presence of both platinum(IV) and platinum(II) in solution before the platinum(III)-platinum(III) bond can be formed.

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**Registry No.** **1**·$H_2O$, 116053-26-0; **2**, 116053-27-1; $K_2Pt(NO_2)_4$, 13815-39-9.

**Supplementary Material Available:** Listings of thermal parameters, least-squares planes, and nonbonded distances and packing diagrams (4 pages); a listing of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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# Glasslike Structure in Crystalline Macrocyclic Complexes: Synthesis, X-ray Diffraction, and Laser-Spectroscopic Investigation of Neodymium(III) and Europium(III) Complexes with 4,13-Dimethyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane[1]

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Nd and Eu nitrates react with the macrocyclic ligand 4,13-dimethyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane, abbreviated $Me_2(2,2)$, to yield crystalline complexes with a 4:3 metal:ligand ratio. Their crystal and molecular structures have been determined at 150 K (Nd) and 293 K (Eu) from single-crystal X-ray diffraction. The two complexes are isostructural, pseudocentric, and disordered and crystallize in the monoclinic space group $C2$ (ITC No. 5) with $Z = 2$. Lattice parameters are $a = 30.140$ (13) Å, $b = 11.031$ (2) Å, $c = 12.494$ (6) Å, $\beta = 112.21$ (4)° for Nd and $a = 31.340$ (9) Å, $b = 11.017$ (3) Å, $c = 12.533$ (2) Å, and $\beta = 116.04$ (2)° for Eu. The structures were solved by Patterson and Fourier techniques and refined by least squares, using soft constraints and unit weights, to final conventional $R$ values of 0.069 (Nd) and 0.065 (Eu). The complexes are comprised of three $[Ln(NO_3)_2\cdot Me_2(2,2)]^+$ cations and one $[Ln(NO_3)_6]^{3-}$ anion. Two equivalent complex cations are in general positions while the other is in a special position with $C_2$ symmetry; the Ln(III) ions are 10-coordinate. The anion has $C_2$ symmetry, close to $C_{2h}$, and contains a 12-coordinate Ln(III) ion. The metal ion sites of the Eu complex have been probed by high-resolution excitation and emission spectra at variable temperature. At 77 K, the $[Eu(NO_3)_6]^{3-}$ anions give rise to a luminescence spectrum dominated by the $^5D_0 \rightarrow {}^7F_1$ transition; this points to anions with a local symmetry very close to $C_{2h}$. Analysis of the spectra generated by the $[Eu(NO_3)_2\cdot Me_2(2,2)]^+$ cations revealed a wide dispersion of the cationic sites. This is due to the complex cations being evenly distributed among different conformations. Such a situation is analogous to what is observed in the vitreous state. These conclusions are supported by the values of the lifetimes determined at 293 and 77 K.

## Introduction

Lanthanide ions react with synthetic ionophores to form guest-host complexes[4] in which the metal ion is partly protected from solvent interaction. Investigation of these complexes is a logical extension[5,6] of the work on alkali-metal and alkaline-earth-metal complexes started in the late 1960s[7] and bears the following specific motivations: (i) systematic study of the coordination properties of rare-earth ions, (ii) design of efficient separation[8,9] and analytical processes,[10] (iii) stabilization of unusual oxidation states, (iv) use of lanthanide macrocyclic complexes as probes in the analysis of biological materials,[11] and (v) synthesis of relaxation agents for NMR-imaging experiments.[12] The subject has been recently reviewed[13] and is presently attracting considerable interest in its synthetic,[14] structural,[15] photophysical,[16,17] kinetic,[18] thermodynamic,[19] and applied[20] aspects.

On the other hand, lanthanide luminescent probes are being increasingly used to solve a variety of structural and analytical problems. In particular, owing to selective laser excitation, the Eu(III) ion probe[21] displays a high sensitivity, which contributes to the determination of the local structures in crystalline materials,[22] glasses,[23] and solutions.[24,25] It facilitates the study of the effects of chemical and thermal treatments on catalysts[26] and potential catalysts[27] and is also provided in the development of immunoassays having a sensitivity comparable to that of radioisotopic methods.[28] In our laboratory, special attention has been given to the relationship between the structure and the

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luminescent properties of Eu-containing and/or Eu-doped lanthanide complexes.[3,29–34] In this work we present the synthesis and the crystal structure determination of the 4:3 complexes between Nd and Eu nitrates and 4,13-dimethyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane, abbreviated $Me_2(2,2)$ or simply L. This article will also show how the photophysical properties of the Eu coronate can contribute to a deeper understanding of the detailed structure of this complex.

## Experimental Section

**Synthesis of the Complexes.** Lanthanide nitrates were synthesized from pure oxides (99.9%, Glucydur) and nitric acid (Merck, p.A.). Acetonitrile (Merck, p.A.) was distilled three times over $P_4O_{10}$ prior to use. The ligand $Me_2(2,2)$ was synthesized according to known procedures,[35] and its purity was checked by elemental analysis and IR spectra. All the reactions were carried out under strictly anhydrous conditions (Ar atmosphere).

A 1-mmol amount of $Me_2(2,2)$ in 30–50 mL of MeCN was heated to reflux before adding a solution of 1 mmol of $Ln(NO_3)_3 \cdot xH_2O$ ($1 < x < 3$) in 20–40 mL of MeCN. The mixture was refluxed for 2–6 h and filtered while hot to eliminate a very fine precipitate of insoluble material. The solution was concentrated to 20–40 mL and allowed to cool. If no crystalline precipitate started to form, more solvent was distilled before storing the solution at −22 °C for 2 days. The microcrystalline material was filtered and dried under vacuum (0.1 mmHg). The crystals were then redissolved in 50–70 mL of MeCN, the solution was heated to reflux, filtered while hot, concentrated, allowed to cool slowly, and stored again 1 day at −22 °C. This recrystallization procedure was repeated until suitable crystals for X-ray analysis were obtained. The complexes gave satisfactory elemental analyses.

**X-ray Structural Studies.** Since both the Nd and Eu complexes are hygroscopic, X-ray analyses were performed on single crystals sealed in Lindemann capillaries. Intensities for the Nd complex were collected at 150 K, whereas intensities for the Eu complex were collected at 293 K since the low-temperature measurements did not improve the disorder problems in the Nd complex.

The cell dimensions (Table I) were accurately determined from the least-squares treatment of 22 (Nd) and 21 (Eu) reflections with $20 \leq 2\theta \leq 27°$ (Nd) and $40 \leq 2\theta \leq 45°$ (Eu). Data were collected on a Syntex $P2_1$ four-circle automatic diffractometer using Nb-filtered Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were evaluated with the Lehman–Larsen algorithm.[36] For each crystal, the intensities of three standard reflections were monitored every 47 (Nd) and 97 (Eu) measurements. They showed a slight decrease, which was accounted for accordingly before correcting for absorption (Gaussian integration method), Lorentz, and polarization effects. Corrections for extinction did not improve the structure refinements and were consequently not considered. For both crystals, the systematic absences *hkl* with $h + k$ odd indicate a *C*-centered monoclinic cell with possible space groups *C*2/*m*, *C*2, and *Cm*.

The crystal structures were solved by the heavy-atom method. The choice of the correct space group was complicated by the higher symmetry of the partial structure of the Ln atoms. The structures were refined in the three possible space groups by combining difference Fourier synthesis and full-matrix least-squares refinement. The minimized function was $\sum(|F_o| - |F_c|)^2$, and unit weights were used. No attempt was made to locate the H atoms, and only the Ln(III) ions were refined anisotropically. Under these conditions the agreement factors for *C*2/*m*, *C*2, and *Cm* were 0.088, 0.075, and 0.092 for Nd and 0.081, 0.071, and 0.086 for Eu. The Hamilton test showed that the better agreement values for *C*2 were significant (the *significance level* is less than 0.01, particularly for the Eu structure) although the number of parameters was larger. A comparison was performed among the three models in relationship to the degree of order in the three independent molecular fragments. In all models the two ions placed at the origin and at ca. (0, 0.5, 0.5) show large thermal ellipsoids and significant electron-density residuals. The second complex cation, at ca. (0.28, 0.50, 0.27), is only ordered in space group *C*2. This observation suggests that there is no mirror plane and that the pseudocentricity is due to the intrinsic higher symmetry of the fragments placed in special positions.

**Table I.** Crystallographic Data for X-ray Diffraction Studies

| | $[Ln(NO_3)_2(C_{14}H_{30}N_2O_4)]_3[Ln(NO_3)_6]$ | |
|---|---|---|
| | Ln = Nd | Ln = Eu |
| formula | $C_{42}H_{90}N_{18}O_{48}Nd_4$ | $C_{42}H_{90}N_{18}O_{48}Eu_4$ |
| fw | 2192.23 | 2223.10 |
| cryst syst | monoclinic | monoclinic |
| space group | *C*2 (ITC No. 5) | *C*2 (ITC No. 5) |
| $a$/Å | 30.140 (13) | 31.340 (9) |
| $b$/Å | 11.031 (2) | 11.017 (3) |
| $c$/Å | 12.494 (6) | 12.533 (2) |
| $\beta$/deg | 112.21 (4) | 116.04 (2) |
| $V$/Å$^3$ | 3845 (3) | 3888 (2) |
| $Z$ | 2 | 2 |
| $d_{calcd}/(g \cdot cm^{-3})$ | 1.89 | 1.90 |
| $d_{exptl}/(g \cdot cm^{-3})$ (flotation in $CCl_4/CH_2Br_2$) | 1.87 | 1.89 |
| cryst size/mm | 0.20 × 0.30 × 0.40 | 0.18 × 0.30 × 0.35 |
| $T$/K | 150 | 293 |
| scan type | $\theta$–$2\theta$ | $\theta$–$2\theta$ |
| scan width/deg | 2 | 2 |
| scan speed/$(deg \cdot s^{-1})$ | 0.042–0.167 | 0.033–0.167 |
| rel bkgd estimation at each end of scan/% | 50 | 25 |
| $2\theta$ interval/deg | 3–50 | 3–55 |
| $\mu$(Mo K$\alpha$)/mm$^{-1}$ | 27.76 | 32.95 |
| transmission factor range | 0.43–0.61 | 0.40–0.66 |
| $F(000)$ | 2184 | 2208 |
| collected octant | $\pm h,-k,+l$ | $\pm h,-k,-l$ |
| no. of unique rflns | 3582 | 5155 |
| no. of obsd rflns ($I > 4\sigma(I)$), $m$ | 2123 | 2641 |
| no. of obsd Friedel pairs | 0 | 189 |
| $R_{int}$ (with abs cor) | 0.032 | 0.022 |
| no. of refined params, $n$ | 245 | 245 |
| no. of correlations (>0.50) | 202 | 165 |
| $R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ | 0.069 | 0.065 |
| $S = \{[\sum(\|F_o\| - \|F_c\|)^2 + \sum w_p(R_p - R_o)^2]/\sum(m + r - n)\}^{1/2}$ [a] | 3.49 | 3.84 |
| Durbin–Watson $D$ statistics | 1.90 | 1.91 |
| final av shift/error | 0.53 | 0.50 |
| residual electron density/(e·Å$^{-3}$) | 1.7 | 1.6 |

[a] $R_p$ = prescribed distance or angle; $R_o$ = observed value; $w_p$ = reciprocal of imposed esd; $r$ = number of soft constraints.

The final refinements were therefore carried out in space group *C*2. Due to the presence of a pseudo mirror plane related to the disorder, many parameters were strongly correlated, with the following consequences: (i) slow convergence, (ii) large thermal parameters and esd's, (iii) relatively large electron residuals simulating the higher symmetry, and (iv) nonconvergence of the enantiomorph-polarity parameter.[37] The origin was fixed on the structure centroids by a dedicated algorithm,[38] and the following soft constraints were used, with the weights equal to the reciprocal values of the given esd's: C–O = 1.420 (5) Å, C–N = 1.480 (5) Å, C–C = 1.520 (5) Å, C–X–C = 113.0 (5)°, C–C–X = 109.5 (5)° (where X is N or O), N–O = 1.240 (1) Å, O–N–O = 120.0 (1)°. In both structures, two possible orientations were found for the pseudosymmetry-related nitrate groups in $[Ln(NO_3)_6]^{3-}$; population parameters were refined in the first stage of refinement only. The N atoms of the ligand could not be located unambiguously. Isotropic thermal parameters of the C atoms were constrained to be equal to those of the N atoms. The enantiomorph-polarity parameters in the two structure refinements did not converge and were arbitrary fixed to unity. For the ligand surrounding the Ln(III) ion in a general position, two distinct and mirror-

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related orientations could be refined, of which one was chosen on the basis of conformational considerations. After convergence was reached with isotropic atoms (except the Ln ions), attempts to further interpret the residual electron density failed. Most of the largest peaks were located 1.3–1.5 Å from the nitrate ions. An attempt to refine them anisotropically showed significant elongations toward the residual peaks. Other residuals were located around the N–$CH_3$ fragments of the ligand molecules.

Atom scattering factors and dispersion corrections were taken from ref 39. Computational work was carried out with XRAY,[40] PARST,[41] and ORTEP[42] programs. Atomic positional parameters for the Nd complex are reported in Table II.

**Table II.** Atomic Fractional Coordinates (×$10^3$) and Isotropic Thermal Parameters (Å$^2$ × $10^3$) for the Nd Complex[a]

| atom | $x$ | $y$ | $z$ | PP | $U_{iso}/U_{eq}$[b] |
|---|---|---|---|---|---|
| Nd(1) | 0 | −5 (2) | 0 | | 34.3 (8)* |
| N(1) | 100.0 (6) | −3 (3) | 153 (2) | | 68 (7) |
| O(11) | 143.2 (6) | −2 (5) | 216 (2) | | 81 (7) |
| O(12) | 84 (1) | −84 (3) | 80 (3) | | 150 (20) |
| O(13) | 74.2 (9) | 84 (3) | 156 (2) | | 86 (9) |
| C(1) | 3 (3) | −321 (8) | 63 (2) | | 290 (90) |
| O(1) | −15 (2) | −210 (4) | 87 (4) | | 440 (80) |
| C(2) | 0 (2) | −189 (4) | 206 (4) | | 130 (20) |
| C(3) | −33 (2) | −93 (5) | 223 (7) | | 400 (100) |
| C(4) | 16 (2) | 91 (7) | 265 (5) | | 456 |
| N(2) | −25 (2) | 27 (4) | 179 (4) | | 460 (60) |
| C(5) | −68 (1) | 103 (5) | 146 (5) | | 160 (30) |
| C(6) | −58 (1) | 218 (4) | 95 (6) | | 140 (30) |
| O(2) | −13 (1) | 205 (3) | 89 (2) | | 90 (10) |
| C(7) | 5 (1) | 314 (4) | 64.1 (9) | | 110 (20) |
| Nd(3) | 277.51 (6) | 498 (1) | 292.9 (1) | | 46.4 (7)* |
| N(7) | 249.3 (9) | 498 (3) | 491 (2) | | 75 (7) |
| O(71) | 236.6 (8) | 498 (4) | 575 (2) | | 92 (7) |
| O(72) | 272 (1) | 411 (2) | 474 (2) | | 72 (8) |
| O(73) | 238 (1) | 584 (2) | 421 (2) | | 90 (10) |
| N(8) | 306.3 (5) | 498 (4) | 94 (1) | | 62 (6) |
| O(81) | 317.8 (6) | 485 (4) | 9 (1) | | 70 (8) |
| O(82) | 336.1 (5) | 479 (3) | 193 (1) | | 58 (7) |
| O(83) | 264.2 (5) | 522 (3) | 80 (1) | | 62 (7) |
| C(8) | 251 (1) | 804 (3) | 197 (4) | | 80 (20) |
| O(4) | 290 (1) | 726 (3) | 255 (4) | | 100 (20) |
| C(9) | 332 (1) | 790 (3) | 323 (4) | | 160 (30) |
| C(10) | 370 (1) | 699 (4) | 384 (3) | | 120 (20) |
| C(11) | 334 (2) | 699 (5) | 531 (4) | | 135 |
| N(9) | 353 (1) | 625 (3) | 462 (3) | | 140 (20) |
| C(12) | 390 (1) | 539 (3) | 534 (3) | | 110 (20) |
| C(13) | 392 (1) | 427 (4) | 467 (5) | | 270 (60) |
| O(5) | 346 (1) | 377 (3) | 412 (3) | | 120 (10) |
| C(14) | 345 (2) | 248 (4) | 417 (3) | | 200 (40) |
| C(15) | 319 (1) | 199 (3) | 296 (3) | | 80 (10) |
| O(6) | 279 (1) | 273 (3) | 237 (3) | | 90 (20) |
| C(16) | 238 (1) | 203 (3) | 179 (5) | | 140 (30) |
| C(17) | 197 (1) | 286 (4) | 111 (3) | | 110 (20) |
| C(18) | 182 (3) | 315 (6) | 289 (4) | | 191 |
| N(10) | 190 (1) | 375 (4) | 191 (3) | | 190 (30) |
| C(19) | 151 (1) | 462 (3) | 130 (3) | | 90 (20) |
| C(20) | 161 (2) | 580 (4) | 195 (5) | | 200 (40) |
| O(7) | 204 (1) | 631 (3) | 191 (3) | | 110 (10) |
| C(21) | 208 (1) | 757 (3) | 216 (5) | | 160 (30) |
| Nd(2) | 0 | 500 (2) | 500 | | 49 (1)* |
| N(3) | 0 | 236 (2) | 500 | | 80 (20) |
| O(31) | 0 | 124 (2) | 500 | | 140 (50) |
| O(32) | 29.8 (7) | 292 (2) | 581 (1) | 0.70 | 27 (7) |
| O(33) | 26 (9) | 292 (2) | 459.0 (4) | 0.30 | 30 (10) |
| N(4) | 0 | 772 (4) | 500 | | 100 (40) |
| O(41) | 0 | 884 (4) | 500 | | 170 (20) |
| O(42) | −32 (2) | 715 (4) | 424 (4) | | 280 (40) |
| N(5) | −67.1 (6) | 502 (3) | 622 (2) | | 71 (7) |
| O(51) | −93.7 (8) | 500 (5) | 677 (2) | | 120 (10) |
| O(52) | −62 (2) | 408 (3) | 572 (3) | 0.70 | 70 (10) |
| O(53) | −51 (1) | 600 (3) | 604 (3) | 0.70 | 40 (10) |
| O(54) | −85 (1) | 480 (20) | 513 (2) | 0.30 | 80 (30) |
| O(55) | −23.0 (6) | 530 (20) | 674 (3) | 0.30 | 70 (30) |
| N(6) | −79.1 (6) | 509 (4) | 267 (1) | | 81 (8) |
| O(61) | −112.4 (7) | 519 (4) | 171 (2) | | 100 (10) |
| O(62) | −88.1 (8) | 497 (8) | 355 (2) | | 120 (10) |
| O(63) | −37.0 (7) | 503 (8) | 273 (2) | | 130 (10) |

[a] Esd's are given in parentheses. Nonreported population parameters, PP, are equal to 1.00. [b] Thermal parameters with an asterisk are the $U$-equivalent parameters corresponding to the anisotropic ellipsoid: $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_i{\cdot}a_j$.

**Spectroscopic Measurements.** Luminescence measurements were performed at 77 K on finely powdered microcrystalline samples. A dye-laser power of 150 mW was used for both excitation and emission spectra. The spectrometer and experimental techniques have been previously described.[33,34]

## Discussion of the Structures

The unsubstituted ligand (2,2) forms 1:1 complexes with all the lanthanide nitrates, but it was shown that the nitrate ions are bound differently in the lighter (La–Sm) and heavier (Gd–Yb) series.[43] It was subsequently demonstrated that the Eu complex is ionic and contains the complex cation $[Eu(NO_3)_2(2,2)]^+$.[32] Similar bis(nitrato) or dichloro complex cations are quite common in lanthanide macrocyclic complexes.[13] With $Me_2(2,2)$, complexes having a 4:3 metal:ligand ratio are isolated from Pr through Lu.[44]

The two investigated Nd and Eu complexes are strictly isostructural. The partial structure of the Ln(III) ions is centrosymmetric, which is not the case for the lighter atoms. This situation, along with the presence of important static disorders, especially in the macrocyclic molecules, did not facilitate the structure refinements, and soft constraints had to be used. The two structures marginally differ in the position of the C, N, and O atoms around the Ln(III) ions, which may be partly traced back to the different temperatures at which the data were collected. Moreover, it should be realized that the atoms of the ligands build kinds of delocalized toroids around the metal ions and that the extracted coordinates represent average values only. The proposed model is considered as the most probable static structural arrangement describing the glasslike multistate disorder of the true crystal packing. A similar situation was observed in the 15-crown-5 sandwich complexes with lanthanide perchlorates and hexafluorophosphates: in this case, no light atoms could be localized upon solving the crystal structure.[45] Selected bond lengths and angles are reported in Table III.

The asymmetric units contain three distinct ions with no substantial interaction between them (Figure 1).[46] One of the $[Ln(NO_3)_2{\cdot}L]^+$ cations is placed in a general position, whereas the second one is in a special position with $C_2$ symmetry. The $[Ln(NO_3)_6]^{3-}$ anion also lies in a special position with $C_2$ symmetry. The complex formulation is therefore similar to that of the other 4:3 lanthanide adducts with synthetic ionophores.[13]

In the $[(Ln(1))(NO_3)_2{\cdot}L]^+$ cation with $C_2$ symmetry, the Ln(III) ions lie approximately in the center of the ligand cavity (Figure 2a). The 2-fold axis is in the mean plane of the ligand molecule. The bidentate and opposite nitrate ions lie on the crystallographic $b$ plane and are perpendicular to the ligand plane. The symmetry of the complex is close to $C_{2h}$, the Ln(III) ion and the N atoms of both the ligand and the two nitrate groups defining a pseudo mirror plane. The $[(Ln(3))(NO_3)_2{\cdot}L]^+$ cation located in a general position exhibits also a pseudosymmetry: a mirror plane perpendicular to the mean ligand plane (Figure 3). Its geometry is close to a $C_{2v}$ arrangement with the 2-fold axis through the two nitrate ions and perpendicular to the main plane of the ligand. The main difference with respect to the cation having the crystallographic $C_2$ symmetry lies in the position of the methyl

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(39) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(40) Stewart, J. M.; Kundell, F. A.; Baldwin, J.-C. "XRAY-72"; Tech. Rep. TR-192; Computing Science Center, University of Maryland: College Park, MD, 1972. Locally modified by D. Schwarzenbach.

(41) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(42) Johnson, C. K. "ORTEP II"; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(43) Desreux, J. F.; Renard, A.; Duyckaerts, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1587.

(44) Jin, L.; Plancherel, D.; Bünzli, J.-C. G. *Inorg. Chim. Acta* **1988**, *144*, 269.

(45) Bünzli, J.-C. G.; Harrison, W. D.; Giorgetti, A.; Pradervand, G.-O.; Alcock, N. W. *Inorg. Chim. Acta* **1985**, *109*, 59.

(46) The two structures being similar, the figures shown represent the Eu complex only, for which a detailed spectroscopic study was carried out.

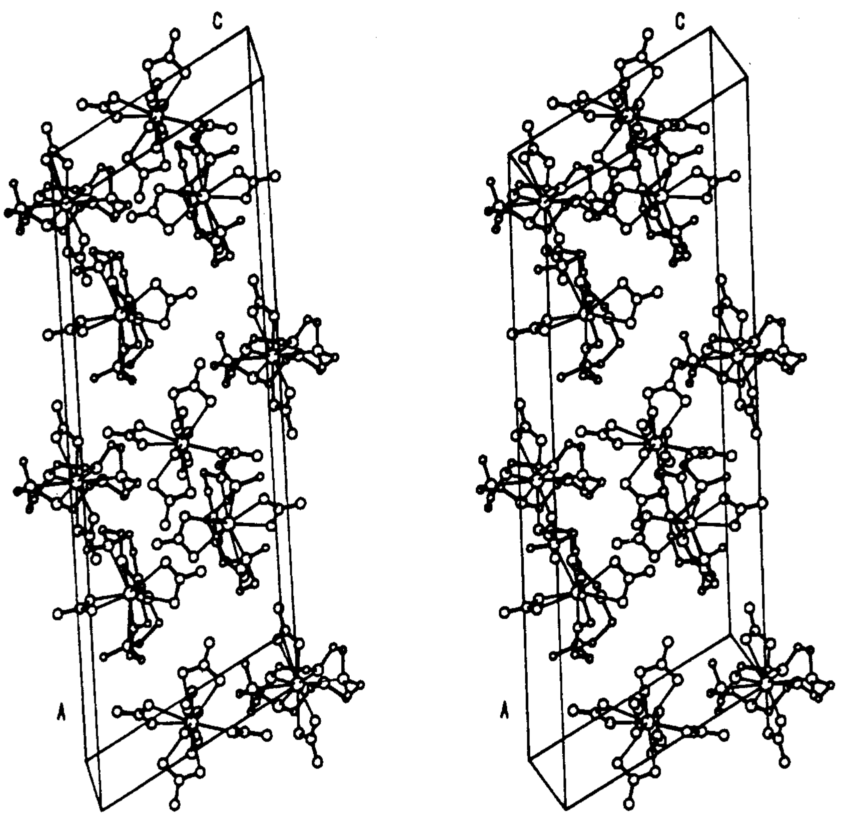

**Figure 1.** Stereoscopic view of the crystal packing in $[Eu(NO_3)_2 \cdot L]_3[Eu(NO_3)_6]$.

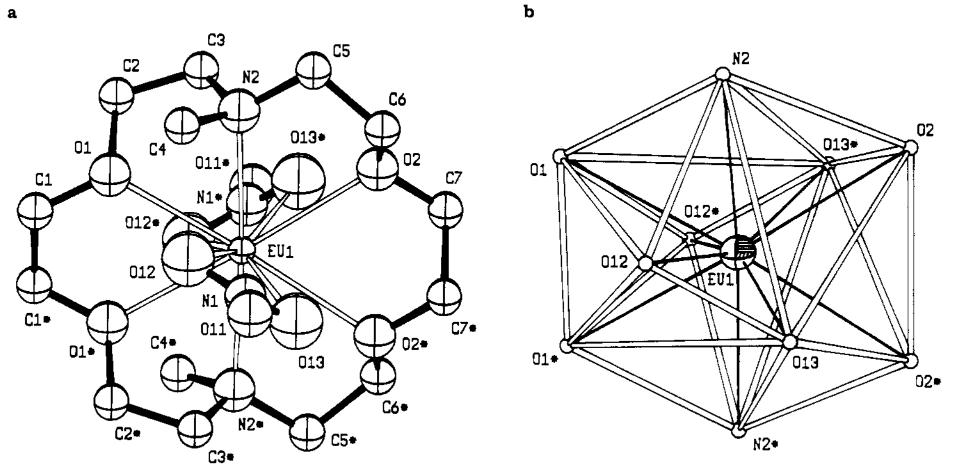

**Figure 2.** (a) ORTEP drawing of $[(Eu(1))(NO_3)_2 \cdot L]^+$ with $C_2$ symmetry, showing the atom-numbering scheme (30% probability contours for all the atoms). (b) Coordination polyhedron around Eu(1).

groups, which are on the same side of the macrocycle mean plane in the $[(Ln(3))(NO_3)_2 \cdot L]^+$ ion (Figure 3a) and on opposite sides in the Ln(1) cation (Figure 2a).

Data for a more detailed comparison of the Nd and Eu complex cations are reported in Tables III, IV, and S5 (cf. the supplementary material). In both structures, the macrocyclic $Me_2(2,2)$ ligand displays some torsion angles significantly different from the energetically favorable synclinal (60°) and antiperiplanar (180°) values, as already observed in the Eu complex with ligand (2,2).[32] Furthermore, it is noteworthy that the angle between the planes of the two opposite nitrate ions is 90° for Ln(3) and ca. 60° for Ln(1), a consequence of the differently positioned methyl groups. With respect to the coordination properties of the ligand, the geometrical arrangement of the heteroatoms around the metal center is a more important factor than the conformation of the ethylene bridges. We have carried out a ring-puckering analysis[41,47] on the $N_2O_4$ moiety, similar to that reported for dicyclohexyl-18-crown-6 and its complexes.[34a] In the cation with $C_2$ symmetry, the $N_2O_4$ ring is almost perfectly planar for Nd ($Q^{48}$ = 0.08), as observed in $[Nd(NO_3)_2(18\text{-crown-}6)]^+$.[13] For the smaller Eu(III) ion, $Q$ = 0.58, $\theta$ = 41°, and $\phi$ = 150°: the $N_2O_4$ ring is no longer planar, displaying a slightly twisted chairlike conformation. In the nonsymmetric cation, the two N atoms are displaced from the mean O atom plane and lie on the same side as the Ln(III) ions (cf. set 8 in Table S5). The $N_2O_4$ entities clearly adopt a boat conformation characterized by the following parameters: $Q$ = 1.24 (Nd) and 1.46 (Eu), $\theta$ = 87° (Nd) and 84° (Eu), $\phi$ = 17° (Nd) and 21° (Eu).

The coordination polyhedra are shown in Figures 2b and 3b. The mean Ln–O(nitrate) distances are the same, within experimental errors, in the two different cations: 2.53 (2) Å for Nd and 2.51 (3) Å for Eu. On the other hand, the Ln–X(ether)

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[47] Boeyens, J. C. A. *J. Cryst. Mol. Struct.* **1978**, *8*, 317.

[48] $Q$ is proportional to the ring deviation from planarity, $\theta$ is the angle characterizing the ring conformation (0 or 180° = "chair", 90 ° = "boat"), and $\phi$ is the angle defining the corresponding conformer.[47]

**Table III.** Selected Bond Lengths (Å) and Angles (deg) for $[Ln(NO_3)_2{\cdot}L]_3[Ln(NO_3)_6]$, Ln = Nd (150 K) and Ln = Eu (293 K)[a]

| | Nd | Eu | | Nd | Eu |
|---|---|---|---|---|---|
| | | (a) $[Ln(NO_3)_2{\cdot}L]^+$, $C_2$ Symmetry | | | |
| Ln(1)–O(12) | 2.49 (3) | 2.53 (3) | Ln(1)–O(13) | 2.54 (3) | 2.48 (3) |
| Ln(1)–O(1) | 2.62 (5) | 2.65 (5) | Ln(1)–N(2) | 2.64 (6) | 2.52 (4) |
| Ln(1)–O(2) | 2.66 (4) | 2.67 (4) | | | |
| O(12)–Ln(1)–O(13) | 50 (1) | 51 (1) | O(1)*–Ln(1)–O(1) | 60 (1) | 59 (2) |
| O(1)–Ln(1)–N(2) | 67 (1) | 58 (1) | N(2)–Ln(1)–O(2) | 53 (1) | 63 (1) |
| O(2)–Ln(1)–O(2)* | 59 (1) | 62 (1) | O(1)–Ln(1)–O(2) | 120 (1) | 120 (1) |
| N(1)···Ln(1)–O(1) | 92 (1) | 88 (1) | N(1)···Ln(1)–N(2) | 90 (1) | 80 (1) |
| N(1)···Ln(1)–O(2) | 90 (1) | 94 (1) | N(1)···Ln(1)···N(1)* | 179 (1) | 177 (1) |
| | | (b) $[Ln(NO_3)_2{\cdot}L]^+$, No Symmetry | | | |
| Ln(3)–O(72) | 2.53 (3) | 2.47 (3) | Ln(3)–O(73) | 2.52 (4) | 2.50 (2) |
| Ln(3)–O(82) | 2.53 (2) | 2.51 (1) | Ln(3)–O(83) | 2.56 (2) | 2.54 (1) |
| Ln(3)–O(4) | 2.61 (4) | 2.53 (4) | Ln(3)–N(9) | 2.82 (3) | 2.86 (5) |
| Ln(3)–O(5) | 2.43 (3) | 2.48 (3) | Ln(3)–O(6) | 2.59 (4) | 2.55 (3) |
| Ln(3)–N(10) | 2.82 (4) | 2.79 (3) | Ln(3)–O(7) | 2.56 (3) | 2.53 (3) |
| O(72)–Ln(3)–O(73) | 50 (1) | 51 (1) | O(82)–Ln(3)–O(83) | 50 (1) | 50 (1) |
| O(4)–Ln(3)–N(9) | 62 (1) | 65 (1) | N(9)–Ln(3)–O(5) | 64 (1) | 68 (1) |
| O(5)–Ln(3)–O(6) | 62 (1) | 61 (1) | O(6)–Ln(3)–N(10) | 61 (1) | 66 (1) |
| N(10)–Ln(3)–O(7) | 64 (1) | 65 (1) | O(7)–Ln(3)–O(4) | 61 (1) | 56 (1) |
| N(7)···Ln(3)–O(6) | 106 (1) | 105 (1) | N(7)···Ln(3)–N(10) | 82 (1) | 79 (1) |
| N(7)···Ln(3)···N(8) | 180 (1) | 178 (1) | N(7)···Ln(3)–O(4) | 105 (1) | 110 (1) |
| N(7)···Ln(3)–N(9) | 77 (1) | 74 (1) | N(7)···Ln(3)–O(5) | 86 (1) | 85 (1) |
| N(7)···Ln(3)···O(7) | 87 (1) | 88 (1) | N(8)···Ln(3)–O(4) | 75 (1) | 68 (1) |
| N(8)···Ln(3)–N(9) | 103 (1) | 105 (1) | N(8)···Ln(3)–O(5) | 94 (1) | 96 (1) |
| N(8)···Ln(3)–O(6) | 74 (1) | 77 (1) | N(8)···Ln(3)–N(10) | 98 (1) | 102 (1) |
| N(8)···Ln(3)–O(7) | 93 (1) | 91 (1) | | | |
| | | (c) $[Ln(NO_3)_6]^{3-}$, $C_2$ Symmetry | | | |
| Ln(2)–O(32) | 2.53 (2) | 2.56 (2) | Ln(2)–O(33) | 2.53 (8) | 2.56 (2) |
| Ln(2)–O(42) | 2.60 (5) | 2.48 (4) | Ln(2)–O(52) | 2.56 (5) | 2.62 (3) |
| Ln(2)–O(53) | 2.59 (4) | 2.59 (3) | Ln(2)–O(54) | 2.63 (4) | 2.64 (3) |
| Ln(2)–O(55) | 2.54 (5) | 2.57 (3) | Ln(2)–O(62) | 2.59 (2) | 2.61 (2) |
| Ln(2)–O(63) | 2.62 (2) | 2.65 (2) | | | |
| O(32)–Ln(2)–O(32)* | 50 (1) | 50 (1) | O(33)–Ln(2)–O(33)* | 50 (1) | 50 (1) |
| O(42)–Ln(2)–O(42)* | 49 (1) | 51 (1) | O(52)–Ln(2)–O(53) | 49 (1) | 49 (1) |
| O(54)–Ln(2)–O(55) | 51 (1) | 49 (1) | O(62)–Ln(2)–O(63) | 49 (1) | 48 (1) |
| N(3)···Ln(2)···N(4) | 180 (1) | 180 (1) | N(3)···Ln(2)···N(5) | 90 (1) | 92 (1) |
| N(3)···Ln(2)···N(6) | 92 (1) | 88 (1) | N(4)···Ln(2)···N(5) | 90 (1) | 88 (1) |
| N(4)···Ln(2)···N(6) | 88 (1) | 92 (1) | N(5)···Ln(2)···N(6) | 93 (1) | 87 (1) |

[a] O(33), O(54), and O(55) with occupancy factor 0.3 correspond to O(32), O(52), and O(53), respectively, with occupancy factor 0.7. The asterisks denote positions equivalent for the 2-fold axis.

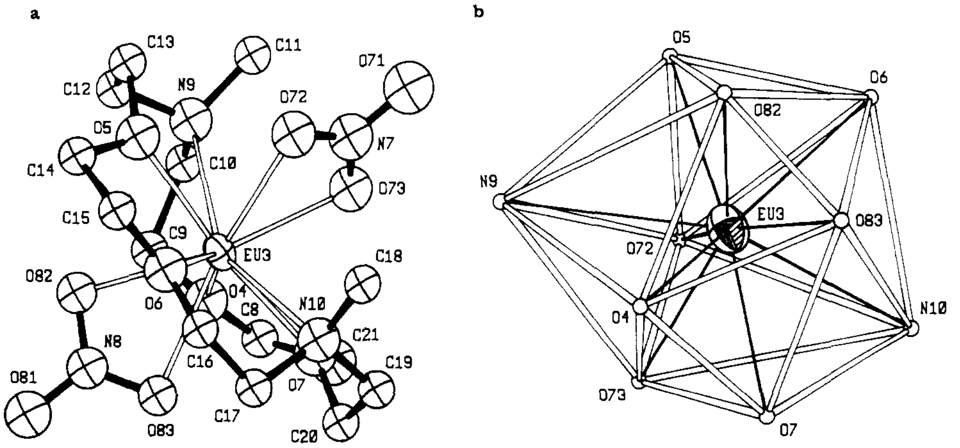

**Figure 3.** (a) ORTEP drawing of the nonsymmetric $[(Eu(3))(NO_3)_2{\cdot}L]^+$ showing the atom-numbering scheme (30% probability contours for all the atoms). (b) Coordination polyhedron around Eu(3).

distances vary considerably, probably due to the disorder in the macrocyclic ligands. In the cations with $C_2$ symmetry they are equal to 2.64 (2) Å (X = O, or N) for Nd and to 2.66 (1) Å (X = O) and 2.52 (4) Å for Eu. In the other cations the Ln–N distances are much longer than the Ln–O mean distances, 2.82 vs 2.55 (7) Å for Nd and 2.83 vs 2.52 (3) Å for Eu, resulting in an elliptically shaped macrocyclic cavity. It is also noteworthy that the mean heteroatom–heteroatom contact distances in $Me_2(2,2)$ increase from 2.63 (Nd) and 2.65 Å (Eu) for Ln(1) to 2.74 (Nd) and 2.77 Å (Eu) for Ln(3). Therefore, in view of the crude model previously reported for $O_6$ rings,[34a] the M–X and X···X distances are comparable when the ligand adopts a flat conformation, while they differ more substantially in the complex cations where the macrocycle has a boat conformation.

**Table IV.** Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for the $Me_2(2,2)$ Molecules in $[Ln(NO_3)_2{\cdot}L]^+$ Cations[a]

| | | | | Nd | | | Eu | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 1–2 | 1–2–3 | 1–2–3–4 | 1–2 | 1–2–3 | 1–2–3–4 |
| | | | | Symmetry $C_2$ | | | | | |
| O(1)* | C(1)* | C(1) | O(1) | 1.41 (10) | 108 (4) | 47 (7) | 1.41 (8) | 111 (3) | 30 (6) |
| C(1)* | C(1) | O(1) | C(2) | 1.52 (5) | 108 (4) | −165 (5) | 1.52 (3) | 111 (3) | 110 (5) |
| C(1) | O(1) | C(2) | C(3) | 1.41 (10) | 112 (4) | −161 (5) | 1.41 (8) | 115 (4) | −176 (5) |
| O(1) | C(2) | C(3) | N(2) | 1.41 (7) | 108 (4) | −69 (6) | 1.43 (9) | 107 (5) | −26 (6) |
| C(2) | C(3) | N(2) | C(5) | 1.52 (9) | 111 (5) | 154 (5) | 1.52 (7) | 109 (4) | −160 (4) |
| C(3) | N(2) | C(5) | C(6) | 1.49 (8) | 111 (5) | −176 (5) | 1.48 (8) | 114 (4) | −119 (5) |
| N(2) | C(5) | C(6) | O(2) | 1.48 (6) | 108 (4) | 5 (6) | 1.50 (6) | 111 (3) | 45 (5) |
| C(5) | C(6) | O(2) | C(7) | 1.50 (8) | 107 (4) | −168 (4) | 1.53 (6) | 108 (3) | 165 (4) |
| C(6) | O(2) | C(7) | C(7)* | 1.41 (6) | 113 (3) | −98 (4) | 1.43 (4) | 116 (3) | 86 (4) |
| O(2) | C(7) | C(7)* | O(2)* | 1.41 (5) | 107 (3) | −52 (4) | 1.42 (6) | 109 (4) | 57 (4) |
| C(4) | N(2) | C(3) | C(2) | 1.48 (7) | 112 (5) | 83 (6) | 1.48 (8) | 111 (4) | 29 (7) |
| C(4) | N(2) | C(5) | C(6) | 1.48 (7) | 110 (5) | 60 (6) | 1.48 (8) | 114 (5) | 112 (6) |
| | | | | No Symmetry | | | | | |
| C(8) | O(4) | C(9) | C(10) | 1.41 (5) | 113 (3) | 178 (4) | 1.40 (5) | 113 (4) | −88 (5) |
| O(4) | C(9) | C(10) | N(9) | 1.41 (5) | 108 (3) | −62 (4) | 1.41 (6) | 108 (4) | −69 (6) |
| C(9) | C(10) | N(9) | C(12) | 1.50 (5) | 109 (4) | −175 (3) | 1.50 (9) | 111 (4) | −76 (6) |
| C(10) | N(9) | C(12) | C(13) | 1.49 (6) | 112 (4) | −80 (4) | 1.48 (7) | 109 (4) | 168 (4) |
| N(9) | C(12) | C(13) | O(5) | 1.47 (5) | 112 (4) | −52 (5) | 1.48 (5) | 110 (4) | −71 (4) |
| C(12) | C(13) | O(5) | C(14) | 1.51 (7) | 110 (4) | −139 (4) | 1.53 (5) | 110 (3) | −114 (4) |
| C(13) | O(5) | C(14) | C(15) | 1.42 (5) | 114 (4) | −127 (4) | 1.45 (6) | 118 (3) | −157 (3) |
| O(5) | C(14) | C(15) | O(6) | 1.42 (6) | 109 (3) | −42 (5) | 1.42 (5) | 108 (3) | −42 (4) |
| C(14) | C(15) | O(6) | C(16) | 1.51 (5) | 109 (3) | −133 (4) | 1.53 (4) | 107 (2) | −176 (3) |
| C(15) | O(6) | C(16) | C(17) | 1.42 (5) | 112 (3) | −175 (3) | 1.40 (4) | 113 (2) | −178 (3) |
| O(6) | C(16) | C(17) | N(10) | 1.41 (5) | 109 (3) | −57 (4) | 1.42 (5) | 110 (3) | 59 (4) |
| C(16) | C(17) | N(10) | C(19) | 1.50 (5) | 109 (3) | 179 (3) | 1.52 (5) | 109 (3) | 179 (3) |
| C(17) | N(10) | C(19) | C(20) | 1.48 (6) | 112 (3) | −151 (4) | 1.51 (5) | 116 (3) | 74 (4) |
| N(10) | C(19) | C(20) | O(7) | 1.47 (5) | 109 (3) | 65 (4) | 1.48 (4) | 112 (3) | 59 (4) |
| C(19) | C(20) | O(7) | C(21) | 1.51 (6) | 109 (4) | 161 (4) | 1.51 (5) | 108 (3) | 138 (4) |
| C(20) | O(7) | C(21) | C(8) | 1.41 (6) | 113 (4) | −174 (4) | 1.43 (7) | 114 (4) | 133 (4) |
| O(7) | C(21) | C(8) | O(4) | 1.42 (5) | 108 (4) | 49 (5) | 1.42 (5) | 109 (4) | −13 (5) |
| C(21) | C(8) | O(4) | C(9) | 1.51 (7) | 108 (3) | −132 (4) | 1.50 (5) | 107 (3) | 159 (4) |
| C(11) | N(9) | C(10) | C(9) | 1.48 (7) | 112 (4) | 47 (5) | 1.46 (8) | 109 (4) | −156 (5) |
| C(11) | N(9) | C(12) | C(13) | 1.48 (7) | 112 (3) | 152 (4) | 1.46 (8) | 112 (5) | −65 (5) |
| C(18) | N(10) | C(17) | C(16) | 1.48 (8) | 112 (4) | 54 (5) | 1.47 (6) | 112 (3) | −53 (4) |
| C(18) | N(10) | C(19) | C(20) | 1.48 (8) | 112 (4) | 82 (5) | 1.47 (6) | 110 (3) | −158 (4) |

[a] Data for Nd and Eu complexes are at 150 and 293 K, respectively.

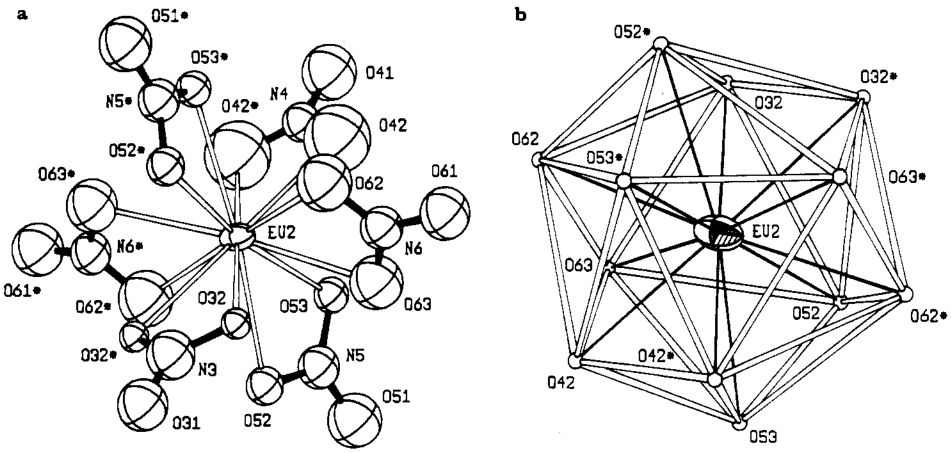

**Figure 4.** (a) ORTEP drawing of $[(Eu(2))(NO_3)_6]^{3-}$ with $C_2$ symmetry, showing the atom-numbering scheme (30% probability contours for all the atoms). (b) Coordination polyhedron around Eu(2).

The hexakis(nitrato) anions (Figure 4) have three disordered nitrates, $(N(3))O_3^-$, $(N(5))O_3^-$, and $(N(5)^*)O_3^-$; two different positions could be resolved for six O atoms (cf. Table III). They have approximate $C_{2h}$ symmetry since, in addition to the $C_2$ axis through N(3) and N(4), there is a pseudo mirror plane containing $(N(6))O_3^-$ and $(N(6)^*)O_3^-$. The mean Ln–O bond lengths are 2.58 (3) and 2.59 (5) Å for Nd and Eu, respectively, in reasonable agreement with the values expected for 12-coordinate Ln(III) ions.[49] The arrangement of the six N atoms around the Ln(III) ions resembles an octahedron, with angles close to their expected values (cf. Tables III and S5) but with nonequivalent Ln–N distances: 2.92–2.99 (3) Å for Nd and 2.85–3.02 (2) Å for Eu.

## Luminescence Study

The Eu(III) ion being highly luminescent and environmentally sensitive, we have turned to laser-luminescence spectroscopy to gain more information on the detailed structure of the europium complex. Excitation spectra of the nondegenerate $^5D_0 \leftarrow {}^7F_0$ transition reflect the number of distinct chemical environments for the Eu(III) ion.[24] They have been measured at three different temperatures by tuning a continuous dye laser over the corresponding spectral range while successively monitoring several components of the $^5D_0 \rightarrow {}^7F_1$ transition. This latter transition

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(49) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

**Table V.** Energy ($\tilde{\nu}$, $cm^{-1}$) and Width at Half-Height ($\Delta\tilde{\nu}_{1/2}$, $cm^{-1}$) of the $^5D_0 \leftarrow {}^7F_0$ Transitions in $[Eu(NO_3)_2{\cdot}Me_2(2,2)]_3[Eu(NO_3)_6]$[a]

| | band H | | band C | | | |
|---|---|---|---|---|---|---|
| $T$/K | $\tilde{\nu}$ | $\Delta\tilde{\nu}_{1/2}$ | $\tilde{\nu}$ | $\Delta\tilde{\nu}_{1/2}$ | $\tilde{\nu}$ | $\Delta\tilde{\nu}_{1/2}$ |
| 294 | 17 253 | 15 | 17 265 | 16 | | |
| 125 | 17 251 | 11 | 17 266 | 11 | | |
| 77 | 17 243 sh | | 17 265 m | 5 | 17 263 m | 5 |
| | 17 245 | 6 | 17 260 sh | | 17 256 s | 5 |
| | | | 17 253 w | 5 | | |

[a] The labels H (hexanitrate) and C (complex cations) refer to Figure 5. Abbreviations: w = weak; m = medium; s = strong; sh = shoulder.

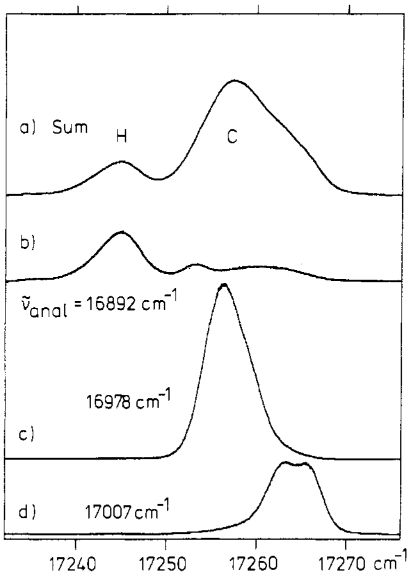

**Figure 5.** Excitation spectra of the $^5D_0 \leftarrow {}^7F_0$ transition of $[Eu(NO_3)_2{\cdot}L]_3[Eu(NO_3)_6]$ at 77 K obtained by analyzing the $^5D_0 \rightarrow {}^7F_1$ transition (excitation bandwidth 1.5 $cm^{-1}$, analyzing bandwidth 6.0 $cm^{-1}$, vertical scale in arbitrary units).

was chosen instead of the usually more intense $^5D_0 \rightarrow {}^7F_2$ transition because it allowed a better differentiation between the various Eu(III) environments. At 294 and 125 K, two broad bands, labeled H and C, are observed (Table V). The low-temperature spectra are more complex (Figure 5). In addition to the expected bathochromic shift and line narrowing, band C split into at least five components while a shoulder appeared on the low-energy side of band H.

To assign the $^5D_0 \leftarrow {}^7F_0$ transitions to specific chemical species, we have selectively excited the Eu(III) ions to their $^5D_0$ levels with energies corresponding to the maxima of bands H and C. The resulting $^5D_0 \rightarrow {}^7F_J$ luminescence spectra are displayed in Figure 6. They are very different, with respect both to the total intensity of emitted light, spectrum H being ca. 15 times less intense than spectrum C, and to the relative $^5D_0 \rightarrow {}^7F_J$ transition probabilities. In particular, $P_{2/1} = P(^5D_0 \rightarrow {}^7F_2)/P(^5D_0 \rightarrow {}^7F_1)$ amounts to 0.9 in spectrum H[50] while it is equal to 3.2 in spectrum C. Comparison with luminescence spectra of the 4:3 Eu complexes with 18-crown-6[33] (18C6) and 21-crown-7[3] (21C7) polyethers[51] readily leads to the assignment of spectrum H to the $[Eu(NO_3)_6]^{3-}$ anion: $\tilde{\nu}(^5D_0 \leftarrow {}^7F_0)$ = 17 245 $cm^{-1}$, as compared to 17 242 $cm^{-1}$ (18C6) and 17 246 $cm^{-1}$ (21C7), (ii) the barycenter of the $^7F_1$ sublevels is equal to 365 $cm^{-1}$ (Table VI), as compared to 365 $cm^{-1}$ (18C6) and 364 $cm^{-1}$ (21C7), and (iii) the patterns of the $^5D_0 \rightarrow {}^7F_{1,2}$ transitions are very similar (cf. Figure 7).

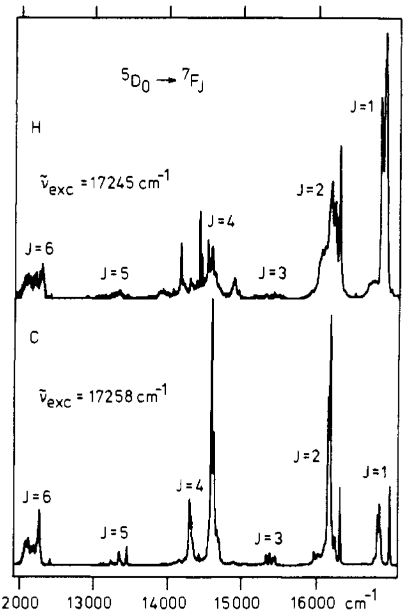

**Figure 6.** Emission spectra of $[Eu(NO_3)_2{\cdot}L]_3[Eu(NO_3)_6]$ at 77 K under selective laser excitation: (top) site H; (bottom) maximum of band C (cf. Figure 5; excitation bandwidth 1.5 $cm^{-1}$, analyzing bandwidth 1.5 $cm^{-1}$, vertical scales in arbitrary units). The bottom spectrum has been scaled down by a factor of 17 with respect to the top spectrum.

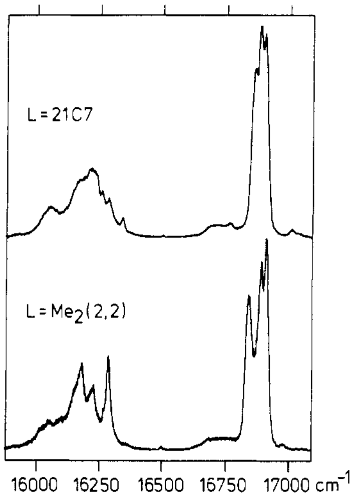

**Figure 7.** $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of $[Eu(NO_3)_6]^{3-}$ in two different $[Eu(NO_3)_2{\cdot}L]_3[Eu(NO_3)_6]$ complexes.

**Table VI.** Identified $^7F_J$ Energy Sublevels ($cm^{-1}$, 77 K) for $[Eu(NO_3)_6]^{3-}$ Anions in $[Eu(NO_3)_2{\cdot}L]_3[Eu(NO_3)_6]$ Complexes (Origin: $^7F_0$ Level)

| level | L = 18C6[33] | L = 21C7[3] | L = $Me_2(2,2)$[a] | |
|---|---|---|---|---|
| $^7F_1$ | 334 | 334 | 336 | |
| | 368 | 363 | 355 | |
| | 394 | 385 | 404 | |
| $^7F_2$ | 989 | 989 | 955 | |
| | 1005 | 1012 | 1014 | |
| | 1024 | 1033 | 1068 | |
| $^7F_3$[b] | 1689 | 1727 | 1682 | 1953 |
| | 1721 | 1747 | 1720 | 1991 |
| | | | 1765 | |
| $^7F_4$ | 3118 | *c* | 2365 | 3051 |
| | | | 2714 | 3077 |
| | | | 2767 | 3183 |
| | | | 2868 | |

[a] This work. [b] Very weak transition. [c] No sublevel identified with certainty.

This assignment is supported by two other experimental findings. First, band H in Figure 5 appears at lower energy than band C, which is assigned to $[Eu(NO_3)_2{\cdot}L]^+$ cations, consistent with the larger total charge of the ligands coordinated to Eu(III)[52] in the hexanitrate, as compared with that of the complex cations.

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(50) Without corrections for vibronic and energy-transfer contributions. The true value of this ratio is probably around 0.5.

(51) Systematic names: 1,4,7,10,13,16-hexaoxacyclooctadecane (18C6) and 1,4,7,10,13,16,19-heptaoxacycloheneicosane (21C7).

**Table VII.** Relative Integrated and Corrected Intensities $P$ (±8%) of the $^5D_0 \rightarrow {}^7F_J$ Transitions and Lifetimes ($\tau$, ms) for $[Eu(NO_3)_2 \cdot Me_2(2,2)]_3[Eu(NO_3)_6]$

| species[a] | $T$/K | $P$ |  |  |  |  |  | $\tau$ |
|---|---|---|---|---|---|---|---|---|
|  |  | $J = 1$[b] | $J = 2$ | $J = 3$ | $J = 4$ | $J = 5$ | $J = 6$ |  |
| H | 293 | 1.0 | 3.8 | 0.08 | 1.8 | *c* | *c* | 0.77 ± 0.02 |
|  | 77 | 1.0 | 0.9 | 0.02 | 0.56 | 0.03 | 0.18 | 5.41 ± 0.27 |
| C | 293 | 1.0 | 3.4 | 0.09 | 2.3 | *c* | *c* | 0.77 ± 0.02 |
|  | 77 | 1.0 | 3.2 | 0.15 | 3.9 | 0.21 | 1.2 | 1.06 ± 0.05 |

[a] Abbreviations: H = hexanitrate; C = complex cations. [b] Taken as reference. [c] Not measured.

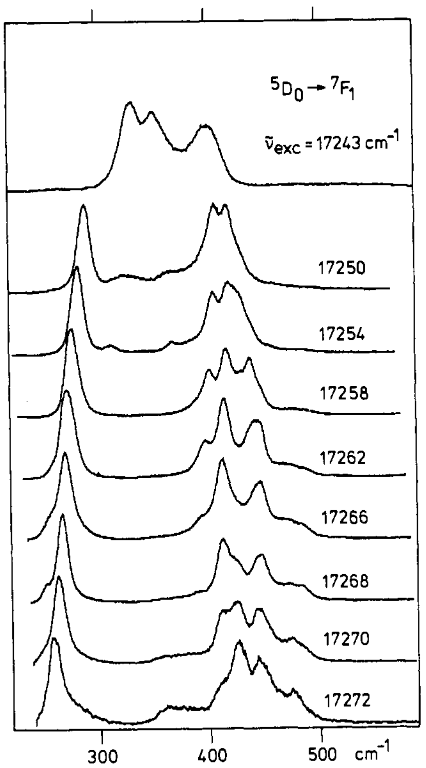

**Figure 8.** $^5D_0 \rightarrow {}^7F_1$ transition reported in energy difference with respect to the excitation energy: (top spectrum) $[Eu(NO_3)_6]^{3-}$; (other spectra) $[Eu(NO_3)_2 \cdot L]^+$ cations (various excitation energies). Experimental conditions are the same as in Figure 6.

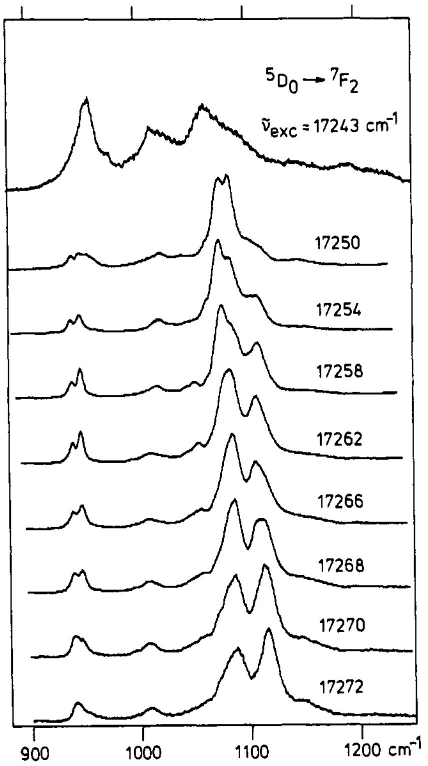

**Figure 9.** $^5D_0 \rightarrow {}^7F_2$ transition reported in energy difference with respect to the excitation energy: (top spectrum) $[Eu(NO_3)_6]^{3-}$; (other spectra) $[Eu(NO_3)_2 \cdot L]^+$ cations (various excitation energies). Experimental conditions are the same as in Figure 6.

Second, we have estimated the Eu(III) site occupancies from the relative $^5D_0 \rightarrow {}^7F_1$ transition probabilities. The oscillator strength of this transition is indeed independent of the Eu(III) environment,[53] and its band area is therefore directly proportional to the number of Eu(III) ions in a given environment. The contribution of species C (three Eu(III) ions) to the $^5D_0 \rightarrow {}^7F_1$ transition measured under broad-band excitation of all four Eu(III) sites[54] is 77 ± 5%, close to the expected 75% value.

The splitting in three components of the magnetic dipole transition to $^7F_1$ in the emission spectrum of the hexanitrate is indicative of a low-symmetry species. The large intensity of this $^5D_0 \rightarrow {}^7F_1$ transition compared to that of the other transitions denotes the possible presence of an inversion center. When such a symmetry element is present, electric dipole transitions to $^7F_2$, $^7F_4$, and $^7F_6$ are indeed forbidden. The situation encountered for spectrum H is, however, not clear-cut, and we interpret it as follows. According to the crystallographic study at 293 K, the $[Eu(NO_3)_6]^{3-}$ anions with $C_2$ symmetry are disordered and display, on average, an approximate $C_{2h}$ symmetry. When the temperature is 77 K, the thermal motions are reduced and the anions become seemingly "frozen" in various conformations. Many of these are close to $C_{2h}$ symmetry while the other ones are more distorted. Despite the high resolution of our measurements, the observed luminescence spectrum H contains contributions from several species with different conformations. When the excitation energy $\tilde{\nu}_{exc}$ is scanned through the narrow excitation band H of Figure 5, the resulting emission spectra undergo small changes only, except for a noticeable variation in the $P_{2/1}$ ratio, which increases when $\tilde{\nu}_{exc}$ is off the maximum of band H: for instance, $P_{2/1}$ = 2.1 for $\tilde{\nu}_{exc}$ = 17 237 cm$^{-1}$ and $P_{2/1}$ = 1.3 for $\tilde{\nu}_{exc}$ = 17 247 cm$^{-1}$. We conclude that at 77 K the average distortion from $C_{2h}$ symmetry is small or, in other words, that there are more $[Eu(NO_3)_6]^{3-}$ anions with $C_{2h}$ symmetry than with a lower symmetry. At 293 K, this is no longer the case: $P_{2/1}$ is much larger than 1 (cf. Table VII), pointing to most anions having a noncentrosymmetric conformation. This is not in contradiction with crystallographic data showing that the Eu and Nd complexes have, on average, the same disordered structure at 293 and 77 K since luminescence spectra are highly sensitive to very small distortions from centric symmetry.

The complex cations $[Eu(NO_3)_2 \cdot Me_2(2,2)]^+$ generate a luminescence specrum C (Figure 6) that is typical of a low-symmetry species without an inversion center and that is relatively insensitive to temperature changes, as far as transition probabilities are

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(54) Xe-lamp excitation of the $^5L_6$ level (25 320 cm$^{-1}$). One component of the $^5D_0 \rightarrow {}^7F_1$ transition in spectrum C is well separated from all the other components arising from species C and H (cf. Figure 8). Its relative intensity was determined both in the broad-band-excited spectrum and in the laser-excited spectrum C, which allowed us to calculate the site occupancies. Two independent estimates were made, taking into account weighted averages of differently excited emission spectra. No correction was, however, allowed for vibronic contributions.

concerned (cf. Table VII). In order to possibly identify the spectra associated with each of the five components observed at 77 K for the $^5D_0 \leftarrow {}^7F_0$ transition, we have recorded the luminescence spectra under variable-excitation and narrow-band-excitation conditions. The observed $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions shown in Figures 8 and 9, respectively, reveal a unique property of the investigated compound. They display two features: (i) The number of components is larger than $2J + 1$; that is, each spectrum is the sum of several spectra originating from Eu(III) ions having different chemical environments. (ii) The general pattern of the spectra is largely dependent upon the excitation energy. The latter effect is particularly important for the $J = 1$ transition (Figure 8): some of its components have a small intensity in one spectrum, have a more intense one in the next, and then disappear. It is noteworthy that the lowest $^7F_1$ sublevel is shifted toward higher energy with decreasing excitation energy, whereas the other sublevels undergo a bathochromic shift larger than the shift in excitation energy. The $Me_2(2,2)$ compound therefore contains a wide dispersion of complex cation sites with a total crystal field splitting for $^7F_1$ ranging from 130 cm$^{-1}$ ($\tilde{\nu}_{exc} = 17\,250$ cm$^{-1}$) to 250 cm$^{-1}$ ($\tilde{\nu}_{exc} = 17\,272$ cm$^{-1}$). This may be again traced back to the large thermal motions of the macrocycle atoms evidenced by the room-temperature crystallographic study and generating several different conformations at 77 K. In view of the intensity distribution of the components of the transitions to $^7F_1$ and $^7F_2$, it appears that none of these conformations are clearly favored. Such a monotonous distribution of metal ion sites is analogous to what is observed in glasses.[23,55]

The above analysis of the emission spectra is confirmed by the lifetimes of the $^5D_0$ levels measured for both the hexanitrate and the complex cations. There is a large increase in the former in going from 293 to 77 K, consistent with the fact that most anions adopt a conformation with $C_{2h}$ symmetry at low temperature. On the other hand, the average lifetime of the complex cations increases by 30% upon cooling, reflecting easy energy migration between the many cationic sites.

## Conclusion

This study confirms the complementarity of crystallographic and luminescence data for gaining information on the structure of materials containing disordered species. While the X-ray determination yields an average representation of the unit cell, the luminescence experiment allows one to probe the detailed local structure of the various moieties present in the microcrystalline material. In the investigated Eu compound, the $[Eu(NO_3)_2\cdot Me_2(2,2)]^+$ cations adopt many different conformations, resulting in large but continuous variations in the crystal field splittings (>100 cm$^{-1}$ for the total splitting of $^7F_1$). A somewhat similar situation has been observed for other macrocyclic compounds, the structures of which also display some degree of disorder. In the 18C6 complex,[33] the differences in the crystal field splittings were very small, amounting to a few wavenumbers only. In the complexes with the dicyclohexyl derivative of 18C6,[34] the luminescence spectra recorded under various excitation conditions presented large differences, but their components could be assigned to specific species with different conformations. For the presently investigated Eu complex, the various excitations produce luminescence spectra, the patterns of which vary in a monotonous way. This situation resembles that found in glasses. On the other hand, the $[Eu(NO_3)_6]^{3-}$ anions have a better defined structure, close to a $C_{2h}$ arrangement at 77 K, and behave as microcrystals within this material.

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**Supplementary Material Available:** Atomic coordinates and isotropic thermal parameters for the Eu complex (Table S1), anisotropic parameters for the heavy atoms (Table S2) and selected least-squares weighted planes and dihedral angles for the Nd and Eu complexes (Table S5), luminescence spectra of the $[Eu(NO_3)_6]^{3-}$ anions under various excitation conditions (Figure F1), and luminescence spectra used in the determination of the site occupancies (Figure F2) (6 pages); observed structure factors for the Nd and Eu complexes (Tables S3 and S4, respectively) (52 pages). Ordering information is given on any current masthead page.

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# Structural Investigations on Tris(tetrahydrothiophene)rhodium(III) Halide Complexes

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Complexes of the type $RhX_3(tht)_3$ (X = Cl, Br, I; tht = tetrahydrothiophene) were prepared and were studied by NMR spectroscopy and X-ray crystallography (X = Cl). The crystals of $RhCl_3(tht)_3$ are monoclinic and belong to the space group $P2_1/n$, with $a = 11.887$ (2) Å, $b = 10.317$ (1) Å, $c = 15.237$ (3) Å, $\beta = 107.266$ (9)°, $V = 1784.4$ (5) Å$^3$, and $Z = 4$. The structure was refined to give final agreement factors of $R = 0.027$ and $R_w = 0.034$ and showed that the complex adopts a meridional configuration. Rh–S bond lengths and other structural parameters were consistent with $\sigma$-bonding between the Rh atom and thioether ligands. Broad signals were observed in the 200-MHz $^1H$ NMR spectra of the complexes at 20 °C due to inversion of the thioether ligands. However, spectra recorded at lower temperatures enabled complete assignment of the signals. These data showed that signals due to the $\alpha$-protons of the axial ligands are downfield of the corresponding signals of equatorial ligands, in contrast with previous observations. No ligand exchange was observed when dimethyl disulfide was added to solutions of the complexes at temperatures required to achieve coalescence of the NMR signals, indicating that ligand inversion occurs by a nondissociative mechanism.

## Introduction

Organo sulfide complexes of rhodium, iridium, ruthenium, and other transition-metal halides are well-known.[1] For example, Chatt et al.[2,3] examined their catalytic properties and Allen and Wilkinson[4,5] studied their structural features. Although claims were made for a *fac* configuration,[6-9] Allen and Wilkinson,[5] using a combination of X-ray, NMR, dipole moment, and electronic spectral studies, clearly demonstrated that complexes of the type $MX_3L_3$ (M = Rh, Ir; X = Cl, Br, I; L = $SMe_2$, $SEt_2$, tetra-

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