

The Crystal Structure of the Adduct between Quinuclidine and the NMR Shift Reagent $\text{Eu}(\text{DPM})_3$

ERIK BYE

Department of Chemistry, University of Oslo, Oslo 3, Norway

The molecular and crystal structure of the quinuclidine adduct of tris-(2,2,6,6-tetramethylheptan-3,5-dionato)Eu(III), $\text{Eu}(\text{DPM})_3$, has been determined by X-ray methods. The crystals are monoclinic, space group $P2_1/n$ with unit cell dimensions $a = 10.718(1) \text{ \AA}$; $b = 20.417(3) \text{ \AA}$; $c = 21.368(3) \text{ \AA}$; $\beta = 106.94(1)^\circ$. The phase problem was solved by the heavy atom method and the model refined to an R -value of 0.046 for 4151 observed reflections. Estimated standard deviations in bond lengths and angles involving the europium ion are 0.006 \AA and $0.2 - 0.6^\circ$, respectively.

The coordination polyhedron is best described as a distorted octahedron with the nitrogen atom located above the center of one of the faces, and the adduct has threefold symmetry. The Eu—N distance is 2.60 \AA , the average Eu—O distance is 2.33 \AA , and the europium ion is situated 0.54 \AA , in average, from the three planar chelate rings.

Since the discovery by Hinckley¹ of lanthanide shift reagents, their use have been widespread. Several investigators have postulated relations between the induced chemical shifts and structural parameters of the substrates. The geometric factor $3 \cos^2\theta - 1/r^3$ given by Horrocks *et al.*,² valid for molecules having axial symmetry ($n \geq 3$) only, has been the most successful so far. Many structure determinations have been reported.³⁻⁵ None of them, however, has been concerned with substrates having threefold axial symmetry. As such a substrate quinuclidine was thought to be suitable combined with the symmetric and frequently used shift reagent $\text{Eu}(\text{DPM})_3$. The present work is a part of the investigations of shift reagents being carried out in this laboratory.⁹⁻¹¹ Fig. 1 shows the molecule with the numbering of atoms.

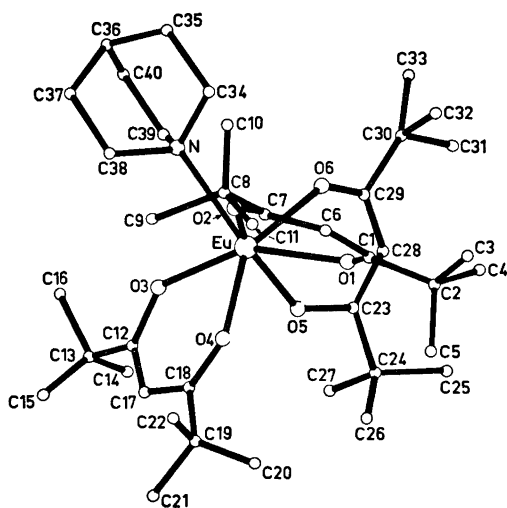


Fig. 1. The adduct between quinuclidine and $\text{Eu}(\text{DPM})_3$, with the numbering of atoms.

EXPERIMENTAL

Single crystals of the 1:1 adduct were obtained by slow evaporation of a benzene solution with equimolecular amounts of $\text{Eu}(\text{DPM})_3$ and quinuclidine. The crystals are colourless, transparent, parallelepipeds. A single crystal of dimensions 0.5 mm \times 0.2 mm \times 0.2 mm, sealed in a thin-walled capillary was used for the experiments.

Oscillation and Weissenberg photographs indicated monoclinic symmetry; systematically absent reflections are $h0l$ and $0k0$ for $h+l$ and k odd, respectively. The space group is thus $P2_1/n$. Unit cell dimensions were determined on a Syntex P1 diffractometer with graphite crystal monochromated $\text{MoK}\alpha$ -radiation. Three-dimensional intensity data were collected using the $2\theta - \theta$ autocollection program with variable

scan rate and a cut-off for low intensities. The scan range was from 0.7° below $2\theta(\alpha_1)$ to 0.7° above $2\theta(\alpha_2)$, and the background was counted 0.7 times the intensity measuring time. The intensities of three standard reflections were measured periodically during the data collection. They showed an average decrease of 5% and the intensities were amended according to this. E.s.d.'s in the intensities were taken as the square root of the total counts with a 2% addition for instrumental instability.

A total of 4332 independent reflections were recorded within the limit of 0.60 for $\sin \theta/\lambda$ of which 4151 had a net count larger than $3\sigma_I$.

The data were corrected for Lorentz and polarization effects and for absorption according to a μ -value of $14.3 \text{ cm}^{-1} (\text{MoK}\alpha)$.

All the calculations were performed on a CDC 3300 computer using the programs described in Ref. 12. Atomic form factors were those of Hanson *et al.*¹³ for Eu, O, N, and C, and of Stewart *et al.*¹⁴ for H.

CRYSTAL DATA

Quinuclidine adduct of tris-(2,2,6,6-tetramethylheptan-3,5-dionato)europium(III), $\text{EuC}_{33}\text{H}_{47}\text{O}_4\text{C}_7\text{H}_{13}\text{N}$, monoclinic. $a = 10.718 (1) \text{ \AA}$,

$b = 20.417 (3) \text{ \AA}$, $c = 21.368 (3) \text{ \AA}$, $\beta = 106.94(1)^\circ$. $V = 4473.0 \text{ \AA}^3$, $M = 812.96$, $Z = 4$. $D_{\text{obs}} = 1.20 \text{ g cm}^{-3}$ (floatation). $D_{\text{calc}} = 1.21 \text{ g cm}^{-3}$.

Systematic absences: $h0l$ and $0k0$ for $h+l$ and k odd, respectively; space group $P2_1/n$.

STRUCTURE DETERMINATION

The coordinates of the europium ions were obtained from a three-dimensional Patterson synthesis based on 1628 reflections within the limit of 0.36 for $\sin \theta/\lambda$. A Fourier map revealed 38 of the 48 atomic positions. Two Fourier refinement including all the 4151 reflections served to establish a model of all the non-hydrogen atoms. Successive cycles of full matrix least-squares refinement with isotropic thermal parameters gave an R -factor of 0.07. The data were then corrected for absorption effects, and anisotropic thermal parameters were introduced for the six *t*-butyl groups. The positional parameters of the 13 quinuclidine hydrogen atoms were calculated from stereochemical con-

Table 1. Fractional coordinates ($\times 10^4$) and isotropic thermal parameters (\AA^2) with e.s.d.'s.

Atom	x	y	z	B
Eu ^a	3147(5)	5553(2)	20647(2)	3.30(01)
O1	1921(6)	674(3)	3062(3)	4.9(1)
O2	2237(6)	137(3)	1932(3)	4.7(1)
O3	-1208(6)	1003(3)	1159(3)	4.3(1)
O4	1209(6)	1506(3)	1790(3)	5.2(1)
O5	-857(6)	1214(3)	2577(3)	4.8(1)
O6	-553(6)	-117(3)	2718(3)	4.2(1)
N	-461(7)	-471(3)	1331(3)	3.7(1)
C1	3150(9)	668(5)	3251(4)	4.4(2)
C6	3907(10)	471(5)	2850(5)	5.1(2)
C7	3433(9)	226(5)	2225(4)	4.2(2)
C12	-1435(9)	1593(5)	931(5)	4.5(2)
C17	-506(10)	2081(5)	1064(5)	5.2(2)
C18	770(10)	2021(5)	1471(5)	5.6(2)
C23	-1118(9)	1176(5)	3123(4)	4.1(2)
C28	-1141(9)	592(5)	3445(4)	4.4(2)
C29	-890(9)	-22(5)	3237(4)	4.0(2)
C34	257(10)	-1052(5)	1652(5)	5.0(2)
C35	-173(11)	-1683(6)	1232(5)	6.3(3)
C36	-1196(11)	-1507(6)	626(6)	6.3(3)
C37	-661(11)	-995(5)	249(5)	6.0(3)
C38	-223(9)	-386(5)	676(5)	4.6(2)
C39	-1879(9)	-582(5)	1228(5)	4.8(2)
C40	-2346(13)	-1195(6)	794(6)	7.5(3)

^a The parameters of the Eu ion ($\times 10^5$).

Table 2. Fractional coordinates and anisotropic thermal parameters ($\times 10^4$) with e.s.d.'s.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B11	B22	B33	B12	B13	B23
C2	3775(11)	922(6)	3959(5)	126(14)	56(6)	19(2)	-4(13)	13(10)	-12(6)
C3	5165(13)	628(9)	4255(6)	154(18)	99(8)	36(4)	48(21)	-41(14)	-23(10)
C4	2926(15)	721(10)	4389(6)	224(23)	135(11)	29(4)	-122(26)	72(16)	-23(11)
C5	3903(18)	1657(7)	3910(7)	439(36)	34(4)	42(5)	-50(22)	38(21)	-16(8)
C8	4360(10)	144(6)	1824(5)	90(12)	44(4)	39(4)	-10(12)	52(11)	-24(7)
C9	3794(13)	278(7)	1111(6)	165(17)	74(6)	29(4)	-1(16)	59(13)	4(7)
C10	4379(15)	-728(6)	1819(7)	256(24)	36(6)	64(6)	34(16)	141(20)	-20(8)
C11	5770(11)	329(7)	2110(7)	96(13)	75(7)	59(6)	-44(14)	73(14)	-51(9)
C13	-2815(10)	1701(5)	487(5)	120(13)	36(4)	35(4)	50(12)	13(11)	16(6)
C14	-3619(16)	1871(14)	926(10)	160(23)	220(19)	77(9)	143(35)	82(23)	-57(21)
C15	-2903(17)	2226(14)	61(15)	177(27)	201(19)	210(20)	-155(36)	-192(37)	329(34)
C16	-3413(17)	1083(9)	171(11)	238(27)	83(9)	133(12)	92(25)	-210(29)	-110(17)
C19	1752(13)	2605(6)	1562(7)	196(20)	39(5)	59(5)	-107(16)	30(17)	7(8)
C20	2147(27)	2796(12)	2109(9)	744(69)	140(14)	65(8)	-541(55)	156(39)	-122(18)
C21	1232(23)	3155(10)	1162(15)	432(47)	76(10)	211(19)	-231(36)	-262(48)	184(23)
C22	2876(22)	2350(11)	1360(17)	403(44)	88(10)	295(26)	-228(36)	526(60)	-101(27)
C24	-1453(11)	1841(5)	3371(5)	159(15)	24(3)	39(4)	20(11)	61(13)	-9(5)
C25	-1444(18)	1832(6)	4102(7)	424(35)	40(5)	44(5)	17(21)	163(22)	-18(8)
C26	-452(16)	2365(6)	3284(8)	326(29)	30(4)	81(7)	-86(18)	192(22)	-36(9)
C27	-2818(15)	2041(7)	2908(8)	245(24)	58(6)	68(6)	144(20)	1(20)	-23(10)
C30	-972(11)	-634(5)	3627(5)	182(16)	25(3)	32(3)	4(12)	81(12)	7(5)
C31	-1747(21)	-540(8)	4114(9)	503(44)	52(8)	88(8)	51(26)	344(34)	39(12)
C32	383(15)	-844(8)	3966(9)	219(24)	64(6)	99(8)	72(21)	79(24)	95(13)
C33	-1516(21)	-1182(7)	3172(8)	552(46)	45(6)	51(6)	-146(26)	135(26)	4(9)

Table 3. Fractional coordinates ($\times 10^3$) for the quinuclidine hydrogen atoms.^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
H1	8	-112	212	H8	-77	3	42
H2	129	-98	172	H9	81	-30	75
H3	-58	-203	151	H10	-243	-16	99
H4	65	-190	111	H11	-205	-66	170
H5	-147	-195	32	H12	-307	-105	35
H6	-143	-86	-19	H13	-276	-154	106
H7	17	-120	12				

^a The hydrogen atoms were given *B*-values of 7.0 Å².

Table 4. Bond lengths (Å) with e.s.d.'s.

Eu-O1	2.327(6)			
Eu-O2	2.323(6)		C2-C3	1.56(2)
Eu-O3	2.322(6)		C2-C4	1.53(2)
Eu-O4	2.316(6)		C2-C5	1.51(2)
Eu-O5	2.322(6)		C8-C9	1.56(2)
Eu-O6	2.337(6)		C8-C10	1.52(2)
			C8-C11	1.59(2)
Eu-N	2.603(7)		C13-C14	1.49(2)
			C13-C15	1.39(2)
O1-C1	1.26(1)		C13-C16	1.49(2)
O2-C7	1.26(1)		C19-C20	1.36(2)
O3-C12	1.29(1)		C19-C21	1.42(2)
O4-C18	1.27(1)		C19-C22	1.48(3)
O5-C23	1.28(1)		C24-C25	1.56(2)
O6-C29	1.28(1)		C24-C26	1.56(2)
C1-C6	1.40(2)		C24-C27	1.56(2)
C6-C7	1.38(1)		C30-C31	1.52(2)
C12-C17	1.38(1)		C30-C32	1.48(2)
C17-C18	1.39(2)		C30-C33	1.49(2)
C23-C28	1.38(1)			
C28-C29	1.38(1)		N-C34	1.47(1)
			N-C38	1.50(1)
			N-C39	1.49(1)
C1-C2	1.55(1)			
C7-C8	1.55(1)		C34-C35	1.56(2)
C12-C13	1.52(1)		C35-C36	1.47(2)
C18-C19	1.57(2)		C36-C37	1.53(2)
C23-C24	1.54(1)		C36-C40	1.52(2)
C29-C30	1.52(1)		C37-C38	1.53(2)
			C39-C40	1.55(2)

siderations, given *B*-values of 7.0 Å² but not refined. No attempts were made to include the other hydrogen atoms in the calculations. The refinement converged at an conventional *R*-value of 0.046 (*R*_w = 0.062).

A complete list of the structure factors may be obtained from the author on request.

The atomic parameters are given in Tables

1-3; the anisotropic thermal parameters are given by

$$\exp - (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$$

The e.s.d.'s in bond lengths and angles involving the europium ion were calculated to be 0.006 Å and 0.2-0.6°, respectively. For the

Table 5. Bond angles (°) with e.s.d.'s.

Angles		Angles	
O1 - Eu - O2	72.9(2)	C1 - C6 - C7	126(1)
O3 - Eu - O4	72.5(2)	C12 - C17 - C18	126(1)
O5 - Eu - O6	72.1(2)	C23 - C28 - C29	126(1)
O1 - Eu - O4	84.0(2)	O1 - C1 - C2	115(1)
O1 - Eu - O5	82.2(2)	O2 - C7 - C8	114(1)
O2 - Eu - O3	118.4(2)	O3 - C12 - C13	114(1)
O2 - Eu - O4	80.1(2)	O4 - C18 - C19	116(1)
O4 - Eu - O5	87.4(2)	O5 - C23 - C24	113(1)
O3 - Eu - O5	79.6(2)	O6 - C29 - C30	115(1)
O3 - Eu - O6	115.1(2)		
O1 - Eu - O6	80.3(2)	C2 - C1 - C6	122(1)
O2 - Eu - O6	112.3(2)	C6 - C7 - C8	122(1)
O2 - Eu - O5	153.1(2)	C13 - C12 - C17	122(1)
O1 - Eu - O3	150.8(2)	C17 - C18 - C19	121(1)
O4 - Eu - O6	155.6(2)	C24 - C23 - C28	123(1)
O1 - Eu - N	131.0(2)	C28 - C29 - C30	121(1)
O2 - Eu - N	76.6(2)		
O3 - Eu - N	78.0(2)	C1 - C2 - C3	111(1)
O4 - Eu - N	127.2(2)	C1 - C2 - C4	110(1)
O5 - Eu - N	129.0(2)	C1 - C2 - C5	107(1)
O6 - Eu - N	77.0(2)	C3 - C2 - C4	109(1)
Eu - O1 - C1	135.7(6)	C3 - C2 - C5	108(1)
Eu - O2 - C7	134.0(6)	C4 - C2 - C5	113(1)
Eu - O3 - C12	133.5(6)	C7 - C8 - C9	108(1)
Eu - O4 - C18	135.7(6)	C7 - C8 - C10	107(1)
Eu - O5 - C23	133.5(6)	C7 - C8 - C11	111(1)
Eu - O6 - C29	133.9(6)	C9 - C8 - C10	110(1)
		C9 - C8 - C11	107(1)
Eu - N - C34	109.6(6)	C10 - C8 - C11	113(1)
Eu - N - C38	110.9(6)	C12 - C13 - C14	106(1)
Eu - N - C39	110.2(6)	C12 - C13 - C15	113(1)
		C12 - C13 - C16	112(1)
O1 - C1 - C6	123(1)	C14 - C13 - C16	103(2)
O2 - C7 - C6	124(1)	C15 - C13 - C16	115(2)
O3 - C12 - C17	123(1)	C18 - C19 - C20	110(1)
O4 - C18 - C17	123(1)	C18 - C19 - C21	113(1)
O5 - C23 - C28	123(1)	C18 - C19 - C22	106(1)
O6 - C29 - C28	123(1)	C20 - C19 - C21	109(2)
C20 - C19 - C22	111(2)		
C21 - C19 - C22	108(2)	C34 - N - C38	109(1)
C23 - C24 - C25	114(1)	C34 - N - C39	109(1)
C23 - C24 - C26	109(1)	C38 - N - C39	109(1)
C23 - C24 - C27	107(1)		
C25 - C24 - C26	109(1)	N - C34 - C35	112(1)
C25 - C24 - C27	111(1)	N - C38 - C37	111(1)
C26 - C24 - C27	107(1)	N - C39 - C40	111(0)
C29 - C30 - C31	114(1)		
C29 - C30 - C32	107(1)	C34 - C35 - C36	109(1)
C29 - C30 - C33	110(1)	C35 - C36 - C37	109(1)
C31 - C30 - C32	111(1)	C35 - C36 - C40	110(1)
C31 - C30 - C33	111(1)	C37 - C36 - C40	107(1)
C32 - C30 - C33	104(1)	C36 - C37 - C38	110(1)
		C36 - C40 - C39	110(1)

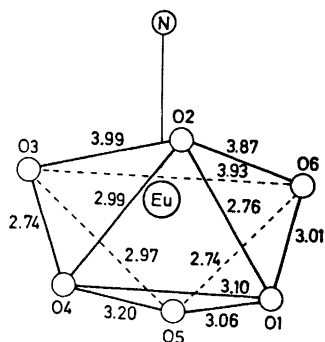


Fig. 2. The coordination polyhedron of the Eu(III) ion.

other atoms the e.s.d's in bond lengths and angles are 0.01–0.02 Å and 1.0–2.0°, respectively.

DISCUSSION

Interatomic distances and angles are given in Tables 4 and 5.

In the present structure the Eu(III) ion has seven-coordination, and Fig. 2 shows that the coordination polyhedron is best described as a distorted octahedron with the quinuclidine nitrogen atom located above the center of one of the faces. This model is called "1:3:3" according

Table 6. Interatomic distances (Å) of the coordination polyhedron ($\sigma = 0.01$ Å).

O1–O6	3.01	O5–O1	3.06
O6–O3	3.93	O5–O6	2.74
O3–O4	2.74	O5–O3	2.97
O4–O1	3.11	O5–O4	3.21
O2–O1	2.76	N–O2	3.06
O2–O6	3.87	N–O6	3.08
O2–O3	3.99	N–O3	3.11
O2–O4	3.99	N–O1	4.49
		N–O4	4.41
		N–O5	4.45

Table 7. Equations of least-squares planes through the three chelate rings, with the deviations ($\text{Å} \times 10^3$) of individual atoms from these planes.

Plane	Equation
A	$(0.0020a + 0.454b + 0.0178c)R - 1.028 = 0$
B	$(-0.0293a + 0.0147b + 0.0381c)R - 3.622 = 0$
C	$(0.0940A + 0.0057c + 0.0250c)R - 0.854 = 0$

Plane	Deviations	Plane	Deviations	Plane	Deviations
A		B		C	
Eu ^a	-458	Eu ^a	527	Eu ^a	629
O1	-40	O3	-52	O5	20
O2	42	O4	48	O6	15
C1	4	C12	2	C23	14
C2	31	C13	25	C24	-6
C6	-16	C17	10	C28	21
C7	-7	C18	7	C29	-2
C8	-15	C19	40	C30	-21

^a The Eu ions do not define the plane.

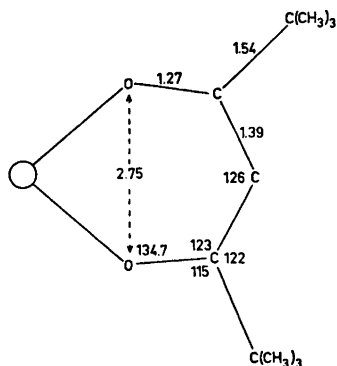


Fig. 3. Averaged bond lengths (Å) and angles (°) of the three planar chelate rings.

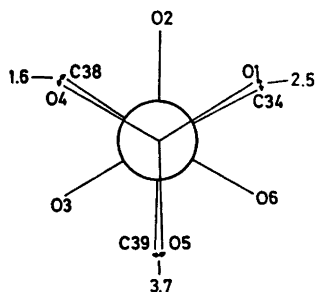


Fig. 4. The orientation of the quinuclidine molecule relative to the oxygen atoms, viewed along the Eu-N line.

to Gillespie.¹⁵ The metal ion is surrounded by six chelate-oxygen atoms at an average distance of 2.325 Å and the nitrogen atom at 2.603 Å. The average Eu-O distance is in agreement with the value 2.347 Å reported by Cramer *et al.*⁸ The slight shortening of the present Eu-N bond length compared to the value 2.649 Å found in the dipyridine adduct of Eu(DPM)₃⁸ is probably significant and may be attributed to the coordination of only one nitrogen atom in the present case.

Adapting the "1:3:3" model¹⁵ the coordination polyhedron is different, for instance, compared with the "1:4:2" model¹⁵ found in Dy(THD)₃H₂O,⁷ with the same coordination number. The preference for the former polyhedron in the present structure is probably due to the non-equivalence of one of the electron pairs and to the space requirements of the quinuclidine molecule.

Some of the interatomic distances of the coordination polyhedron are given in Table 6. The Eu ion is situated 0.51 Å and 1.46 Å from the faces (O2,O3,O6) and (O1,O4,O5), respectively, and the dihedral angle between the two faces is only 3.1°.

As found in acetylacetonato complexes without bridging ligands, the chelate rings are planar. The europium ion is displaced 0.46 Å, 0.53 Å, and 0.63 Å from the three planes A, B, C listed in Table 7 (0.54 Å in average). The bond lengths and angles may be compared to earlier reported dimensions of similar ring

Table 8. Dihedral angles (°), ($\sigma = 0.7^\circ$).

O1-Eu-N-C34	2.5	O3-Eu-N-C34	-178.4
O4-Eu-N-C38	1.6	O6-Eu-N-C34	-178.1
O5-Eu-N-C39	3.7	O2-Eu-N-C39	-174.5

Table 9. Average (r, θ)-values together with those derived from NMR experiments.¹⁸

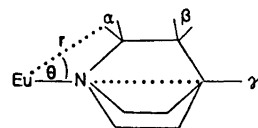
	r (distance, Å)		θ (angle, °)	
	X-ray	NMR	X-ray	NMR
Eu- α	3.5	3.4	37	39
Eu- β	5.5	5.5	23	28
Eu- γ	6.3	6.3	0	0

systems,^{5,7,8,16,17} and the average values are shown in Fig. 3. The mean "bite" distance of 2.75 Å agrees well with the value 2.734 Å found by Cramer *et al.*⁸ They are, however, somewhat shorter than the value 2.87 Å, predicted by Lingafelter *et al.*¹⁶⁻¹⁷

Fig. 4 shows the orientation of the quinuclidine moiety relative to the oxygen atoms. The dihedral angles O-Eu-N-C are listed in Table 8, and indicate the threefold axial symmetry of the complex. The axis is passing through the europium and nitrogen atoms, and the three dihedral angles O1-Eu-N-C34 (2.5°), O4-Eu-N-C38 (1.6°) and O5-Eu-N-C39 (3.7°) are equal within the limits of experimental error.

The present calculated (r, θ)-values are listed in Table 9 together with those derived from

NMR experiments,¹⁸ utilizing the $3 \cos^2 \theta - 1/r^3$ relation. The α -, β -, and γ -hydrogen atoms of quinuclidine are as follows.



Bearing in mind the large experimental errors in the parameters of the hydrogen atoms, the agreement between corresponding values in Table 9 probably indicates that the complex maintains the same structure in solution.

Fig. 5 illustrates the crystal structure as seen along the a -axis.

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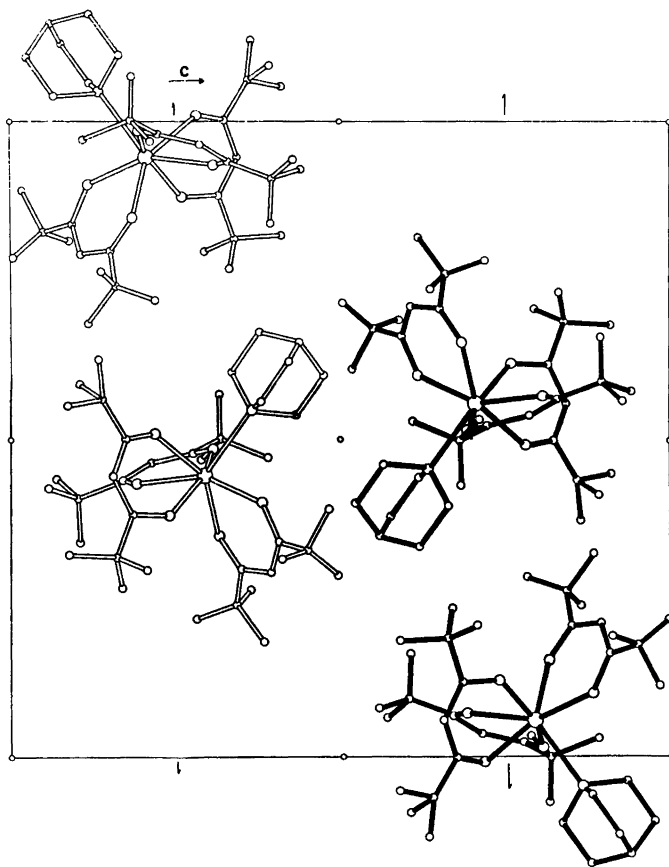


Fig. 5. The crystal structure as seen along the a -axis.

REFERENCES

1. Hinckley, C. C. *J. Amer. Chem. Soc.* **91** (1969) 5160.
2. Horrocks, W. DeW., Jr. and Sipe, J. P., III *J. Amer. Chem. Soc.* **93** (1971) 6800.
3. Phillips, T., II, Sands, D. E. and Wagner, W. F. *Inorg. Chem.* **7** (1968) 2295.
4. Burns, J. H. and Danford, M. D. *Inorg. Chem.* **8** (1969) 1780.
5. Erasmus, C. S. and Boeyens, J. C. A. *Acta Crystallogr. B* **26** (1970) 1843.
6. Horrocks, W. DeW., Jr., Sipe, J. P., III and Lubber, J. R. *J. Amer. Chem. Soc.* **93** (1971) 5258.
7. Erasmus, C. S. and Boyens, J. C. A. *J. Cryst. Mol. Struct.* **1** (1971) 83.
8. Cramer, R. E. and Seff, K. *Acta Crystallogr. B* **28** (1972) 3281.
9. Kristiansen, P. and Ledaal, T. *Tetrahedron Lett.* **30** (1971) 2817.
10. Kristiansen, P. and Ledaal, T. *Tetrahedron Lett.* **46** (1971) 4457.
11. Kjekshus, A. and Ledaal, T. *Acta Chem. Scand.* **27** (1973) 2665.
12. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømming, C. *Acta Chem. Scand.* **24** (1970) 2232.
13. Hanson, H. P., Herman, F., Lea, J. D. and Skillmann, S. *Acta Crystallogr.* **17** (1964) 1040.
14. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
15. Gillespie, R. J. *Can. J. Chem.* **38** (1960) 818.
16. Lingafelter, E. C. *Coord. Chem. Rev.* **1** (1966) 151.
17. Lingafelter, E. C. and Braun, R. L. *J. Amer. Chem. Soc.* **88** (1966) 2951.
18. Ledaal, T. *To be published.*

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