accuracy of the structure do not allow detailed discussion of this aspect.

The thiosulfate ligand coordinates to Pt *via* S and is H-bonded to the cation *via* the interaction O(100)$\cdots$H(200) at 2·04 (8) Å.

We thank the SERC for support of this work.

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609.
HURSTHOUSE, M. B., WALKER, N. C. P., WARRENS, C. P. & WOOLLINS, J. D. (1985). *J. Chem. Soc. Dalton Trans.* pp. 1043–1047.
JONES, R., KELLY, P. F., WARRENS, C. P., WILLIAMS, D. J. & WOOLLINS, J. D. (1986). *J. Chem. Soc. Chem. Commun.* pp. 711–713.
JONES, R., KELLY, P. F., WILLIAMS, D. J. & WOOLLINS, J. D. (1985). *Polyhedron*, **4**, 1947–1950.
KELLY, P. F. (1987). PhD thesis. Univ. of London, England.
KELLY, P. F. & WOOLLINS, J. D. (1986). *Polyhedron*, **5**, 607–632.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
SHELDRICK, G. M. (1980). *SHELX*80 – enlarged version of *SHELX*76. Program for crystal structure determination. Univs. of Cambridge (1976) and Göttingen (1980).

Acta Cryst. (1988). C**44**, 1733–1738

Structure of the 4:3 Complex Between Gadolinium Nitrate and 18-Crown-6 Ether: $[Gd(NO_3)_2(C_{12}H_{24}O_6)]_3[Gd(NO_3)_6]$*

BY FRANCESCO NICOLÒ AND JEAN-CLAUDE G. BÜNZLI†

*Institut de Chimie minérale et analytique, Université de Lausanne, CH-*1005 *Lausanne, Switzerland*

AND GERVAIS CHAPUIS

*Institut de Cristallographie, Université de Lausanne, BSP, CH-*1015 *Lausanne, Switzerland*

(*Received* 11 *April* 1988; *accepted* 31 *May* 1988)

Abstract. Tris[dinitrato(1,4,7,10,13,16-hexaoxacyclooctadecane)gadolinium(III)] hexanitratogadolinate(III), $M_r = 2166{\cdot}02$, monoclinic, $C2$, $a = 28{\cdot}640$ (4), $b = 11{\cdot}087$ (2), $c = 11{\cdot}993$ (2) Å, $\beta = 112{\cdot}40$ (1)°, $V = 3521$ (1) Å^3, $Z = 2$, $D_m = 2{\cdot}01$ (by flotation in CCl_4/CH_2Br_2), $D_x = 2{\cdot}04$ g cm^{-3}, graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å), μ(Mo $K\alpha$) = 38·57 cm^{-1}, $F(000) = 2120$, $\mu r \simeq 0{\cdot}80$, transmission range 0·19–0·29, $T = 295$ K, $R = 0{\cdot}049$ for 4361 unique reflections. The complex contains a $[Gd(NO_3)_6]^{3-}$ anion with symmetry 2 (C_2) and two types of $[Gd(NO_3)_2(18\text{-crown-}6)]^+$ cations, one in special position with symmetry 2 and the other in a general position, in the ratio 1:1:2, respectively. The polar crystal packing is pseudo-centrosymmetric and the ions with the crystallographic symmetry 2 exhibit approximate $2/m$ (C_{2h}) symmetry. This property is the cause of very strong correlation parameters between atoms related by the pseudo-mirror plane and complicates the refinement. The cation located on a general position is well defined and displays interesting differences with respect to the analogous ion with the metal at the origin. The explanation is given by a conformational analysis on the six-membered ring arrangement of the O(ether) atoms around Gd. The mean Gd—O$_{\rm eth}$ and Gd—O$_{\rm nit}$ distances are respectively 2·55 (2) and 2·46 (1) Å in the crown complexes, while in the hexanitrate the Gd—O average bond length is 2·57 (1) Å.

Introduction. The guest–host complexes obtained by reacting lanthanide ions with synthetic ionophores have several potential applications (Bünzli, 1987). In our laboratory, special attention is given to the relationship between the crystal and molecular structure of these complexes and their luminescent properties (*cf.* Nicolò, Plancherel, Bünzli & Chapuis, 1987; Plancherel, Jin, Massara & Bünzli, 1987).

Following the structure determination of the 4:3 complex between $Nd(NO_3)_3$ and 18C6 (18-crown-6 ether: 1,4,7,10,13,16-hexaoxacyclooctadecane) (Bünzli, Klein, Wessner, Schenk, Chapuis, Bombieri & De Paoli, 1981), we have undertaken a detailed photophysical study of the corresponding Eu- and Eu-doped Gd complexes (Bünzli & Pradervand, 1986). This investigation revealed that the two compounds are isostructural and contain $[Ln(NO_3)_6]^{3-}$ anions with an inversion centre and two types of $[Ln(NO_3)_2(18C6)]^+$ cations with approximate symmetry $2mm$ (C_{2v}), in the ratio 1:1:2. The structure of the Eu complex was solved

---

* Part 35 of the series 'Complexes of Lanthanoid Salts with Macrocyclic Ligands'.

† To whom correspondence should be addressed.

0108-2701/88/101733-06\$03.00

by Fan, Yu, Lu, Jin, Yu, Zhang & Ni (1986) and refined to $R_F = 0{\cdot}063$ in space group $C2/m$, the same that was used for the Nd complex. They found similar results: the $[Eu(NO_3)_6]^{3-}$ anion has symmetry $2/m$; the two types of $[Eu(NO_3)_2(18C6)]^+$ cations have symmetry $2/m$ and 1, in the ratio 1:1:2.

The structure determination and refinement of the 4:3 complexes are difficult to perform owing to the centrosymmetric arrangement of the Ln^{III} ions and of the static disorder in the ligands. In this communication, we present the crystal and molecular structure of the Gd complex, in an attempt to understand the origin of the discrepancies between the X-ray and spectroscopic investigations.

Experimental. A colourless air-sensitive crystal ($0{\cdot}30 \times 0{\cdot}38 \times 0{\cdot}49$ mm), synthesized according to Wessner & Bünzli (1985), was sealed in a Lindemann capillary tube and mounted on a Nicolet *R*3*m* four-circle automatic diffractometer. Cell constants were refined from 34 accurately centred reflections with $15 < 2\theta < 30°$; 5390 intensities were recorded at 295 K by the θ–2θ scan method up to $2\theta = 55°$ ($-35 \le h \le 35$, $-1 \le k \le 14$, $-1 \le l \le 15$) and the e.s.d.'s were evaluated statistically. Three reference reflections, monitored periodically every 97 measurements, showed slight irregular variation. A ψ-scan collection (range $= 0$–$360°$ and step $= 10°$) was performed on nine strong reflections with $\chi \ge 70°$. Their intensities were used to refine the six parameters of the pseudo-ellipsoid simulating the crystal absorption effect. The general systematic extinction *hkl* with $h + k$ odd (used in data collection) indicated a *C*-centred monoclinic cell with a *C*2, *Cm* or $C2/m$ space-group symmetry. In addition, 1284 reflections were collected over the four quadrants of the Ewald sphere (equivalent in the $2/m$ Laue symmetry) in the range $25 < 2\theta < 35°$. A difference analysis was carried out on the three corresponding sets of Bijvoet pairs (Parthasarathy, 1967). The theoretical Bijvoet ratio $\delta = |I_h - I_{-h}|/[\frac{1}{2}(I_h + I_{-h})]$ is 0·12 for the pairs related by a symmetry operation not belonging to the space group. The experimental values, computed before (after) the empirical absorption correction, are 0·082 (0·064), 0·095 (0·078) and 0·061 (0·061) respectively for the 2, *m* and $2/m$ symmetry correspondences. They are significantly lower than the expected ratios if the corresponding symmetry relations are absent. In addition they show an evident preference for the axial symmetry over the mirror symmetry. This situation may be explained by a crystal arrangement having a polar space group with a nearly centrosymmetric character. Indeed, the best refinement was obtained in *C*2 with the heavy atoms forming a centrosymmetric partial structure.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}/U_{iso}
Gd(1)	0	0	0	40 (1)*
N(1)	−1011 (3)	−12 (14)	−1675 (9)	78 (3)*
O(11)	−1446 (3)	68 (19)	−2418 (10)	126 (4)*
O(12)	−832 (5)	793 (14)	−928 (14)	148 (4)*
O(13)	−748 (6)	−880 (14)	−1703 (15)	161 (4)*
C(1)	105 (14)	3412 (15)	−498 (25)	219 (7)
O(1)	238 (7)	2196 (17)	−602 (13)	196 (6)
C(2)	185 (11)	2018 (14)	−1818 (14)	163 (6)
C(3)	32 (7)	696 (18)	−2093 (25)	184 (7)
O(2)	484 (9)	26 (14)	−1526 (18)	285 (7)
C(4)	447 (9)	−1022 (17)	−2235 (14)	119 (6)
C(5)	580 (9)	−2075 (15)	−1343 (26)	227 (7)
O(3)	303 (16)	−1869 (18)	−600 (24)	467 (7)
C(6)	37 (6)	−2948 (33)	−599 (8)	261 (7)
Gd(2)	0	4998 (3)	5000	40 (1)*
N(2)	0	2372 (14)	5000	303 (5)*
O(21)	0	1262 (14)	5000	97 (4)*
O(22)	322 (5)	2927 (14)	5826 (10)	166 (4)*
N(3)	0	7650 (6)	5000	30 (3)*
O(31)	0	8759 (6)	5000	112 (4)*
O(32)	341 (3)	7095 (6)	5780 (8)	53 (3)*
N(4)	−646 (5)	5033 (10)	6432 (10)	73 (3)*
O(41)	−885 (6)	5055 (19)	7093 (15)	158 (4)*
O(42)	−567 (11)	4067 (9)	6030 (24)	175 (5)*
O(43)	−511 (5)	5983 (9)	6115 (10)	46 (3)*
N(5)	889 (2)	5084 (14)	7307 (5)	75 (3)*
O(51)	1265 (3)	5147 (29)	8249 (6)	134 (4)*
O(52)	938 (3)	5031 (17)	6333 (6)	72 (3)*
O(53)	469 (3)	4950 (18)	7347 (8)	83 (3)*
Gd(3)	2274 (1)	2 (2)	7106 (1)	46 (1)*
N(6)	2606 (4)	65 (9)	5164 (7)	80 (4)*
O(61)	2719 (7)	75 (16)	4271 (11)	130 (4)*
O(62)	2562 (7)	1021 (10)	5634 (14)	78 (4)*
O(63)	2498 (9)	−893 (10)	5526 (15)	97 (4)*
N(7)	1970 (3)	153 (15)	9107 (5)	74 (4)*
O(71)	1833 (4)	23 (24)	9955 (7)	115 (4)*
O(72)	1656 (3)	132 (26)	8065 (6)	100 (3)*
O(73)	2422 (2)	220 (23)	9296 (8)	119 (4)*
O(4)	3192 (5)	−510 (10)	8096 (9)	89 (4)
C(7)	3570 (4)	304 (9)	8815 (12)	82 (4)
C(8)	3411 (5)	1540 (9)	8224 (16)	91 (5)
O(5)	2911 (4)	1718 (9)	8163 (13)	86 (4)
C(9)	2774 (5)	2922 (11)	7771 (21)	136 (6)
C(10)	2238 (4)	3080 (12)	7737 (13)	121 (6)
O(6)	1951 (5)	2135 (9)	6988 (12)	115 (5)
C(11)	1517 (5)	2671 (15)	6104 (18)	174 (7)
C(12)	1412 (7)	1934 (11)	4955 (11)	138 (6)
O(7)	1524 (4)	722 (11)	5347 (13)	98 (4)
C(13)	1069 (4)	54 (11)	4831 (16)	143 (6)
C(14)	1232 (7)	−1268 (10)	4908 (10)	112 (5)
O(8)	1575 (6)	−1437 (11)	6117 (10)	113 (4)
C(15)	1742 (7)	−2653 (13)	6222 (13)	148 (6)
C(16)	2038 (5)	−2856 (14)	7570 (13)	107 (5)
O(9)	2416 (5)	−1946 (11)	7926 (14)	114 (4)
C(17)	2867 (5)	−2475 (12)	7921 (20)	189 (7)
C(18)	3293 (6)	−1642 (12)	8695 (17)	173 (7)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

The reflections were corrected for absorption and for Lorentz–polarization effects. The structure was solved by the heavy-atom method and successive difference-Fourier syntheses with the *SHELXTL-PLUS* package (Sheldrick, 1987). From the 4361 unique reflections ($R_{int} = 0{\cdot}020$), 3563 were considered observed with $I > 3\sigma(I)$. The refinement was carried out in space group *C*2 by a full-matrix least-squares technique minimizing the function $\sum w(|F_o| - |F_c|)^2$ with the *SHELX*76 program (Sheldrick, 1976). Bond-length and -angle constraints had to be used to compensate for the strong correlation and disorder: N—O = 1·23 Å and O—N—O = 120° for nitrate groups; C—C = 1·53, C—O = 1·42 Å while C—C—O and C—O—C were forced to unique values in the crown rings. Atomic scattering factors and dispersion corrections were taken

Table 2. *Selected distances* (Å), *angles* (°) *and torsion angles* (°)

$[\mathrm{Gd(1)(NO_3)_2(18C6)}]^+$, symmetry 2			
Gd(1)–O(12)	2·38 (1)	Gd(1)–O(13)	2·52 (1)
Gd(1)–O(1)	2·70 (2)	Gd(1)–O(2)	2·68 (2)
Gd(1)–O(3)	2·46 (3)	Gd(1)···N(1)	2·82 (1)
O(13)–Gd(1)–O(12)	51·3 (5)	O(3)–Gd(1)–O(2)	58·5 (8)
O(2)–Gd(1)–O(1)	63·8 (6)	O(3)–Gd(1)–O(1)	121·9 (9)
O(3)–Gd(1)···N(1)	99·7 (6)	O(2)–Gd(1)···N(1)	99·8 (5)
O(1)–Gd(1)···N(1)	96·3 (4)		
O(1′)–C(1′)–C(1)–O(1)	19 (3)	C(1′)–C(1)–O(1)–C(2)	151 (2)
C(1)–O(1)–C(2)–C(3)	−149 (2)	O(1)–C(2)–C(3)–O(2)	−77 (2)
C(2)–C(3)–O(2)–C(4)	−149 (2)	C(3)–O(2)–C(4)–C(5)	−130 (2)
O(2)–C(4)–C(5)–O(3)	46 (3)	C(4)–C(5)–O(3)–C(6)	129 (2)
C(5)–O(3)–C(6)–C(6′)	153 (2)	O(3)–C(6)–C(6′)–O(3′)	58 (3)
$[\mathrm{Gd(2)(NO_3)_6}]^{3-}$, symmetry 2			
Gd(2)–O(22)	2·53 (1)	Gd(2)–O(32)	2·56 (1)
Gd(2)–O(42)	2·60 (3)	Gd(2)–O(43)	2·57 (1)
Gd(2)–O(52)	2·55 (1)	Gd(2)–O(53)	2·62 (1)
Gd(2)···N(2)	2·91 (2)	Gd(2)···N(3)	2·94 (1)
Gd(2)···N(4)	2·97 (1)	Gd(2)···N(5)	2·96 (1)
O(22)–Gd(2)–O(22′)	49·8 (5)	O(32)–Gd(2)–O(32′)	49·2 (3)
O(43)–Gd(2)–O(42)	48·6 (4)	O(53)–Gd(2)–O(52)	48·7 (2)
N(2)···Gd(2)···N(3)	180·0 (2)	N(2)···Gd(2)···N(4)	90·8 (3)
N(2)···Gd(2)···N(5)	91·8 (2)	N(3)···Gd(2)···N(4)	88·3 (3)
N(3)···Gd(2)···N(5)	88·2 (2)	N(4)···Gd(2)···N(5)	87·9 (2)
N(4)···Gd(2)···N(5′)	92·1 (3)		
$[\mathrm{Gd(3)(NO_3)_2(18C6)}]^+$, symmetry 1			
Gd(3)–O(62)	2·48 (2)	Gd(3)–O(63)	2·43 (2)
Gd(3)–O(72)	2·45 (1)	Gd(3)–O(73)	2·51 (1)
Gd(3)–O(4)	2·50 (1)	Gd(3)–O(5)	2·60 (1)
Gd(3)–O(6)	2·52 (1)	Gd(3)–O(7)	2·50 (1)
Gd(3)–O(8)	2·48 (1)	Gd(3)–O(9)	2·34 (1)
Gd(3)···N(6)	2·83 (1)	Gd(3)···N(7)	2·62 (1)
O(63)–Gd(3)–O(62)	51·3 (1)	O(73)–Gd(3)–O(72)	50·8 (3)
O(5)–Gd(3)–O(4)	61·4 (4)	O(6)–Gd(3)–O(5)	61·1 (3)
O(7)–Gd(3)–O(6)	58·3 (4)	O(8)–Gd(3)–O(7)	61·6 (4)
O(9)–Gd(3)–O(8)	65·6 (4)	O(9)–Gd(3)–O(4)	67·0 (4)
O(4)–Gd(3)···N(6)	77·0 (4)	O(5)–Gd(3)···N(6)	89·4 (3)
O(6)–Gd(3)···N(6)	99·3 (4)	O(7)–Gd(3)···N(6)	75·4 (4)
O(8)–Gd(3)···N(6)	94·9 (4)	O(9)–Gd(3)···N(6)	108·0 (4)
O(4)–Gd(3)···N(7)	102·5 (3)	O(5)–Gd(3)···N(7)	86·0 (3)
O(6)–Gd(3)···N(7)	76·7 (4)	O(7)–Gd(3)···N(7)	104·6 (3)
O(8)–Gd(3)···N(7)	89·5 (4)	O(9)–Gd(3)···N(7)	76·2 (5)
N(6)···Gd(3)···N(7)	175·0 (1)		
O(4)–C(7)–C(8)–O(5)	55 (1)	C(7)–C(8)–O(5)–C(9)	172 (1)
C(8)–O(5)–C(9)–C(10)	−179 (1)	O(5)–C(9)–C(10)–O(6)	−55 (2)
C(9)–C(10)–O(6)–C(11)	−128 (1)	C(10)–O(6)–C(11)–C(12)	145 (1)
O(6)–C(11)–C(12)–O(7)	38 (2)	C(11)–C(12)–O(7)–C(13)	118 (1)
C(12)–O(7)–C(13)–C(14)	162 (1)	O(7)–C(13)–C(14)–O(8)	49 (1)
C(13)–C(14)–O(8)–C(15)	−179 (1)	C(14)–O(8)–C(15)–C(16)	−171 (1)
O(8)–C(15)–C(16)–O(9)	−56 (2)	C(15)–C(16)–O(9)–C(17)	−97 (1)
C(16)–O(9)–C(17)–C(18)	−161 (1)	O(9)–C(17)–C(18)–O(4)	−62 (2)
C(17)–C(18)–O(4)–C(7)	−178 (1)	C(18)–O(4)–C(7)–C(8)	−173 (1)

N–O	1·23 (1)	C–C	1·53 (2)	C–O	1·42 (3)
O–N–O	120·0 (1)	C–C–O	105 (1)	C–O–C	107 (2)

from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974).

The final agreement was $R = 0{\cdot}049$, $wR = 0{\cdot}056$ with a corresponding goodness of fit $S = 2{\cdot}75$. $(\Delta/\sigma)_{\max} = 0{\cdot}22$. The polyethers were refined isotropically and no H atoms were included. The weighting scheme was $w = 2{\cdot}252/[\sigma^2(F_o) + 0{\cdot}0011F_o^2]$. Attempts to determine the enantiomorph were unsuccessful, owing to the high pseudo-centrosymmetric character of the structure. On the last difference Fourier map, the highest electron residuals were about $1{\cdot}2\ \mathrm{e\,Å^{-3}}$ and mainly located on the pseudo-mirror plane in the vicinity of $[\mathrm{Gd(NO_3)_6}]^{3-}$ nitrates. Attempts to interpret this disorder with different $\mathrm{NO_3^-}$ orientations did not improve the refinement.

The geometrical calculations and drawings were obtained from the program *PARST* (Nardelli, 1983) and the Nicolet graphic package (*SHELXTL-PLUS*), respectively. Atomic positions and equivalent isotropic displacement parameters are reported in Table 1, while Table 2 carries the main information on ion geometries.*

Discussion. The best refinement was obtained in space group *C*2. In the unit cell, the Gd$^{\mathrm{III}}$ atoms have indeed an arrangement corresponding to space group *C*2/*m* (Fig. 1); Gd(1) and Gd(2) are placed on the twofold axis, but $[\mathrm{Gd(1)(NO_3)_2(18C6)}]^+$ and $[\mathrm{Gd(2)(NO_3)_6}]^{3-}$ have approximate $2/m$ (C_{2h}) symmetry. The resulting correlation between the atoms related by the pseudo-mirror plane generates a substantial imprecision on the position and displacement parameters. A similar case has been reported for similar Nd and Eu complexes (Nicolò, Plancherel, Chapuis & Bünzli, 1988). The ambiguity is certainly due to the high flexibility of the crown ring which can adopt several different conformations even at low temperature. In the X-ray structure determination, these independent configurations and the centrosymmetric distribution of the heavy atoms in the cell appear globally as an *average* arrangement with a symmetry

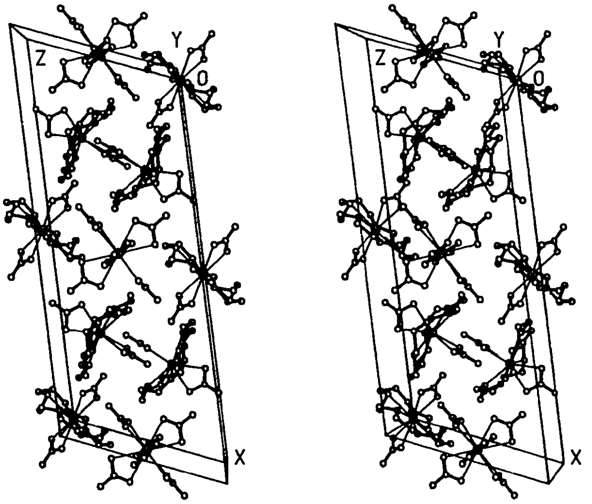

Fig. 1. Stereoview of the crystal packing with arbitrary atom radii.

---

* Lists of anisotropic displacement parameters, selected weighted least-squares-planes data, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51091 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

close to $C2/m$. It is then reasonable to admit that the inversion centre is destroyed by the conformational disorder of the ligands. This model is confirmed by the structure of the Eu complex refined in $C2/m$. The two Eu and Gd crystals are indeed similar: their cell parameters are identical, except for the slight change in the lanthanide radius and an origin translation of $(0\frac{1}{2}\frac{1}{2})$. Since the refinement in space group $C2$ yields better results than with $C2/m$ ($R_F = 0{\cdot}049$ compared with 0·063 for the Eu complex) we propose the following explanation. The crystal packing is pseudo-centrosymmetric due to the local symmetry $2/m$ of the ions. The true space group is certainly the polar space group $C2$.

The twofold axis of the hexanitrate (Fig. 2*a*) contains N(2) and N(3). The Gd(2) atom lies on the pseudo-mirror plane bisecting the N(4) and N(5) nitrates. The six N atoms of the bidentate nitrates form an octahedral arrangement around the Gd(2) ion with the Gd···N distances ranging from 2·91 to 2·97 Å [mean: 2·94 (2) Å], and N···Gd···N angles ranging from 88·2 to 92·1° [mean: 90 (2)°], and N(2)···Gd···N(3) equals 180°. The coordination polyhedron (Fig. 2*b*) has a symmetry close to $2/m$ (C_{2h}) and the atoms related by pseudosymmetry display anomalous displacement parameters owing to the strong correlations in the refinement. The same situation was reported for the hexanitrate in the $[La(NO_3)_2L]_3[La(NO_3)_6]$ structure ($L = C_{12}H_{24}O_6$) solved in the polar space group $I2$ (standard $C2$) (Bünzli, Pfefferlé, Ammann, Chapuis & Zuniga, 1984). The Gd(2)—O bond lengths range from 2·53 to 2·62 Å with the average value 2·57 (3) Å. This is shorter than the mean distance 2·64 (4) Å found in $[La(NO_3)_6]^{3-}$ and comparable with the corresponding 2·58 (1) Å of the Eu complex. The effective ionic radius (Shannon, 1976) of the 12-coordinate Gd^{III} ion amounts to 1·26 (3) Å, in agreement with the value obtained from extrapolation of ionic *vs* coordination number plots: 1·24 Å.

The asymmetric unit contains two independent $[Gd(NO_3)_2(18C6)]^+$ cations in the ratio 1:2. In the first cation Gd(1) lies on the twofold axis and in the other Gd(3) is in a general position. In both ions, the 10-coordinate Gd ion is held at the centre of the polyether cavity by two bidentate nitrates located on opposite sides of the ligand mean plane (Fig. 3*a*). The dihedral angle between the planes containing the nitrate ions is 58 and 83° for Gd(1) and Gd(3), respectively. The two cations show additional differences. (i) In the complex with Gd(1) at the origin, large correlations increase the deviations of the position and displacement parameters. The geometrical arrangement deviates more from the symmetry $2/m$ than in the hexanitrate (*cf.* the atomic coordinates in Table 1). (ii) The average Gd—O(nitrate) distance is 2·45 (1) and 2·47 (2) Å for Gd(1) and Gd(3), respectively. These values are significantly smaller than in $[Gd(2)(NO_3)_6]^{3-}$ owing to the lower coordination number. They are similar to the average Gd—O(nitrate) distance found in $[Gd(NO_3)_3(H_2O)_3]$.18C6 (Backer-Dirks, Cooke, Galas, Ghota, Gray, Hart & Hursthouse, 1980). (iii) An important difference lies in the conformation of the crown ethers and in the Gd—O(ether) bond lengths: 2·46–2·70 [average: 2·61 (2)] and 2·34–2·61 Å [average: 2·49 (2) Å] for Gd(1) and Gd(3), respectively.

The difference in the mean Gd—O(ether) distances may be better understood in terms of a puckering analysis (Boeyens, 1978) of the six-membered ring formed by the O(ether) atoms. This simple model has already been applied to the dicyclohexyl-18C6 complexes (Nicolò, Plancherel, Bünzli & Chapuis, 1987). The Q parameter, proportional to the off-plane deformation, is 0·27 (3) and 1·17 (1) for the Gd(1) and Gd(3) ions, respectively. The θ coordinate, characterizing the ring conformation (0 or 180° = chair,

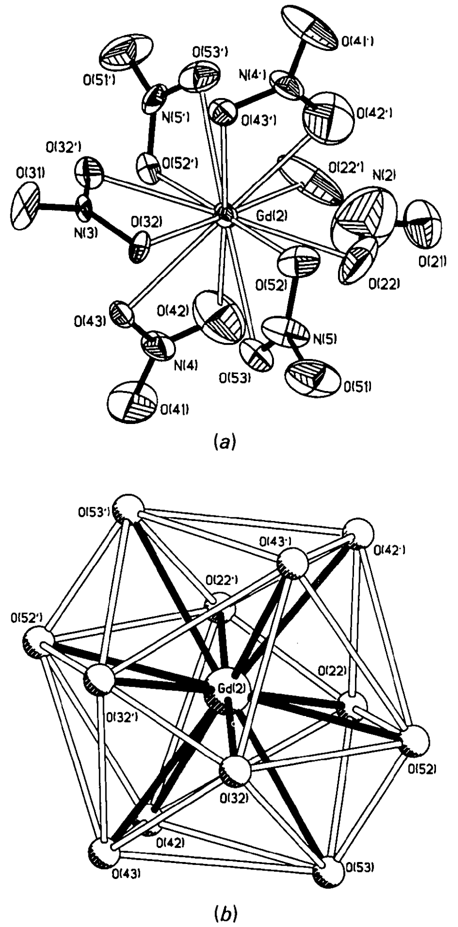

Fig. 2. View of the $[Gd(2)(NO_3)_6]^{3-}$ anion on the twofold axis. (*a*) Drawing showing the numbering scheme (thermal ellipsoids with 30% probability); (*b*) coordination polyhedron displaying the regular geometry with almost perfect $2/m$ symmetry (arbitrary atom radii).

90° = boat), is equal to 25 (4) and 89 (1)°, respectively. These values are in agreement with the consideration that the O_6 conformation is the result of a compromise between the contraction of the ligand cavity induced upon coordination and the repulsive effect of the $(O\cdots O)_{eth}$ interactions. In $[Gd(1)(NO_3)_2(18C6)]^+$, the O_6 ring has a flat chair conformation and cannot contract further without generating strong O···O repulsions. In the Gd(3) complex the O_6 ring displays the boat arrangement which allows a larger deformation from planarity without shortening significantly the $O\cdots O_{eth}$ distances. Therefore the coordination ring is more puckered than around Gd(1); the $Gd—O_{eth}$ bond lengths are shorter while the oxygen–oxygen interactions remain almost the same. Both cations have indeed the same mean O···O separation, 2·59 Å [range: 2·33–2·85 for Gd(1) and 2·45–2·68 Å for Gd(3)], which is smaller than the sum of the oxygen covalent radii (2·80 Å). The Gd(3) complex has no crystallographic symmetry and its O(ether) ring adopts a more general conformation (*cf.* Fig. 3*b*). This model explains also the mean Gd—O(ether) distances of 2·54 Å reported for the $[GdCl_3(18C6)]$ complex in which the Gd^{III} ion is 9-coordinate and the O_6 ring has a boat conformation (Forsellini, Benetollo, Bombieri, Cassol & De Paoli, 1985).

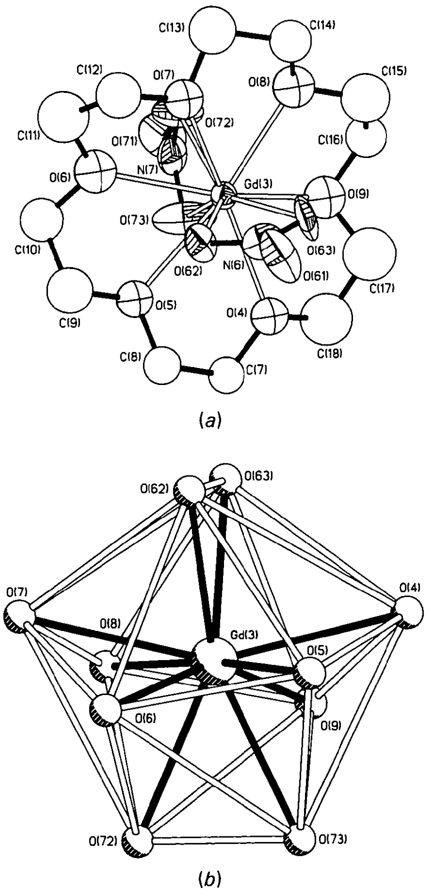

Fig. 3. View of the $[Gd(3)(NO_3)_2(18C6)]^+$ cation in general position. (*a*) Drawing showing the numbering scheme (thermal ellipsoids with 30% probability); (*b*) coordination polyhedron displaying the boat conformation of the corresponding crown O_6-ring (arbitrary atom radii).

The differences in the conformation of the macrocycles are reflected in the effective ionic radii: 1·24 (13) and 1·17 (6) Å for the Gd(1) and Gd(3) ions, respectively, if the same corrections as described previously (Bünzli, Klein, Chapuis & Schenk, 1982) are applied. The predicted value for the 10-coordinate Gd^{III} is 1·17 Å.

The results are compatible with the laser-spectroscopic study mentioned previously. Indeed, the photophysical investigation revealed that each metal ion site does not generate a single luminescence spectrum but rather a series of similar spectra arising from molecules with slightly different conformations. The X-ray analysis yields an average model of the various conformations, hence the imprecision on the position and displacement parameters of several atoms. Therefore in the Eu and Gd complexes, most $[Ln(NO_3)_6]^{3-}$ anions have a conformation with local symmetry 2/*m*, while most $[Ln(NO_3)_2(18C6)]^+$ cations have a conformation with 2 or no local symmetry, which is easier to achieve than the more strained 2/*m* conformation. Nevertheless, some moieties are close to this latter conformation, hence the difficulty in interpreting the luminescence spectra.

We thank the Swiss National Science Foundation for financial support and Dr D. Plancherel for the synthesis of the Gd complex.

References

Backer-Dirks, J. D., Cooke, J. E., Galas, A. M. R., Ghota, J. S., Gray, C. J., Hart, F. A. & Hursthouse, M. B. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2191–2198.

Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317.

Bünzli, J.-C. G. (1987). In *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner Jr & L. Eyring, Vol. 9, ch. 60, pp. 321–394. Amsterdam: Elsevier.

Bünzli, J.-C. G., Klein, B., Chapuis, G. & Schenk, K. (1982). *Inorg. Chem.* **44**, 808–811.

Bünzli, J.-C. G., Klein, B., Wessner, D., Schenk, K. J., Chapuis, G., Bombieri, G. & De Paoli, G. (1981). *Inorg. Chim. Acta Lett.* **54**, L43–L46.

Bünzli, J.-C. G., Pfefferlé, J.-M., Ammann, B., Chapuis, G. & Zuniga, F.-J. (1984). *Helv. Chim. Acta*, **67**, 1121–1127.

Bünzli, J.-C. G. & Pradervand (1986). *J. Phys. Chem.* **85**, 2489–2497.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2.B and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Fan, Y., Yu, J., Lu, P., Jin, Z., Yu, F., Zhang, S. & Ni, J. (1986). *Chin. J. Appl. Chem.* **3**, 35–41.

Forsellini, E., Benetollo, F., Bombieri, G., Cassol, A. & De Paoli, G. (1985). *Inorg. Chim. Acta*, **109**, 167–171.

Nardelli, M. (1983). *Comput. Chem.* **7**, 78–95.

NICOLÒ, F., PLANCHEREL, D., BÜNZLI, J.-C. G. & CHAPUIS, G. (1987). *Helv. Chim. Acta*, **70**, 1798–1805.
NICOLÒ, F., PLANCHEREL, D., CHAPUIS, G. & BÜNZLI, J.-C. G. (1988). *Inorg. Chem.* In the press.
PARTHASARATHY, S. (1967). *Acta Cryst.* **22**, 98–103.
PLANCHEREL, D., JIN, L., MASSARA, R. & BÜNZLI, J.-C. G. (1987). *Helv. Chim. Acta*, **70**, 1807–1815.
SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination (version locally modified by F. NICOLÒ). Univ. of Cambridge, England.
SHELDRICK, G. M. (1987). *SHELXTL-PLUS Crystallographic System*, version 2. Nicolet XRD Corporation, Madison, Wisconsin, USA.
WESSNER, D. & BÜNZLI, J.-C. G. (1985). *Inorg. Synth.* **23**, 149–157.

Acta Cryst. (1988). C**44**, 1738–1740

cis-Tetracarbonyl(methoxycarbonyl)(triphenylphosphine)manganese, $Mn(CO)_4(PPh_3)(COOCH_3)$

BY DONALD E. WILLIAMS, SANTOSH K. MANDAL AND DOROTHY H. GIBSON

Department of Chemistry, University of Louisville, Louisville, KY 40292, *USA*

(*Received* 4 *January* 1988; *accepted* 8 *June* 1988)

Abstract. $[Mn(C_2H_3O_2)(C_{18}H_{15}P)(CO)_4]$, M_r = 488·32, monoclinic, $P2_1/n$, a = 20·497 (10), b = 10·099 (10), c = 22·157 (10) Å, β = 93·69 (4)°, V = 4576·8 Å^3, Z = 8, D_x = 1·42 g cm^{-3}, λ = 0·7107 Å, μ = 6·6 cm^{-1}, $F(000)$ = 2000, room temperature, 4251 reflections measured, R = 0·058, wR = 0·063 for 2826 observed reflections with $I > 3\sigma(I)$. The manganese has octahedral coordination, with the triphenylphosphine group *cis* to the methoxycarbonyl group. There are two molecules in the asymmetric unit which have only minor differences in structure.

Introduction. Metallocarboxylates are an important class of organometallic compounds which are implicated as intermediates in the water gas shift (WGS) reaction; little structural information is available for these compounds, however (Ford & Rokicki, 1988). During the course of another investigation, a sample of the ester, $Mn(CO)_4(PPh_3)(COOCH_3)$, became available; the determination of its structure is reported herein.

Experimental. To a saturated methanolic solution containing 1·00g of $[Mn(CO)_5(PPh_3)]BF_4$ and maintained at 273 K was added 1·1 ml of a 25% solution of Et_4NOH in methanol. Reaction was complete after about 1 min; solvent was removed and the residue was extracted with hexane. The hexane extracts were concentrated and then chilled to 263 K; pale yellow crystals, m.p. 359–360 K, were collected by filtration.

X-ray diffraction data were obtained with an Enraf–Nonius CAD-4H diffractometer, Mo $K\alpha$ radiation, incident-beam graphite monochromator, from a yellow needle crystal 0·1 × 0·3 × 0·5 mm glued on a glass fiber. The cell dimensions were taken from a least-squares fit to 25 reflections whose θ angles ranged from 8 to 14°. The space group was uniquely determined from the observed extinctions ($h0l$): $h+l = 2n+1$; ($0k0$): $k = 2n+1$. Intensity data were taken by $\omega/2\theta$ scan with ω scan width (0·8 + 0·34tanω)°; the maximum θ was 22·5°. Three reference reflections were remeasured every 2 h of exposure; no significant change in intensity occurred. Intensities were corrected for Lp and equivalent reflections averaged to give 4251 unique reflections, of which 2826 had $I > 3\sigma(I)$. The structure was solved by direct methods using *MULTAN*82 (Main *et al.*, 1982); the manganese and phosphorus atoms of both molecules were visible on the E map, as well as sets of three carbons on P and several carbons around the manganese atoms. The remaining nonhydrogen atoms were located by successive difference Fourier syntheses. Refinement was by full-matrix least squares with hydrogens placed in calculated positions, with

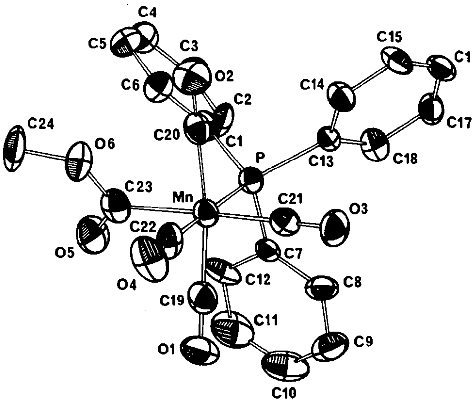

Fig. 1. *ORTEP* plot of molecule 1 showing the atomic numbering system. The thermal ellipsoids are plotted at the 30% probability level. Molecule 2 is similar but with small differences in bond lengths and bond angles as shown in Table 2.