether during 2 h. The complex was filtered off, dried over P_4O_{10} under vacuum (10^{-2} mm Hg), and stirred with triethyl orthoformate for 12 h. Additional drying over $P_4O_{10}/10^{-2}$ mm Hg gave the anhydrous complex. Elemental analysis: found, %C 23.87, %H 4.02, %La 13.66; theor, %C 23.69, %H 3.97, %La 13.70. Block-shaped crystals of this compound were grown by slow evaporation of an acetonitrile solution. They gave broad diffraction peaks but there was no obvious sign of twinning. The crystals are cubic with a = 30.50(3) Å and systematic absences $h + k$, $k + l$, $(l + h) \neq 2n$ indicate a face-centered lattice. The measured density of 1.82 g cm^{-3} corresponds to 32 molecules per cell. Of the 1318 reflections collected, 649 were considered observed ($I/\sigma(I) \geqslant 3.0$), and examination of statistics of normalized structure factors strongly suggested a centrosymmetric space group. The lack of systematic absences other than those due to the F-centered lattice narrows the possible space groups to $Fm3$ *or* $Fm3m$; sorting and averaging reflections in Laue groups $m3$ and $m3m$ marginally favoured the former, hence the possibility of a trial solution in $Fm3$ was examined. Both heavy atom (Patterson) and direct (Multan 80) methods have been tried without success in several F-centered cubic space groups. It is difficult to envisage any solution containing a $[Eu(15\text{-crown-}5)_2]^{3+}$ cation (maximum point group symmetry C_{2v}) without extensive disorder. Luminescence spectra were recorded at 77 K on a previously described laser-spectrofluorimeter [8]. The relative intensities given in the text represent the area of all the components of a transition, calculated from spectra that have been corrected for the instrumental response. The accuracy of these intensities is ±5–7%.

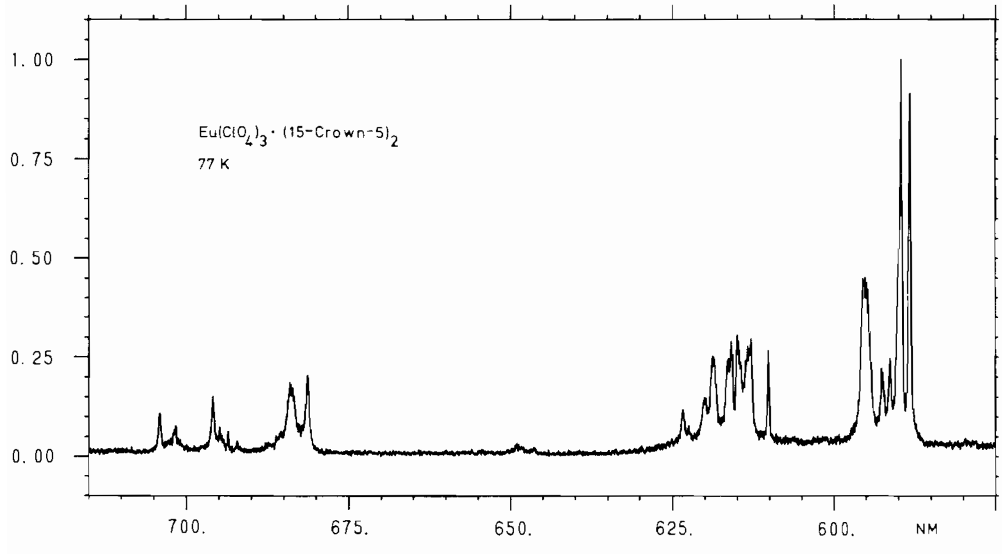

Fig. 1. Corrected luminescence spectrum of $Eu(ClO_4)_3(C_{10}H_{20}O_5)_2$ at 77 K, under excitation to the $^5L_6$ level (395 nm).

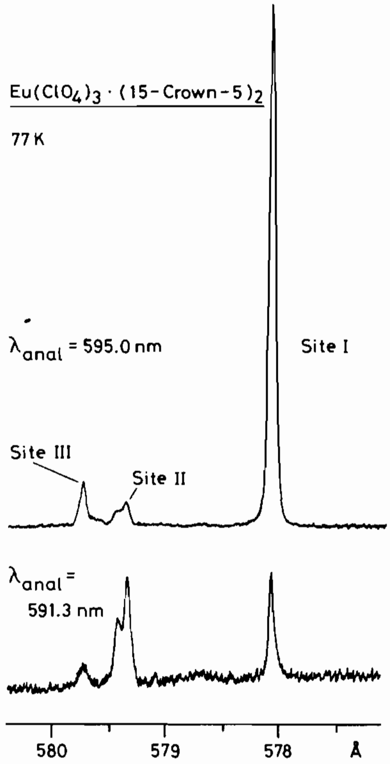

Fig. 2. Part of the excitation spectra of $Eu(ClO_4)_3(C_{10}H_{20}O_5)_2$ at 77 K.

TABLE I. Observed ^7F_J Energy Sublevels in cm^{-1}, from the Emission Spectra at 77 K.

J	Site I	Site II	Site III
0	0	0	0
1	300	311	304
	338	347	370
	498[a]	450	433
2	908	941	935
	1004	991	948
	1022	1023	963
	1039	1100	1184
	1171		1209
3	1827	b	1822
	1878		1848
	1891		1874
	2017		1908
4	2620	2622	2592
	2906	2643	2613
	2929		2880
	3048		3013
	3097		

[a] Average of two closely spaced components. [b] Too weak to be observed.

Results and Discussion

In the absence of any appreciable cation/anion interaction, as is generally the case for perchlorates and hexafluorophosphates, 1:2 sandwich complexes are isolated when the ratio of ionic diameter to cavity diameter is larger than 1:1. Such complexes with 15-crown-5 ether are isolated for Ln = La–Eu (X = ClO_4^-) and for Ln = La–Sm (X = PF_6^-) [4]. For the perchlorate complexes, the possible space groups compatible with the crystallographic study imply a minimum C_{4h} symmetry at the metal site, which is difficult to accommodate without disorder. Disorder has been noted in previously determined structures, usually of a fluxional type and restricted to a portion of the molecule, as for instance $-CH_2-CH_2-$ groups in $Eu(NO_3)_3(C_{10}H_{20}O_5)$ [8]. A similar situation is observed for the lanthanum hexafluorophosphate complex, which is cubic and in which the minimum site symmetry of the metal cation would be C_3 assuming only one metal site in a 32-fold position.

Vibrational spectra clearly indicate the coordination of both polyethers [7]; in order to get more structural information we have analyzed the luminescence spectrum of $Eu(ClO_4)_3(C_{10}H_{20}O_5)_2$ at 77 K (Fig. 1). Under excitation to the $^5L_6$ level (*ca.* 395 nm), the relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 0.25, 100, 66, 1, and 69 for J = 0, 1, 2, 3, and 4 respectively. High resolution excitation spectra obtained with a dye laser (Fig. 2) reveal that the $^5D_0 \leftarrow {}^7F_0$ transition comprises four components, which points to the presence of at least four differently coordinated species. One of these components (578.05 nm, I) is well separated from the other (579.33/579.41 nm, II and 579.73 nm, III); II is a closely spaced doublet and may be considered as one site only. Selective excitations of these three sites result in the spectra displayed in Fig. 3*; very little energy transfer occurs between the sites.

The spectrum of Site I, which accounts for about 2/3 of the total Eu-emission under excitation to $^5L_6$ may be assigned to a species with an inversion centre [9]: (i) the relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 100, 33, and 82 for J = 1, 2, and 4, respectively and (ii) the $^5D_0 \rightarrow {}^7F_0$ transition is extremely weak. Since the $^5D_0 \rightarrow {}^7F_1$ transition has three components, Site I has a low symmetry, either D_{2h}, C_{2h} or C_i. The observation of five components for $^5D_0 \rightarrow {}^7F_2$ restricts the possible point groups to the last two, but it is not possible to distinguish between them since we do not have polarization data. The resulting coordination around the metal ion is probably similar to that found for the potassium iodide sandwich complex with benzo-15-crown-5 ether. That compound has an irregular penta-

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*A listing of 91 transitions, with assignment, is available upon request (5 pages).

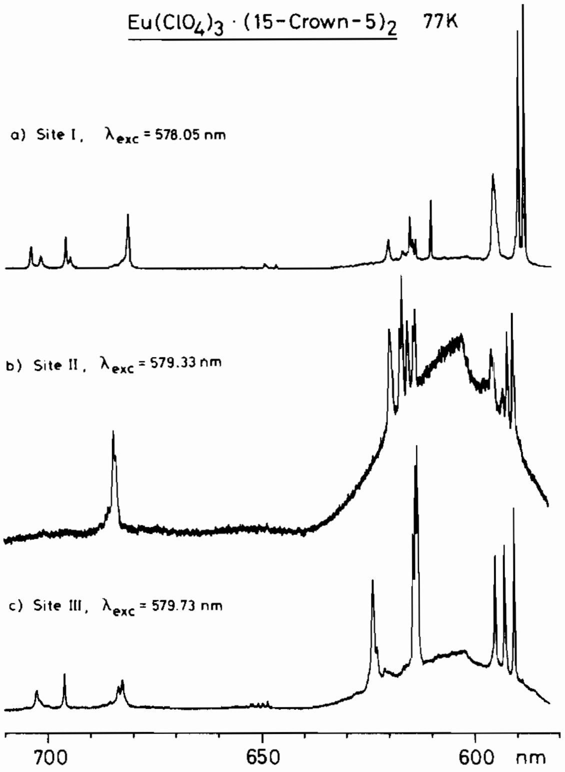

Fig. 3. Corrected luminescence spectra of $Eu(ClO_4)_3(C_{10}H_{20}O_5)_2$ at 77 K, under selective laser-excitation. The vertical scale, in arbitrary units, is not the same for the three spectra.

gonal antiprismatic configuration around the potassium and possesses the crystallographic symmetry $\bar{1}$, with almost C_{2h} symmetry because each ligand molecule has an approximate mirror plane perpendicular to the oxygen plane [10]. The actual spacing of the three components of the $^5D_0 \rightarrow {}^7F_1$ transition (a singlet and a doublet, Table I) suggests that the site symmetry of the europium(III) ion arises from a distortion of an idealized, more symmetrical coordination polyhedron, which could be a regular pentagonal antiprism (D_{5d}). Such pseudosymmetries have been reported for $Eu(NO_3)_3(C_{10}H_{20}O_5)$ [8] and for $[Eu(NO_3)_5]^{2-}$ ions [11].

Excitation of the two components of the $^5D_0 \leftarrow {}^7F_0$ transition labelled Site II yielded quite similar spectra, an example of which is displayed in Fig. 3b. These spectra have a weak intensity and are characterized by a broad and intense band centered at *ca.* 605 nm* and by weak and sharp components assigned to the f–f transitions. The magnetic dipole transition to the $^7F_1$ level has an intensity more or less equal to that of the transitions to $^7F_2$ and $^7F_4$, the relative intensities being 100, 90 and 105 for J = 1, 2, and 4, respectively. The overall f–f spectrum resembles that of site I, except for $^5D_0 \rightarrow {}^7F_4$, which only shows one intense doublet. Moreover, three of the four components of the $^5D_0 \rightarrow {}^7F_2$ transition appear as closely spaced doublets (6–15 cm^{-1}) similar to those observed in the luminescence spectrum of $Eu(NO_3)_3C_8H_{16}O_4$ and assigned to interactions between the electronic and vibrational levels [12, 13].

In the luminescence spectrum of Site III, the f–f transitions are more intense and their pattern is different. The $^5D_0 \rightarrow {}^7F_1$ transition comprises three equally spaced components with approximately the same intensity. The relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions are 100, 216 and 138 for J = 1, 2, and 4, respectively, pointing to a site with low symmetry and without an inversion centre.

The spectrum of $La(PF_6)_3(C_{10}H_{20}O_5)_2$ doped with europium displays only weak and broad bands that cannot be analyzed in detail. The complex is photosensitive and decomposes rapidly under light exposure.

Conclusion

The differently coordinated species giving rise to the observed luminescence spectra of the europium perchlorate complex (2) may be seen as being frozen configurations corresponding to minima in a potential energy curve describing a fluxional behaviour of this compound. Site I, with an inversion centre, and Site III, without symmetry, would then be the two extreme configurations, Site II representing an intermediate situation. The apparent discrepancy between the spectroscopic and crystallographic data may arise because the X-ray scattering is dominated by the Eu-atoms, which form a body-centered lattice with high symmetry. The crystals were not of best quality, giving rise to somewhat broad diffraction patterns, hence the large standard deviation on the cell dimensions. However, the presence of an inversion centre is established by the crystallographic data and by the luminescence spectra, at least for one of the sites. We therefore conclude that the sandwich Eu-complex has a coordination polyhedron close to the ideal pentagonal antiprism, with a fluxional behaviour that prevents the exact determination of the structure. The crystallographic and spectroscopic data for the hexafluorophosphate complex are less informative; they are both consistent with a highly disordered species, even at low temperature.

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*This broad band may be an artifact arising from the plasma of the laser discharge and which is seen when the spectra are weak and, therefore, when a large amplification is used.

Acknowledgements

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References

1 J.-C. G. Bünzli and D. Wessner, *Coord. Chem. Rev.* (1984) in press.
2 C. J. Pedersen, *J. Am. Chem. Soc., 89,* 7017 (1967).
3 N. S. Poonia, in R. M. Izatt and J. J. Christensen (eds.), 'Progress in Macrocyclic Chemistry, Vol. 1', Wiley, New York, 1979, ch. 3.
4 J.-C. G. Bünzli and D. Wessner, *Isr. J. Chem.,* (1984) in press.
5 W. D. Harrison, A. Giorgetti and J.-C. G. Bünzli, *J. Chem. Soc., Dalton Trans.,* in press.
6 T. J. Lee, H.-R. Sheu, T. T. Chiu and C. T. Chang, *Acta Crystallogr., Sect. C:, 39,* 1357 (1983).
7 J.-C. G. Bünzli, Huyhn Tham Oanh and B. Gillet, *Inorg. Chim. Acta, 53,* L219 (1981).
8 J.-C. G. Bünzli, B. Klein, G. Chapuis and K. J. Schenk, *Inorg. Chem., 21,* 808 (1982).
9 P. Porcher and P. Caro, *J. Lumin., 21,* 207 (1980).
10 P. R. Mallinson and M. R. Truter, *J. Chem. Soc., Perkin Trans., 2,* 1818 (1972).
11 J.-C. G. Bünzli, B. Klein, G.-O. Pradervand and P. Porcher, *Inorg. Chem., 22,* 3763 (1983).
12 J.-C. G. Bünzli, B. Klein, D. Wessner and N. W. Alcock, *Inorg. Chim. Acta, 59,* 269 (1982).
13 C. J. Barnett, A. F. Drake, R. Kuroda, S. F. Mason and S. Savage, *Chem. Phys. Lett., 70,* 8 (1980).