f-Element/Crown Ether Complexes 2.* The Synthesis and Crystal Structure of $Y(NO_3)_3$(12-Crown-4)

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Abstract. $Y(NO_3)_3$(12-crown-4) was prepared via reaction of the crown ether and $Y(NO_3)_3 \cdot nH_2O$ in acetonitrile. $Y(NO_3)_3$(12-crown-4) crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.084(5)$, $b = 8.524(4)$, $c = 15.150(6)$ Å, $\beta = 91.62(3)^0$ and $D_{calc} = 1.92$ g cm^{-3} for $Z = 4$. The structure was refined by least-squares to a final conventional R value of 0.105 using 1249 independent observed reflections $[I \geqslant 3\sigma(I)]$. The title compound is isostructural with its Eu(III) analog. The yttrium ion is ten-coordinate, bonded to three bidentate nitrate groups and to the four oxygens of the crown ether. The coordination polyhedron is best described as a 4A, 6B-extended dodecahedron. The Y-O(nitrate) and Y-O(ether) separations average 2.44(5) and 2.46(4) Å, respectively.

Key words: 12-crown-4, yttrium, complex, X-ray crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82040 (10 pages).

1. Introduction

Rare earth crown ether chemistry has attracted considerable attention [1,2], including ours. In the literature one finds two major types of *f*-element crown ether complexes, those with direct metal-crown interactions and those with the crown ether hydrogen bonded to a metal coordinated water molecule. As an example of the former, the structure of [Gd(18-crown-6)Cl$_2$(EtOH)]Cl, prepared from anhydrous GdCl$_3$, has recently been published [3] as has that of [La(NO$_3$)$_3$(18-crown-6)] [4]. A growing number of structures containing metal-water-crown interactions have also been determined including [Sm(15-crown-5)(OH$_2$)$_4$][ClO$_4$]$_3$ · (15-crown-5) · H$_2$O [5], [Gd(NO$_3$)$_3$(OH$_2$)$_3$] · (18-crown-6) [4], [Y(OH$_2$)$_8$]Cl$_3$ · (15-crown-5) [6], and [Y(NO$_3$)$_2$(OH$_2$)$_5$][NO$_3$] · 2(15-crown-5) [7].

We have begun to study the solid state structures of a variety of *f*-element/crown ether complexes in order to elucidate the 'how' and 'why' of the exclusion of water of hydration. It is possible that the exclusion of water and the formation of direct metal-crown interactions are important in the separations behavior of these crown ether complexes. [Y(OH$_2$)$_8$]Cl$_3$ · (15-crown-5) and [Y(NO$_3$)$_2$(OH$_2$)$_5$][NO$_3$] · 2(15-crown-5) were both prepared from the hydrated yttrium(III) salt and no metal-crown interactions were observed. When we initially determined that the title compound prepared from Y(NO$_3$) · nH$_2$O and 12-crown-4 (IUPAC name 1,4,7,10-tetraxacyclododecane), was isostructural with Eu(NO$_3$)$_3$(12-crown-4) [8] we were somewhat surprised that the anhydrous product was obtained and decided to carry out a full structure determination. The synthetic and structural results of our study of Y(NO$_3$)$_3$(12-crown-4) are reported here.

★ For Part 1 see reference [6]   **Author for correspondence.

2. Experimental

2.1. PREPARATION OF Y(NO₃)₃(12-CROWN-4)

10 mmol of 12-crown-4 in 50 ml of CH_3CN was added dropwise to a stirring solution of 10 mmol of $Y(NO_3)_3 \cdot nH_2O$ in 50 ml of the same solvent. The solution was heated to 60° for 24 h and allowed to cool to 20 °C. Crystals deposited along the walls of the flask as the solution cooled to room temperature. Melting Point: decomposed at 264 °C. Anal. Calcd.: C, 21.29; H, 3.57; N, 9.32; Found: C, 20.72; H, 3.63; N, 9.01.

Infrared frequencies (cm^{-1}) for the nitrate ions were observed at 1770 ($v_2 + v_5$), 1730 ($v_2 + v_6$), 1500 ($v_1(A_1)$), 1310 ($v_4(B_2)$), 1020 ($v_2(A_1)$), 820 ($v_3(B_1)$), 750 ($v_6(B_1)$), and 710 ($v_5(B_2)$). The assignment of the nitrate bands is based upon the presence of bidentate nitrate groups with C_{2v} local symmetry. The separation of the two combinations in the 1700–1800 cm^{-1} region falls in the range 25–50 cm^{-1} indicating the presence of bidentate nitrates [9].

The v_s(CCO) vibration at 1100 cm^{-1} for free 12-crown-4 is shifted 40 cm^{-1} to a lower frequency upon complexation. The v_{as} vibration which occurs at 1060 cm^{-1} in free 12-crown-4, is shifted -10 cm^{-1}. The other crown vibrations at 1350 cm^{-1}, 940–980 cm^{-1} and 850 cm^{-1} are shifted $+75$ cm^{-1}, -50 cm^{-1} and $+25$ cm^{-1}, respectively.

Table I. Crystal data and summary of intensity data collection and structure refinement

Compound	Y(NO₃)₃(12-crown-4)
Mol wt.	451.13
Space group	$P2_1/c$
Cell constants	
a, Å	12.084(5)
b, Å	8.524(4)
c, Å	15.150(6)
β, deg	91.62(3)
Cell vol, Å³	1559.9
Molecules/unit cell	4
ρ(calc), g cm^{-3}	1.92
μ(calc), cm^{-1}	39.4
Range of transmission factors	0.33–0.25
Radiation	Mo$K\alpha$ ($\lambda = 0.71069$)
Max crystal dimensions, mm	0.28 × 0.35 × 0.52
Scan width	0.80 + 0.20 tan θ
Scan speeds, deg min^{-1}	variable, 1.6–16
Standard reflections	(0,4,0)(6,0,0)(0,0,10)
Decay of standards	± 2%
Reflections measured	2943
2θ range	$4° \leqslant 2\theta \leqslant 50$
Reflections collected [I $\geqslant 3\sigma(I)$]	1249
No. of parameters varied	226
Weights	$[1/\sigma_{F_o}^2 + 1/0.0007F_o^2]$
GOF	6.1
R	0.105
R_w	0.138

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT FOR Y(NO₃)₃(12-CROWN-4)

Clear single crystals of the title compound were mounted in air on a pin placed on the goniometer head. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections ($\theta > 13.5°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P2_1/c$ from the systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ-2θ scan technique. A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization effects, and for absorption. The empirical absorption correction was carried out using the intensity profiles of nine reflections with $80° < $ chi $ < 90°$ [10].

Calculations were carried out with the SHELX system of computer programs [11]. Neutral atom scattering factors for Y, O, N, C and H were taken from reference [11] and the scattering was corrected for the real and imaginary components of anomalous dispersion [11].

The fractional coordinates of the isostructural europium compound [8] were used as a starting point in the refinement of the title compound. Least-squares refinement with isotropic thermal parameters led to

$$R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.140.$$

We were disturbed by the high R value and decided to investigate other crystals. We collected and refined three data sets with the reported refinement the best we could obtain. We suspect the presence of a small twinning problem and note that this was also observed in the analogous Eu complex [8]. It is also possible that the empirical absorption correction used did not

Table II.   Final fractional coordinates for Y(NO₃)₃(12-crown-4)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Y	0.2541(2)	0.1856(3)	−0.0477(2)	C(5)	0.301(2)	0.542(3)	0.011(2)
O(1)	0.135(1)	0.070(2)	0.062(1)	C(6)	0.193(2)	0.532(3)	0.059(2)
O(2)	0.350(1)	0.113(2)	0.089(1)	C(7)	0.073(2)	0.326(3)	0.109(2)
O(3)	0.366(1)	0.398(2)	0.024(1)	C(8)	0.036(2)	0.163(3)	0.086(2)
O(4)	0.152(1)	0.379(2)	0.043(1)	H(1)[C(1)]	0.129(2)	−0.040(3)	0.176(2)
O(5)	0.249(1)	−0.092(2)	−0.067(1)	H(2)[C(1)]	0.205(2)	−0.125(3)	0.103(2)
O(6)	0.256(2)	0.041(2)	−0.189(1)	H(3)[C(2)]	0.333(2)	−0.004(3)	0.205(2)
O(7)	0.250(2)	−0.214(2)	−0.194(1)	H(4)[C(2)]	0.265(2)	0.162(3)	0.201(2)
O(8)	0.158(2)	0.367(2)	−0.149(1)	H(5)[C(3)]	0.468(2)	0.183(3)	0.176(2)
O(9)	0.063(1)	0.166(2)	−0.107(1)	H(6)[C(3)]	0.506(2)	0.188(3)	0.074(2)
O(10)	−0.010(2)	0.330(2)	−0.202(1)	H(7)[C(4)]	0.478(2)	0.443(3)	0.120(2)
O(11)	0.377(2)	0.322(2)	−0.152(1)	H(8)[C(4)]	0.354(2)	0.401(3)	0.154(2)
O(12)	0.440(1)	0.123(2)	−0.078(1)	H(9)[C(5)]	0.345(2)	0.631(3)	0.038(2)
O(13)	0.547(2)	0.240(2)	−0.172(1)	H(10)[C(5)]	0.286(2)	0.563(3)	−0.053(2)
N(1)	0.254(1)	−0.095(3)	−0.152(2)	H(11)[C(6)]	0.141(2)	0.614(3)	0.035(2)
N(2)	0.068(2)	0.291(3)	−0.154(1)	H(12)[C(6)]	0.206(2)	0.548(3)	0.123(2)
N(3)	0.455(2)	0.225(3)	−0.137(1)	H(13)[C(7)]	0.110(2)	0.324(3)	0.169(2)
C(1)	0.183(2)	−0.022(3)	0.128(2)	H(14)[C(7)]	0.008(2)	0.399(3)	0.110(2)
C(2)	0.287(2)	0.067(3)	0.167(2)	H(15)[C(8)]	−0.017(2)	0.168(3)	0.034(2)
C(3)	0.444(2)	0.209(3)	0.114(2)	H(16)[C(8)]	−0.001(2)	0.114(3)	0.137(2)
C(4)	0.411(2)	0.375(3)	0.109(2)				

entirely account for the absorption and effects such as the N(1) ellipsoid may be due to this. The hydrogen atoms were placed in calculated positions 1.00 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.105$ and $R_w = 0.138$. A final difference Fourier showed no feature greater than 1.2 e$^-$/Å^3. The weighting scheme was based on $[(1/\sigma_{Fo}^2) + (1/pF_o^2)]$ where $p = 0.0007$; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

3. Results and Discussion

The molecular structure and atom labelling scheme for $Y(NO_3)_3$(12-crown-4) are presented in Figure 1. Bond distances and angles are given in Table III. The problems encountered in the refinement of this structure (see Section 2) have affected the standard deviations, which are all high. Although this limits the discussion, valid comparisons with other structures and the isostructural $Eu(NO_3)_3$(12-crown-4) [8], are still possible. There are four discrete molecules in the unit cell with no significant intermolecular interactions. (The shortest intermolecular contact is $O(13)\cdots H(3)[C(2)]$ $(1-x,y,z) = 2.54$ Å.)
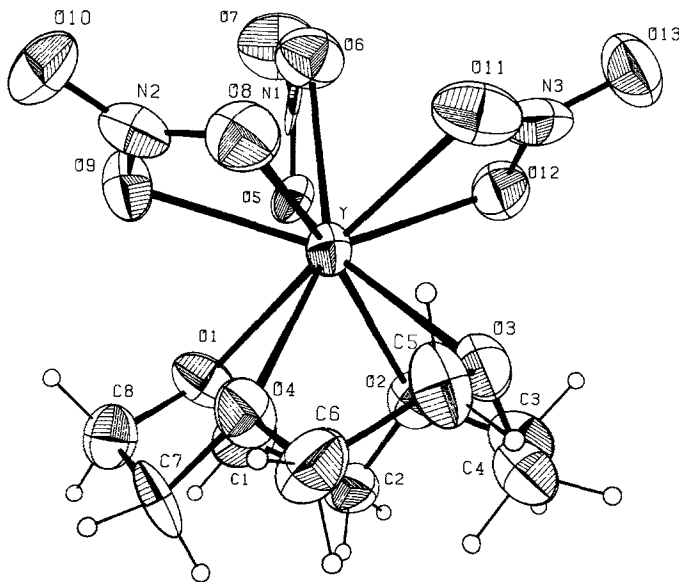

Fig. 1. $Y(NO_3)_3$(12-crown-4) structure and atom labelling scheme. The atoms are represented by their 50% probability ellipsoids for thermal motion.

The yttrium(III) ion is coordinated by all four crown ether oxygen atoms and by the three bidentate nitrate groups. The mean Y—O distance is 2.45(4) Å. The Y—O(nitrate) and Y—O(crown ether) separations are essentially the same (2.44(5) and 2.46(4) Å, respectively). Other comparable Y—O(nitrate) bond lengths have been observed including 2.44(3) Å in $[Y(NO_3)_2(OH_2)_5][NO_3] \cdot 2(15\text{-crown-5})$ [7], 2.51(7) Å in $[Y(NO_3)_3(OH_2)_4]$ [12] and 2.45(3) Å in $[Y(NO_3)_3(OH_2)_3] \cdot 2C_{10}H_8N_2$ [13].

Table III. Selected bond distances (Å) and angles (°) for $Y(NO_3)_3$-(12-crown-4)

Atoms	Distance	Atoms	Distance
Y—O(1)	2.43(1)	Y—O(2)	2.42(2)
Y—O(3)	2.49(2)	Y—O(4)	2.50(2)
Y—O(5)	2.38(2)	Y—O(6)	2.47(2)
Y—O(8)	2.45(2)	Y—O(9)	2.46(2)
Y—O(11)	2.48(2)	Y—O(12)	2.37(2)
O(1)—C(1)	1.39(3)	O(1)—C(8)	1.49(3)
O(2)—C(2)	1.47(3)	O(2)—C(3)	1.44(3)
O(3)—C(4)	1.41(3)	O(3)—C(5)	1.47(3)
O(4)—C(6)	1.42(3)	O(4)—C(7)	1.46(3)
O(5)—N(1)	1.29(3)	O(6)—N(1)	1.29(3)
O(7)—N(1)	1.20(2)	O(8)—N(2)	1.27(3)
O(9)—N(2)	1.29(2)	O(10)—N(2)	1.22(3)
O(11)—N(3)	1.27(3)	O(12)—N(3)	1.26(3)
O(13)—N(3)	1.26(3)	C(1)—C(2)	1.58(4)
C(3)—C(4)	1.48(4)	C(5)—C(6)	1.51(3)
C(7)—C(8)	1.50(3)		

Atoms	Angle	Atoms	Angle
		C(1)—O(1)—C(8)	116(2)
C(2)—O(2)—C(3)	111(2)	C(4)—O(3)—C(5)	115(2)
C(6)—O(4)—C(7)	114(2)	O(5)—N(1)—O(6)	115(2)
O(5)—N(1)—O(7)	123(3)	O(6)—N(1)—O(7)	122(3)
O(8)—N(2)—O(9)	116(2)	O(8)—N(2)—O(10)	123(2)
O(9)—N(2)—O(10)	121(2)	O(11)—N(3)—O(12)	117(2)
O(11)—N(3)—O(13)	121(2)	O(12)—N(3)—O(13)	121(3)
O(1)—C(1)—C(2)	108(2)	O(2)—C(2)—C(1)	105(2)
O(2)—C(3)—C(4)	109(2)	O(3)—C(4)—C(3)	106(2)
O(3)—C(5)—C(6)	111(2)	O(4)—C(6)—C(5)	106(2)
O(4)—C(7)—C(8)	109(2)	O(1)—C(8)—C(7)	108(2)

The polyether resides on one side of the yttrium coordination sphere as found for the isostructural europium analog [8] and in contrast to the coordination of 18-crown-6 in $La(NO_3)_3$(18-crown-6) [4]. [In the latter compound the lanthanum ion is centered in the crown cavity with two nitrate groups coordinated on one side of the crown and one on the other.] The Y—O(crown ether) distances average 0.06 Å less than found for the europium analog.

The coordination polyhedron found for the ten-coordinate Y(III) ion can best be described as a 4A, 6B-extended dodecahedron (Figure 2). The dimensions of the polyhedron are given in Table IV. The bidentate nitrates occupy edges a', b, b.

The three bidentate nitrate groups are normal. They have C_{2v} symmetry and are planar to 0.04 Å. As expected, the average coordinated N—O distance (1.28(1) Å) is larger than the average terminal N—O bond length (1.23(3) Å). In addition the average O–N–O angle involving the bidentate oxygens is 116(1)°, less than the 122(1)° average of the remaining O–N–O angles.

Torsion angles for the complexed crown ether are presented in Table V and the crown itself is depicted in Figure 3. The four O–C–C–O angles are almost synclinal and are in agreement
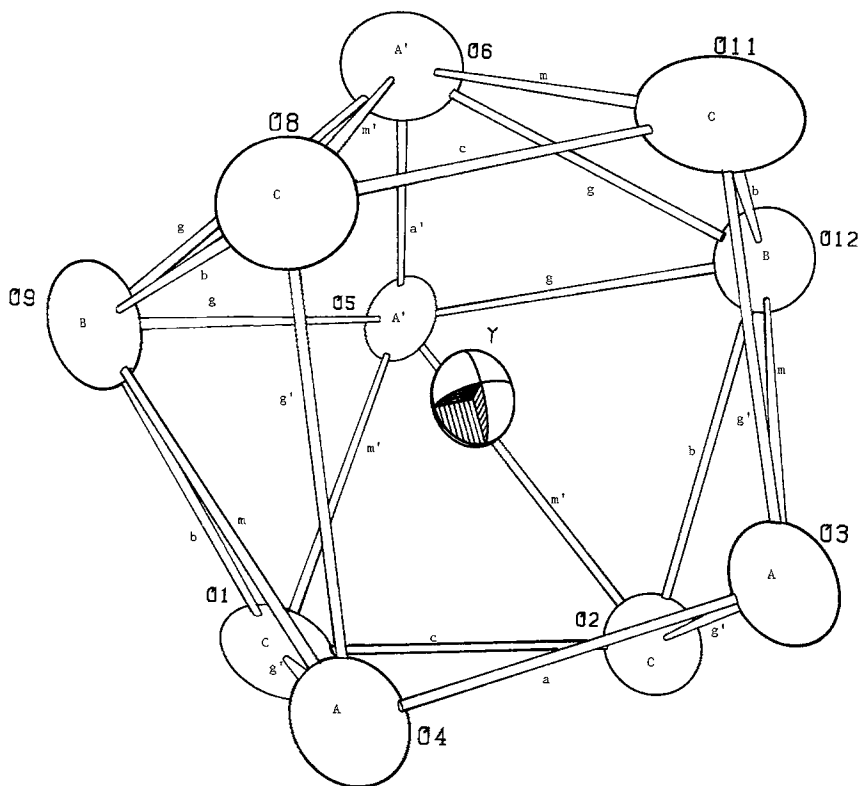
Fig. 2. Yttrium coordination polyhedron.

Table IV. Shape characteristics of the 4A, 6B-expanded dodecahedron in $Y(NO_3)_3(12\text{-crown-4})$

Edge		Distance (Å)	
a	(3–4)	2.62	
a'	(5–6)	2.18	
b	(1–9, 2–12, 8–9, 11–12)	2.58	
c	(1–2, 8–11)	2.66	
g	(5–9, 5–12, 6–9, 6–12)	2.96	
g'	(1–4, 2–3, 3–11, 4–8)	2.68	
m	(3–12, 4–9)	3.01	
m'	(1–5, 2–5, 6–8, 6–11)	2.97	
Shape determining angle[a]		Value (°)	Ideal value (°)
θ_A		31.5	32.8
$\theta_{A'}$		26.8	34.9
θ_B		71.5	65.8
$\theta_{B'}$		81.2	77.8
θ_C		77.0	63.8

[a] θ_A, $\theta_{A'}$, θ_B, $\theta_{B'}$ are defined as in a dodecahedron.
θ_C is defined in reference [14]. Ideal values are quoted from [14].

Table V. 12-crown-4 ether torsion angles (°)

Atoms	Angle
O(1)—C(1)—C(2)—O(2)	−49.1
C(1)—C(2)—O(2)—C(3)	175.1
C(2)—O(2)—C(3)—C(4)	−92.8
O(2)—C(3)—C(4)—O(3)	−53.3
C(3)—C(4)—O(3)—C(5)	163.9
C(4)—O(3)—C(5)—C(6)	−70.8
O(3)—C(5)—C(6)—O(4)	−41.9
C(5)—C(6)—O(4)—C(7)	157.4
C(6)—O(4)—C(7)—C(8)	−179.6
O(4)—C(7)—C(8)—O(1)	44.6
C(7)—C(8)—O(1)—C(1)	96.8
C(8)—O(1)—C(1)—C(2)	−100.9
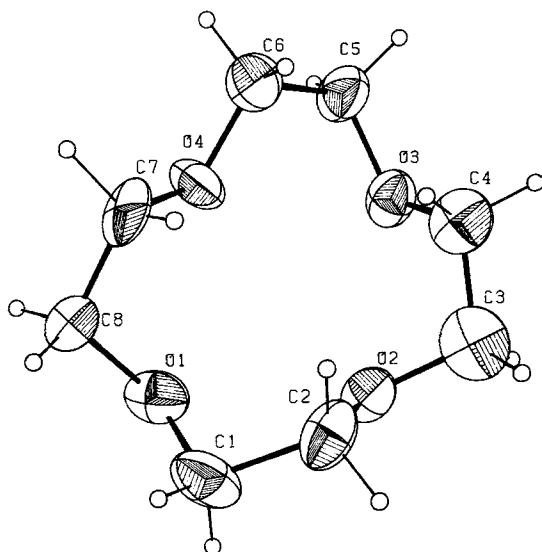
Fig. 3.   12-crown-4 ether configuration.

with other reported structures [8, 16, 17]. The resulting crown conformation tends to equalize the Y—O(crown ether) bond lengths, a fact also observed in the $Eu(NO_3)_3$ complexes with 12-crown-4 and 15-crown-5 [8, 16] and in the 18-crown-6 complex of $Nd(NO_3)_3$ [17]. The average C—C and C—O distances and C–C–O and C–O–C angles are 1.52(4) Å, 1.44(3) Å, 107(2)° and 114(2)°, respectively. These values compare well with the averages reported by Bunzli [8] for $Eu(NO_3)_3(12$-crown-4).

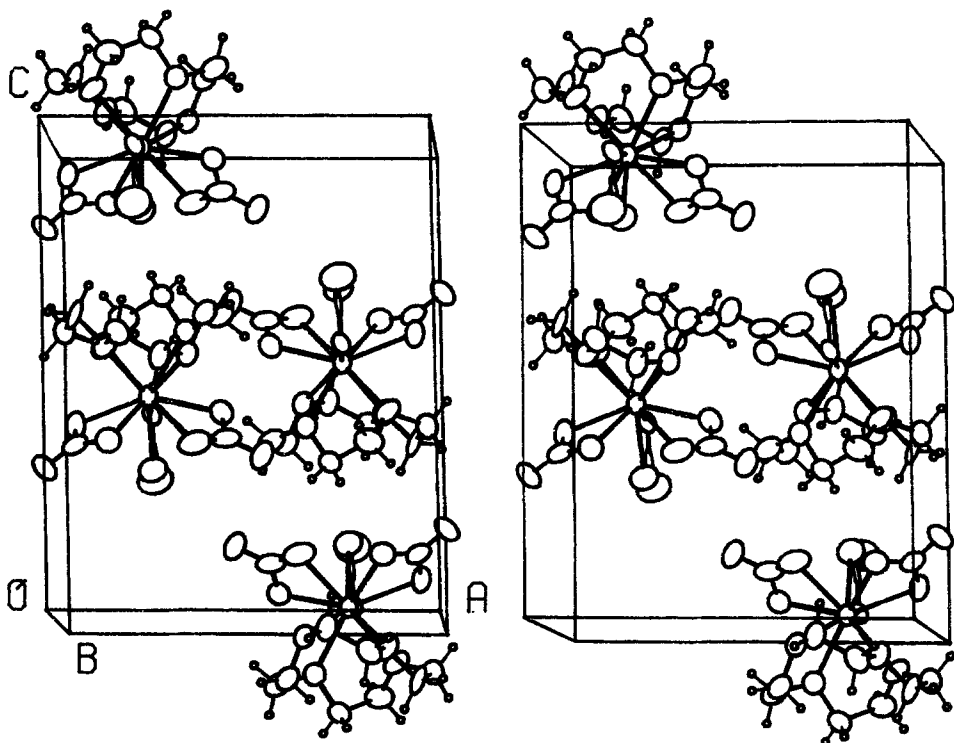A stereoview of the unit cell contents is presented in Figure 4.

Fig. 4.   Stereoview of the unit cell contents.

Acknowledgements

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