Preparation, Characterization and Crystal Structure of a Binuclear Thorium(IV) Complex with a Pentadentate Compartmental Schiff Base

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Abstract

The interaction of the potentially pentadentate compartmental Schiff base, (H_3L), derived by condensation of 2,6-diformyl-4-chlorophenol and *o*-aminophenol with thorium(IV) salts has been studied and the crystal structure of the ionic complex $[Mg-[Th_2L_3]_2\cdot 6H_2O$ determined by X-ray crystallography. The compound is monoclinic, space group $P2_1/c$, with $a = 12.488(6)$, $b = 22.044(5)$, $c = 24.316(5)$ Å, and $\beta = 104.82(3)°$; $D_c = 1.66$ g cm^{-3} for $Z = 2$. The structure was refined to the final conventional R of 0.067 based on 5455 observed reflexions. The two independent Th atoms of the monoanionic $[Th_2L_3]^-$ complex are nona-coordinate and bridged by three oxygen atoms. The Mg^{2+} cations, which are on crystallographic centres of symmetry, are octahedrally surrounded by H_2O molecules. Selected bond distances are: Th–O (bridging) 2.47 Å (mean value), Th–O 2.31 Å (mean value), Th–N 2.74 Å (mean value), Mg···O 2.09 Å (mean value).

Introduction

Binuclear Schiff bases have been extensively studied and used for the preparation of homo- and hetero-dinuclear complexes [1–7]. These ligands are generally planar and especially designed to incorporate, in a planar fashion, two identical or different metal ions. The compartmental ligands represent a particular case of the above compounds and give rise to complexes with metal sharing of at least one donor atom of the ligand. They contain adjacent sites in which the central donor atom behaves as a bridging group between the two metal ions [4, 7] (Fig. 1).

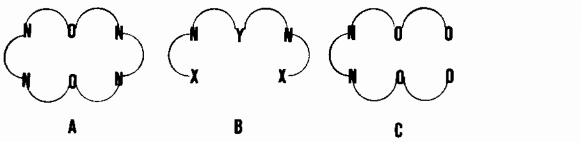
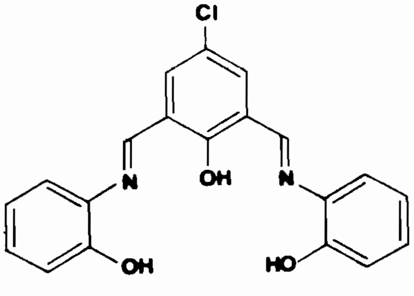


Fig. 1. Schematic representation of compartmental ligands: A, macrocycle (N_2O_4); B, 'end-off' (N_2YX_2; X = N, O, S; Y = O, S); C, 'side-off' (N_2O_4).

The 'side-off' and 'cyclic' ligands have been successfully used in the preparation of homo- and hetero-dinuclear complexes, containing actinide ions [8]. On the contrary, the 'end-off' ligands seem to be not suitable for coordination of actinides owing to their coordination geometry and ionic radii [9, 10], which are considerably different from those of the d-metal ions used for the synthesis of binuclear complexes. For instance, thorium(IV) is usually eight- or nine-coordinate in the square antiprismatic, dodecahedral, monocapped square antiprismatic, or trigonal tricapped prismatic coordination geometry [11]. Reaction of thorium(IV) salts with the Schiff base H_3L:



H_3L

obtained by condensation of 2,6-diformyl-4-chlorophenol with *o*-aminophenol, shows the compartmental behaviour of this ligand with large metal ions. We report here the synthesis, the chemical properties and the crystal structure of the complex $Mg[Th_2L_3]_2\cdot 6H_2O$.

Experimental

2,6-Diformyl-4-chlorophenol was prepared and purified according to the literature [12]; *o*-aminophenol, $Mg(CH_3COO)_2 \cdot 4H_2O$, LiOH and the solvents were commercial products and were used without purification.

Preparation of $Mg[Th_2L_3]_2 \cdot 6H_2O$

To a pale yellow methanolic (50 ml) solution of 2,6-diformyl-4-chlorophenol (184.5 mg, 1 mmol), *o*-aminophenol (218 mg, 2 mmol) was added. The red precipitate obtained was dissolved by addition of LiOH (72 mg, 3 mmol). To this wine red solution, $Th(NO_3)_4 \cdot 4H_2O$ (369 mg, 0.66 mmol) in methanol (20 ml) and $Mg(CH_3COO)_2 \cdot 4H_2O$ (40 mg, 0.17 mmol) in methanol (10 ml) were added. The orange-red solution was refluxed for 15 min and a microcrystalline orange precipitate was obtained. It was filtered, washed with methanol and dried *in vacuo*. *Anal.* Calc. for $Mg[Th_2L_3]_2 \cdot 6H_2O$: C, 44.44; H, 2.61; N, 5.18. Found: C, 43.90; H, 2.80; N, 4.92%.

Well formed crystals of $Mg[Th_2L_3]_2 \cdot 6H_2O$ have been obtained from the mother liquor.

The crude product dissolved in the minimum volume of dimethylformamide (dmf), together with a few drops of methanol, was maintained in an atmosphere saturated by diethyl ether. After 2 days well formed single crystals were obtained in high yield. *Anal.* Calc. for $Mg[Th_2L_3]_2 \cdot 6H_2O \cdot$dmf: C, 44.55; H, 2.77; N, 5.49. Found: C, 44.32; H, 2.80; N, 5.34%.

Crystals of $Mg[Th_2L_3]_2 \cdot 6H_2O \cdot$dmf are not stable in air. Stable crystals, suitable for X-ray investigations, were obtained by dissolving $Mg[Th_2L_3]_2 \cdot 6H_2O \cdot$dmf in dimethylformamide and maintaining the solution in an atmosphere saturated by water at 45 °C. These crystals are identical to those obtained from the mother liquor.

Physical Measurements

The infrared spectra were obtained using KBr pellets on a Perkin-Elmer Model 580B infrared spectrophotometer.

Thorium, magnesium and chlorine ratios were conveniently determined by the integral counting of back-scattered X-ray fluorescence radiation from a Philips SEM Model 505 scanning electron microscope equipped with an EDAX data station.

Samples suitable for SEM analysis were prepared by suspending the microcrystalline powders in petroleum ether. Some drops of the resulting suspension were placed on a graphite plate and after evaporation of the solvent the samples were metallized with gold or graphite using an Edward's S150B model sputter coater.

X-ray Data

A crystal of $Mg[Th_2L_3]_2 \cdot 6H_2O$ was mounted on a glass fibre and used for the X-ray work. Unit cell parameters were determined from accurate settings of 25 reflextions with $5 < 2\vartheta < 20$ on a Philips four-circle diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å).

TABLE I. Crystal and Intensity Data for $Mg[Th_2L_3]_2 \cdot 6H_2O$

Formula	$Mg[Th_2L_3]_2 \cdot 6H_2O$
Formula weight	3135.13
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	12.488(6)
b (Å)	22.044(5)
c (Å)	24.316(5)
β (deg)	104.82(3)
V (Å^3)	6471
Z	2
D_c (g cm^{-1})	1.66
Radiation	Mo Kα
λ(Mo Kα)	0.7107 Å
Maximum crystal size (mm)	0.2
ϑ-scan speed	2 deg min^{-1}
2ϑ range	2–50 deg
Reflexions recorded	8667
Reflexions observed, $I > 3\sigma(I)$	5455
Parameters varied	344
R (observed reflexions)	0.067

Crystal data are given in Table I, together with data collection conditions. Two standard reflexions monitored every 100 measurements indicated no significant systematic fluctuation. Insensities were converted to structure amplitudes after applying Lorentz and polarization corrections. Because of the relatively high absorption coefficient, an absorption correction was also made [13].

The structure was solved by direct methods using programs incorporated in SHELX [14] and by Fourier difference maps. Non-hydrogen atoms were refined in blocks by full-matrix least-squares, minimizing the function $\Sigma w \Delta F^2$ with $w = 1$. Ring carbon atoms were refined as rigid bodies (C–C = 1.395 Å). At convergence the maximum shift on the parameters refined was 0.4σ, and in the final difference Fourier map there were no significant residuals of electron density.

Scattering factors for Th were taken from ref. 15 and for other atoms were from ref. 14. A correction was applied for the anomalous dispersion of Th. Final positional and thermal parameters are in Table II. Tables III and IV list bond lengths and angles. The equations of selected mean planes are reported in Table V.

Results and Discussion

By condensation of 2,6-diformyl-4-chlorophenol and *o*-aminophenol in alcoholic solution the potentially pentadentate compartmental Schiff base H_3L

TABLE II. Atomic Parameters for $Mg[Th_2L_3]_2 \cdot 6H_2O$

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Atomic coordinates			
Th1	0.06233(7)	0.19279(3)	0.89640(3)
Th2	0.13393(8)	0.32936(3)	0.81510(3)
O1	−0.0755(12)	0.1785(6)	0.9449(6)
O2	0.1943(9)	0.2743(5)	0.9072(4)
O3	0.2227(16)	0.3191(8)	0.7407(6)
N1	0.0605(12)	0.2731(6)	0.9825(6)
N2	0.3384(16)	0.2812(7)	0.8412(8)
Cl1	0.5518(7)	0.3604(4)	1.0937(3)
O4	0.0098(11)	0.0992(5)	0.8546(5)
O5	−0.0186(10)	0.2908(5)	0.8549(5)
O6	0.2523(13)	0.4042(5)	0.8532(5)
N3	−0.1276(15)	0.1889(7)	0.8140(7)
N4	0.0758(16)	0.4027(6)	0.8958(6)
Cl2	−0.4472(7)	0.4017(3)	0.8453(5)
O7	0.1816(12)	0.1522(6)	0.9763(5)
O8	0.1129(12)	0.2179(5)	0.8076(4)
O9	−0.0011(13)	0.3945(5)	0.7656(6)
N5	0.2529(15)	0.1399(8)	0.8824(6)
N6	−0.0271(14)	0.2843(7)	0.7238(6)
Cl3	0.1827(8)	0.0639(3)	0.6250(3)
Mg1	0.0000(0)	0.5000(0)	0.5000(0)
O20	0.0711(16)	0.4921(7)	0.4305(7)
O21	0.1272(15)	0.5581(6)	0.5394(7)
O22	0.0898(15)	0.4259(7)	0.5389(6)
C1	−0.1071(11)	0.2193(5)	0.9778(5)
C2	−0.2088(11)	0.2132(5)	0.9911(5)
C3	−0.2470(11)	0.2592(5)	1.0206(5)
C4	−0.1834(11)	0.3113(5)	1.0368(5)
C5	−0.0817(11)	0.3174(5)	1.0234(5)
C6	−0.0436(11)	0.2714(5)	0.9939(5)
C7	0.1414(16)	0.3026(9)	1.0140(8)
C8	0.2525(8)	0.3082(6)	1.0009(5)
C9	0.3380(8)	0.3286(6)	1.0460(5)
C10	0.4452(8)	0.3340(6)	1.0393(5)
C11	0.4670(8)	0.3190(6)	0.9875(5)
C12	0.3814(8)	0.2986(6)	0.9424(5)
C13	0.2742(8)	0.2932(6)	0.9491(5)
C14	0.4111(18)	0.2827(9)	0.8882(9)
C15	0.3668(15)	0.2601(8)	0.7909(6)
C16	0.4509(15)	0.2188(8)	0.7898(6)
C17	0.4737(15)	0.2038(8)	0.7383(6)
C18	0.4125(15)	0.2301(8)	0.6878(6)
C19	0.3284(15)	0.2714(8)	0.6889(6)
C20	0.3056(15)	0.2864(8)	0.7405(6)
C21	−0.0565(11)	0.0895(6)	0.8032(4)
C22	−0.0462(11)	0.0384(6)	0.7711(4)
C23	−0.1143(11)	0.0316(6)	0.7162(4)
C24	−0.1927(11)	0.0760(6)	0.6934(4)
C25	−0.2029(11)	0.1272(6)	0.7254(4)
C26	−0.1349(11)	0.1339(6)	0.7803(4)
C27	−0.2123(18)	0.2232(9)	0.8030(9)
C28	−0.2091(11)	0.2842(4)	0.8300(5)
C29	−0.3117(11)	0.3105(4)	0.8278(5)
C30	−0.3169(11)	0.3687(4)	0.8495(5)
C31	−0.2196(11)	0.4006(4)	0.8733(5)
C32	−0.1171(11)	0.3743(4)	0.8754(5)
C33	−0.1118(11)	0.3161(4)	0.8537(5)
C34	−0.0236(19)	0.4114(9)	0.8984(9)

(continued)

TABLE II. *(continued)*

Atom	x/a	y/b	z/c
C35	0.1643(9)	0.4406(6)	0.9224(5)
C36	0.1637(9)	0.4773(6)	0.9691(5)
C37	0.2555(9)	0.5132(6)	0.9935(5)
C38	0.3480(9)	0.5124(6)	0.9712(5)
C39	0.3486(9)	0.4757(6)	0.9246(5)
C40	0.2568(9)	0.4398(6)	0.9002(5)
C41	0.2868(12)	0.1347(7)	0.9819(7)
C42	0.3542(12)	0.1228(7)	1.0360(7)
C43	0.4632(12)	0.1037(7)	1.0425(7)
C44	0.5048(12)	0.0965(7)	0.9948(7)
C45	0.4373(12)	0.1084(7)	0.9407(7)
C46	0.3283(12)	0.1276(7)	0.9342(7)
C47	0.2724(17)	0.1200(9)	0.8363(9)
C48	0.2044(11)	0.1342(6)	0.7796(4)
C49	0.2208(11)	0.0971(6)	0.7359(4)
C50	0.1602(11)	0.1071(6)	0.6800(4)
C51	0.0834(11)	0.1543(6)	0.6676(4)
C52	0.0671(11)	0.1915(6)	0.7112(4)
C53	0.1276(11)	0.1814(6)	0.7672(4)
C54	−0.0193(18)	0.2367(10)	0.6945(9)
C55	−0.1159(13)	0.3230(6)	0.7094(7)
C56	−0.2223(13)	0.3066(6)	0.6786(7)
C57	−0.3092(13)	0.3481(6)	0.6718(7)
C58	−0.2896(13)	0.4058(6)	0.6956(7)
C59	−0.1832(13)	0.4222(6)	0.7263(7)
C60	−0.0963(13)	0.3808(6)	0.7332(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters[a] $U_{(i,j)} \times 10^{-4}$						
Th1	623(5)	321(4)	324(4)	−14(3)	194(4)	−78(4)
Th2	753(6)	321(4)	306(4)	−39(3)	244(4)	−102(4)
O1	787(107)	487(88)	638(94)	−172(72)	402(83)	−266(77)
O2	375(77)	597(85)	299(70)	−130(62)	112(59)	−92(63)
O3	1353(164)	989(137)	459(100)	−120(94)	452(106)	−261(123)
N1	385(97)	427(91)	353(94)	−41(74)	127(77)	−35(75)
N2	965(154)	482(105)	503(126)	−94(91)	461(120)	−194(101)
Cl1	1133(62)	1560(83)	521(45)	90(48)	−108(41)	−851(59)
O4	788(105)	290(71)	362(79)	−3(58)	47(73)	−42(68)
O5	511(86)	291(69)	474(80)	−43(58)	136(67)	−63(59)
O6	961(124)	395(81)	492(92)	−95(69)	442(89)	−103(79)
N3	819(136)	325(92)	563(118)	−102(84)	232(103)	−120(92)
N4	882(148)	309(86)	356(101)	−115(76)	237(97)	−100(90)
Cl2	987(61)	730(51)	2837(116)	−119(61)	1019(70)	146(44)
O7	727(109)	638(97)	402(84)	40(72)	181(77)	−26(80)
O8	913(109)	387(73)	216(70)	−114(57)	272(72)	−38(70)
O9	887(118)	327(76)	585(100)	−20(67)	178(87)	28(74)
N5	787(140)	625(117)	331(101)	−10(86)	200(95)	−143(101)
N6	720(130)	535(110)	431(103)	24(86)	264(95)	−115(93)
Cl3	1509(100)	656(45)	743(49)	−145(37)	865(59)	238(53)
Mg1	1113(102)	419(60)	580(72)	−38(52)	340(70)	136(62)
O20	1420(176)	576(103)	662(112)	−94(86)	394(115)	123(107)
O21	1147(147)	551(99)	893(127)	−170(90)	521(113)	9(96)
O22	1165(147)	704(109)	513(97)	−67(82)	256(97)	128(102)
C1	531(55)					
C2	664(65)					
C3	789(77)					

(continued)

TABLE II. *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C4	790(78)					
C5	540(56)					
C6	456(51)					
C7	460(50)					
C8	496(51)					
C9	585(60)					
C10	721(70)					
C11	623(64)					
C12	520(55)					
C13	396(48)					
C14	496(55)					
C15	677(65)					
C16	1090(100)					
C17	1070(99)					
C18	1220(113)					
C19	1066(99)					
C20	707(71)					
C21	498(54)					
C22	596(61)					
C23	916(89)					
C24	906(84)					
C25	766(76)					
C26	544(56)					
C27	560(56)					
C28	511(54)					
C29	774(73)					
C30	749(73)					
C31	661(65)					
C32	543(55)					
C33	403(47)					
C34	544(58)					
C35	436(48)					
C36	755(75)					
C37	836(79)					
C38	690(67)					
C39	643(66)					
C40	505(54)					
C41	653(66)					
C42	1063(101)					
C43	1417(133)					
C44	1560(140)					
C45	1032(97)					
C46	610(62)					
C47	487(53)					
C48	564(59)					
C49	728(71)					
C50	712(70)					
C51	651(65)					
C52	473(50)					
C53	502(53)					
C54	577(59)					
C55	657(65)					
C56	905(84)					
C57	1430(134)					
C58	1267(115)					
C59	992(94)					
C60	683(69)					

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[a] Anisotropic thermal parameters are in the form $T = \exp 2\pi^2(U_{ij}H_iH_jA_i{}^*Aj^*)$.

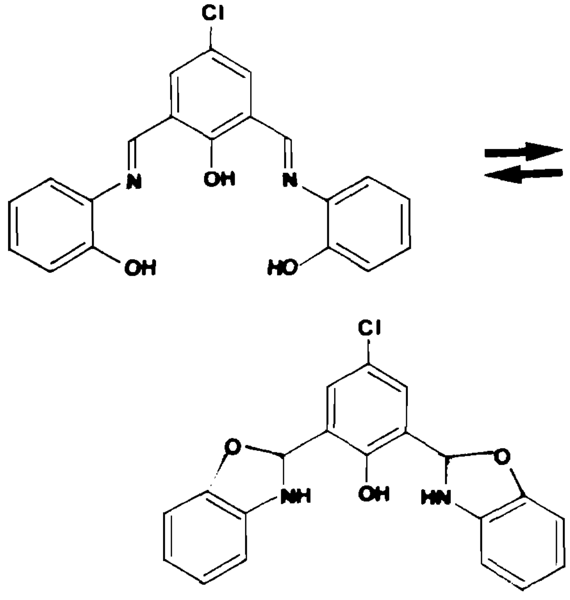
TABLE III. Bond Lengths (Å) for $Mg[Th_2L_3]_2 \cdot 6H_2O$

Coordination					
Th(1)–O(1)	2.34(2)	Th(2)–O(2)	2.49(1)		
Th(1)–O(2)	2.41(1)	Th(2)–O(3)	2.36(2)		
Th(1)–O(4)	2.32(1)	Th(2)–O(5)	2.50(1)		
Th(1)–O(5)	2.49(1)	Th(2)–O(6)	2.25(1)		
Th(1)–O(7)	2.31(1)	Th(2)–O(8)	2.47(1)		
Th(1)–O(8)	2.46(1)	Th(2)–O(9)	2.31(1)		
Th(1)–N(1)	2.75(2)	Th(2)–N(2)	2.69(2)		
Th(1)–N(3)	2.69(2)	Th(2)–N(4)	2.78(2)		
Th(1)–N(5)	2.75(2)	Th(2)–N(6)	2.77(2)		
Ligand 1		Ligand 2		Ligand 3	
O(1)–C(1)	1.33(2)	O(4)–C(21)	1.33(2)	O(7)–C(41)	1.34(2)
C(6)–N(1)	1.41(2)	C(26)–N(3)	1.45(2)	C(46)–N(5)	1.39(2)
N(1)–C(7)	1.28(2)	N(3)–C(27)	1.27(3)	N(5)–C(47)	1.28(3)
C(7)–C(8)	1.51(2)	C(27)–C(28)	1.49(2)	C(47)–C(48)	1.46(2)
Cl(1)–C(10)	1.72(1)	Cl(2)–C(30)	1.76(2)	Cl(3)–C(50)	1.72(2)
C(13)–O(2)	1.30(2)	C(33)–O(5)	1.28(2)	C(53)–O(8)	1.32(2)
C(12)–C(14)	1.50(3)	C(32)–C(34)	1.42(3)	C(52)–C(54)	1.45(3)
C(14)–N(2)	1.26(3)	C(34)–N(4)	1.27(3)	C(54)–N(6)	1.28(3)
N(2)–C(15)	1.43(3)	N(4)–C(35)	1.40(2)	N(6)–C(55)	1.37(2)
C(20)–O(3)	1.26(3)	C(40)–O(6)	1.28(2)	C(60)–O(9)	1.28(2)
$Mg^{2+}(H_2O)_6$					
Mg···O(20)	2.11(2)	Mg···O(21)	2.08(2)	Mg···O(22)	2.07(2)
O(4)···O(20^I)	2.71(2)	Th(1)···Th(2)	3.831(1)		
O(7)···O(22^I)	2.74(2)				

TABLE IV. Selected Bond Angles (deg) for $Mg[Th_2L_3]_2 \cdot 6H_2O$ (estimated standard deviations in parentheses refer to the last significant digit)

Angles involving Th	
Th(1)–O(2)–Th(2)	103.0(4)
Th(1)–O(5)–Th(2)	100.5(5)
Th(1)–O(8)–Th(2)	101.8(5)
N(1)–Th(1)–N(3)	114.2(5)
N(1)–Th(1)–N(5)	122.9(5)
N(3)–Th(1)–N(5)	121.5(5)
Th(1)–O(1)–C(1)	126(1)
Th(1)–O(2)–C(13)	134(1)
Th(1)–O(4)–C(21)	126(1)
Th(1)–O(5)–C(33)	131(1)
Th(1)–O(7)–C(41)	127(1)
Th(1)–O(8)–C(53)	129(1)
Th(1)–N(8)–C(7)	129(1)
Th(1)–N(3)–C(27)	132(1)
Th(1)–N(5)–C(47)	128(1)
N(2)–Th(2)–N(4)	117.8(5)
N(2)–Th(2)–N(6)	120.0(5)
N(4)–Th(2)–N(6)	120.5(5)
Th(2)–O(2)–C(13)	123(1)
Th(2)–O(3)–C(20)	127(1)
Th(2)–O(5)–C(33)	128(1)
Th(2)–O(6)–C(40)	130(1)
Th(2)–O(8)–C(53)	129(1)
Th(2)–O(9)–C(60)	128(1)
Th(2)–N(2)–C(14)	128(2)
Th(2)–N(2)–C(34)	124(1)
Th(2)–N(6)–C(54)	127(1)
Ligand 1	
C(6)–N(1)–C(7)	122(2)
N(1)–C(7)–C(8)	123(2)
C(12)–C(14)–N(2)	121(2)
C(14)–N(2)–C(15)	120(2)
Ligand 2	
C(26)–N(2)–C(27)	117(2)
N(3)–C(27)–C(28)	121(2)
C(32)–C(34)–N(4)	128(2)
C(34)–N(4)–C(35)	123(2)
Ligand 3	
C(40–N(5)–N(47)	119(2)
N(5)–C(47)–C(48)	124(2)
C(52)–C(54)–N(6)	124(2)
C(54)–N(6)–C(55)	122(2)
Angles involving Mg	
O(20)–Mg–O(21)	89.5(7)
O(20)–Mg–O(22)	90.6(7)
O(21)–Mg–O(22)	90.8(6)

was obtained as a orange–red microcrystalline powder. Spectroscopic and mass spectrometry data gave evidence that the equilibrium of Scheme 1 occurs [16]. By reaction of the preformed H_3L ligand or of the precursors with $Th(NO_3)_4 \cdot 4H_2O$ in the presence of the stoichiometric amount of LiOH and $Mg(CH_3COO)_2 \cdot 4H_2O$, an orange complex was obtained which, on the basis of scanning electron microprobe and elemental analysis, was formulated as $Mg[Th_2L_3]_2 \cdot 6H_2O$. Infrared spectra of the powder and of the crystals (obtained by slow evaporation of the mother liquor or by recrystallization from dimethylformamide/diethyl ether of the crude product) show an identical shape along the whole range investigated, apart from the additional bands associated with dimethylformamide for the crystals grown from this solvent. In particular, this compound shows an intense IR band at 1680 cm^{-1} due to ν(C=O). In both complexes the ν(C=N) of the coordinated Schiff bases lies at 1618 cm^{-1}. A correct comparison with the free ligand is difficult, since it is mainly in the oxazoline form. However, the band at 3403 cm^{-1} due to ν(NH) disappears and bands at 1642 and 1634 cm^{-1}, also associable with ν(C=N), are lowered upon coordination.



Scheme 1.

Crystals of $Mg[Th_2L_3]_2 \cdot 6H_2O \cdot dmf$ are not stable in air; it is possible that dimethylformamide is partially lost in air with the consequent destruction of the crystalline packing.

$Mg[Th_2L_3]_2 \cdot 6H_2O \cdot dmf$, dissolved in dimethylformamide and maintained in an atmosphere of aqueous vapour, transforms into $Mg[Th_2L_3]_2 \cdot 6H_2O$ which is identical, also by a crystallographic point of view, to the complex obtained from the mother liquor.

TABLE V. Selected Mean Planes for the $[Th_2L_3]^-$ Anion[a]

Plane I: O(1), O(4), O(7)
$-0.276X - 0.835Y + 0.476Z = 9.164$
Th(1) 1.36

Plane II: O(2), O(5), O(8)
$-0.378X - 0.790Y + 0.483Z = 6.745$
Th(1) 1.89, Th(2) 1.94

Plane III: O(3), O(6), O(9)
$-0.341X - 0.786Y + 0.515Z = 4.055$
Th(2) 1.26

Plane IV: N(1), N(3), N(5)
$-0.378X - 0.784Y + 0.492Z = 8.668$

Plane V: N(2), N(4), N(6)
$-0.384X - 0.766Y + 0.515Z = 5.825$

Plane VI: C(1) to C(6)
$-0.244X + 0.434Y - 0.867Z = -16.026$

Plane VII: C(8) to C(13)
$-0.117X + 0.943Y - 0.312Z = -0.584$

Plane VIII: C(15) to C(20)
$0.650X + 0.751Y + 0.120Z = 6.317$

Plane IX: C(21) to C(26)
$0.797X + 0.478Y - 0.369Z = -10.571$

Plane X: C(28) to C(33)
$0.213X + 0.389Y - 0.896Z = -16.707$

Plane XI: C(35) to C(40)
$-0.239X + 0.749Y - 0.618Z = -5.240$

Plane XII: C(41) to C(46)
$0.295X + 0.952Y + 0.079Z = 3.928$

Plane XIII: C(48) to C(53)
$0.774X + 0.619Y - 0.135Z = -2.427$

Plane XIV: C(55) to C(60)
$0.426X + 0.337Y - 0.839Z = -14.094$

Planes	Angle	Planes	Angle
Angles (°) between the planes			
I–II	6.4	VI–VIII	86.4
I–IV	6.6	IX–X	46.6
II–IV	0.6	X–XI	37.4
II–III	2.8	IX–XI	66.7
II–V	2.3	XII–XIII	36.2
III–V	2.7	XIII–XIV	49.3
VI–VII	44.9	XII–XIV	67.7
VII–VIII	53.6		

[a] X, Y, Z are orthogonal coordinates which are related to the crystallographic coordinates x, y, z by the expression $X = 12.488x - 6.221z$, $Y = 22.044y$, $Z = 23.507z$. Distances (Å) of atoms from the planes are in parenthesis.

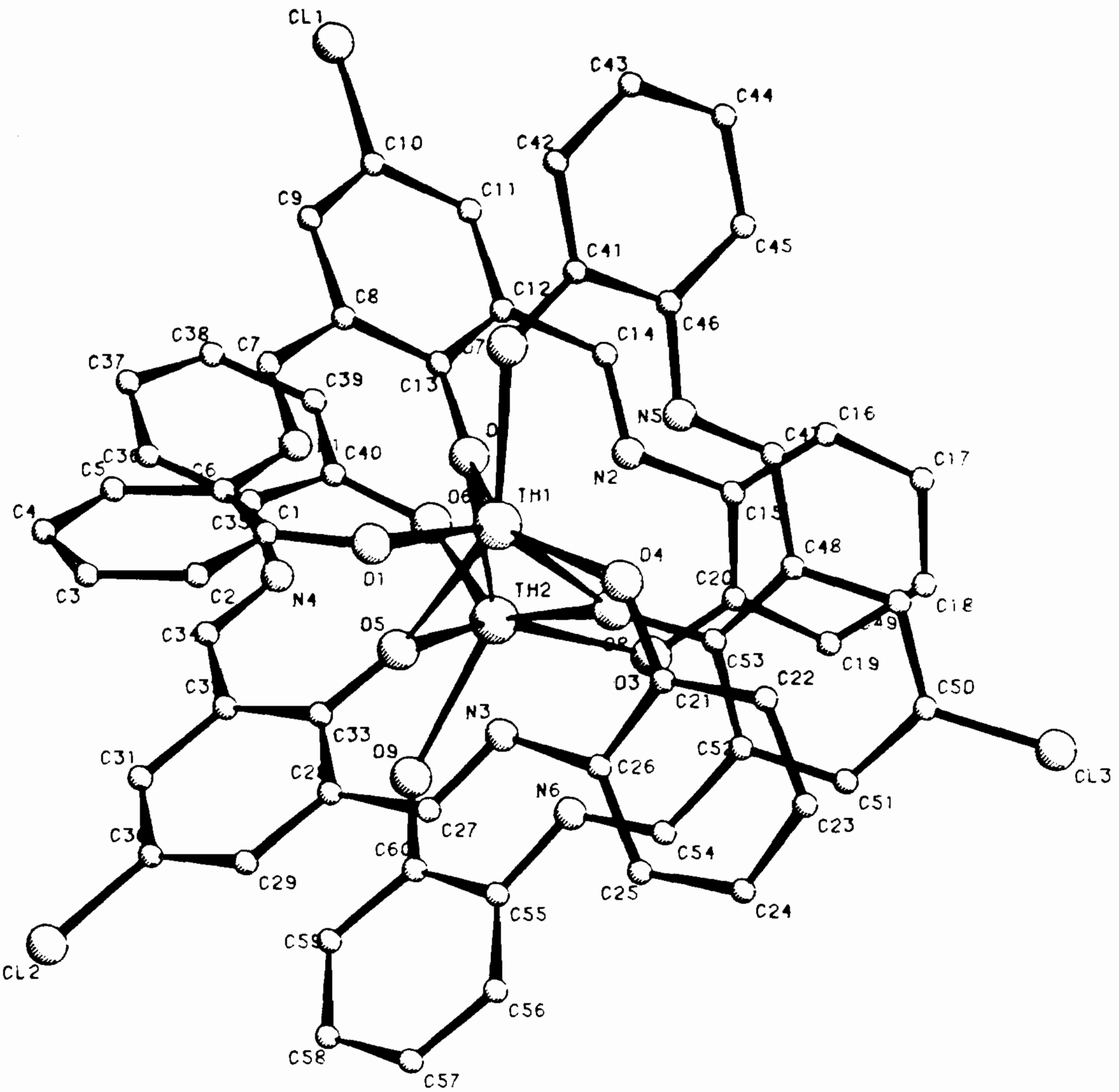


Fig. 2. The structure of the $[Th_2L_3]^-$ anion.

Crystal Structure of $Mg[Th_2L_3]_2 \cdot 6H_2O$

Two formula units of the ionic complex $Mg[Th_2L_3]_2 \cdot 6H_2O$ occur in the monoclinic unit cell of the crystal; the complex anions $[Th_2L_3]^-$ and the H_2O molecules are in general positions, whereas the Mg^{2+} cations are in special positions on inversion centres at (0, 0, 0) and $(0, \frac{1}{2}, \frac{1}{2})$. As shown in Fig. 2 each anion is a dinuclear unit in which two Th atoms are bridged by three oxygen atoms from three different ligands. Each ligand, which is trianionic pentadentate, is coordinated with two atoms to the first Th atom, with two atoms to the second Th atom, and with the central oxygen atom to both Th atoms. Thus ligand 1, which comprises the five donor atoms O(1), N(1), O(2), N(2) and O(3), is coordinated to Th(1) through O(1) and N(2), to Th(2) through N(2) and O(3), and bridges both Th atoms through O(2). The pentadentate ligands are not planar, the two terminal phenylene rings being inclined with respect to the central ring of each ligand by 36° to 54°, as shown in Table V. The two independent Th atoms are nona-coordinate in slightly distorted tricapped trigonal prisms, whose structural details are shown in Figs. 3 and 4.

Th(1) is displaced by 1.36 and 1.89 Å from the outer and the inner trigonal faces of the coordination polyhedron, the corresponding values being 1.26 and 1.94 Å for Th(2) (Table V). The two trigonal faces of each polyhedron are approximately parallel, and are not exactly eclipsed, being rotated from each other by about 16°, as shown in Figs. 3 and 4. The angles between the directions of the Th–N directions (the nitrogen atoms are the caps of the tricapped polyhedrons) are 124°, 114° and 122° for the Th(1)

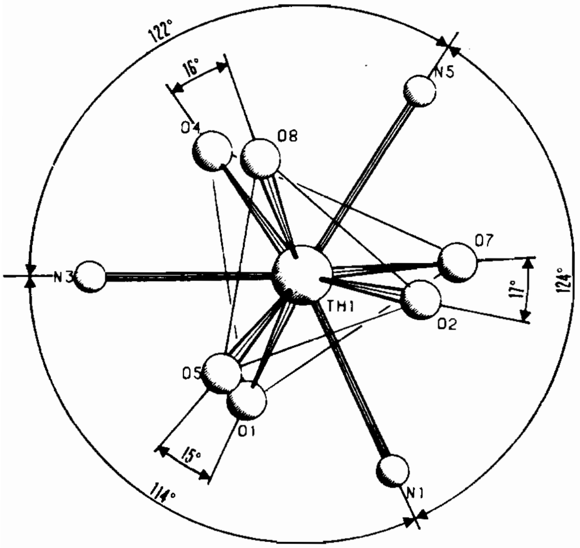


Fig. 3. Coordination polyhedron around Th(1).

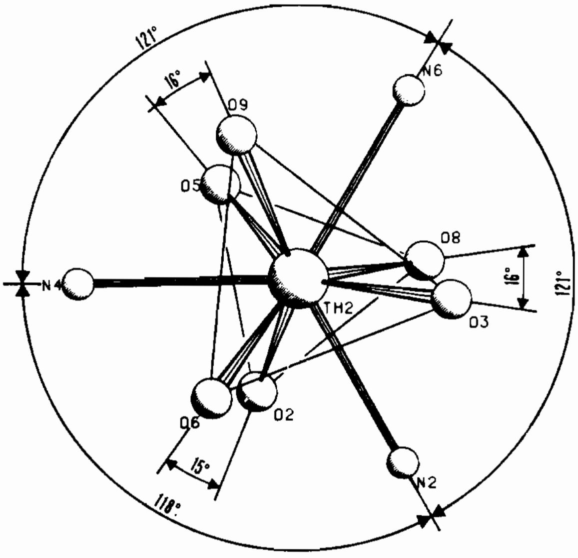


Fig. 4. Coordination polyhedron around Th(2).

polyhedron and 118°, 121° and 121° for the Th(2) polyhedron; that is they differ only by a few degrees from the ideal value of 120°.

Th–O bonds are of two types: bonds with non-bridging oxygen atoms are in the range 2.25–2.36 Å, with a mean of 2.32 Å for Th(1)–O and 2.31 Å for Th(2)–O; bonds with bridging oxygen atoms are, as expected, significantly longer, in the range 2.41–2.50 Å, with a mean of 2.45 Å for Th(1)–O and 2.49 Å for Th(2)–O.

Th–N bonds are much longer than the corresponding Th–O bonds, being between 2.89 and 2.77 Å, with a mean of 2.73 Å for Th(1)–N and 2.75 Å for Th(2)–N. A similar feature, concerning U–N and U–O distances, has already been observed in uranyl complexes with multidentate ligands containing nitrogen and oxygen donor atoms, as for example in $UO_2[o\text{-}OC_6H_4\text{–}CH{=}N(CH_2)_2]_2S$ [17], in $UO_2[o\text{-}OC_6H_4\text{–}CH{=}N(CH_2)]_2C_6H_5PO$ [18] and in $UO_2[o\text{-}OC_6H_4\text{–}C(CH_3){=}N(CH_2)_2]_2NH$ [18]. This fact, which is not restricted only to uranium and thorium metals, was tentatively explained by Pearson on the basis of the 'hard' and 'soft' acid–base concept [19]. Structural details in the ligand are normal. C=N double bonds are localized at N(1)=C(7) and N(2)=C(14) for ligand 1, at N(3)=C(27) and N(4)=C(34) for ligand 2, and at N(5)=C(47) and N(6)=C(54) for ligand 3, as expected.

The Mg^{2+} cations are octahedrally surrounded by six water molecules. The distances of the O(4) and O(7) ligand oxygens from two water molecules are compatible with $O\cdots H_2O$ hydrogen bonding.

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References

1 D. E. Fenton, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta, 95*, 187 (1984).
2 D. E. Fenton, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta, 62*, 57 (1982).
3 R. D. Willett, D. Gatteschi and O. Kahn, 'Magneto-structural Correlations in Exchange Coupled Systems', Nato ASI Series, D. Reidel, Dordrecht, 1983.
4 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Coord. Chem. Rev., 8*, 199 (1979).
5 S. E. Groh, *Isr. J. Chem., 15*, 277 (1976/1977).
6 F. L. Urbach, in H. Siegel (ed.), 'Metal Ions in Biological Systems', Vol. 13, Dekker, New York/Basle, 1981, p. 73, and refs. therein.
7 D. E. Fenton, in A. G. Sykes (ed.), 'Advances in Inorganic and Bioinorganic Mechanisms', Vol. 2, Academic Press, London, 1983, p. 187.
8 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 119*, 215 (1986) and refs. therein.
9 P. T. Moseley, *MTP Int. Rev. Sci. Inorg. Chem., 2*, 65 (1975).
10 D. Brown, 'Halides of the Lanthanides and Actinides', Wiley, London, 1968.
11 G. Bombieri and G. De Paoli, in A. J. Freeman and C. Keller (eds.), 'Handbook on the Physics and Chemistry of the Actinides', Vol. 3, Elsevier, Amsterdam, 1985, p. 75, and refs. therein.
12 A. Zinke, F. Hanus and E. Ziegler, *J. Prakt. Chem., 152*, 126 (1939).
13 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A, 24*, 351 (1968).
14 G. M. Sheldrick, 'SHELX', Program for crystal structure determination, University of Cambridge, U.K., 1975.
15 'International Tables for X-ray Crystallography', Vol. 4, 2nd edn., Kynoch Press, Birmingham, 1974.

16 P. Guerriero, E. Bullita, P. A. Vigato, B. Pelli and P. Traldi, *J. Heterocyclic Chem.*, in press.
17 D. E. Fenton, P. A. Vigato, U. Casellato, R. Graziani and M. Vidali, *Inorg. Chim. Acta, 51*, 195 (1981).
18 U. Casellato, P. A. Vigato, S. Tamburini, S. Sitran and R. Graziani, *Inorg. Chim. Acta, 95*, 147 (1984).
19 R. C. Pearson, *J. Am. Chem. Soc., 85*, 3553 (1963).