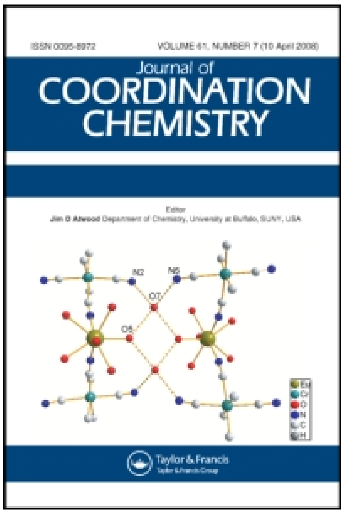

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SYNTHESIS, CRYSTAL STRUCTURE AND FLUORESCENCE EMISSION OF COMPLEXES OF LANTHANIDE PICRATES WITH *N,N'*-DIMETHYL-*N,N*-DIPHENYL-3,6-DIOXAOCTANEDIAMIDE

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SYNTHESIS, CRYSTAL STRUCTURE AND FLUORESCENCE EMISSION OF COMPLEXES OF LANTHANIDE PICRATES WITH *N,N′*-DIMETHYL-*N,N′*-DIPHENYL-3,6-DIOXAOCTANEDIAMIDE

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Lanthanide picrate complexes with the ligand *N,N′*-dimethyl-*N,N′*-diphenyl-3,6-dioxaoctanediamide (DDD) $[Ln(Pic)_3(DDD)]$ (Ln = La, Pr, Sm, Eu, Er, Y) have been prepared in nonaqueous medium and characterized by elemental analysis, conductivity measurements, IR, and ^1H NMR spectra. The Sm(III) complex $[Sm(Pic)_3(DDD)]\cdot\frac{1}{2}H_2O$ is triclinic, space group $P1$, with $a = 12.421(1)$ Å, $b = 13.081(2)$ Å, $c = 14.609(1)$ Å, $\alpha = 82.61(1)^\circ$, $\beta = 86.67(1)^\circ$, $\gamma = 86.83(1)^\circ$, $U = 2347.2(4)$ Å^3, $D_c = 1.698\ g\cdot cm^{-3}$ for $Z = 2$. The structure was refined to $R = 0.035$ based on 8727 observed reflections. The results reveal that DDD forms a ring-like structure with its four O atoms coordinating to the metal ions as a multidentate ligand, together with one O atom of the bidentate picrate. The Eu(III) complex shows strong emission when excited with 433 nm radiation in the solid state. The intensity ratio value $\eta(^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1)$ is 16.8.

Keywords: Lanthanide picrate; complex; X-ray structure; fluorescence

INTRODUCTION

Acyclic polyethers offer many advantages over the use of crown ethers in the extraction and analysis (ion-selective electrodes) of the rare earths.[1–5] *N,N,N′,N′*-tetraphenyl-3,6-dioxaoctanediamide (TDD) has the largest

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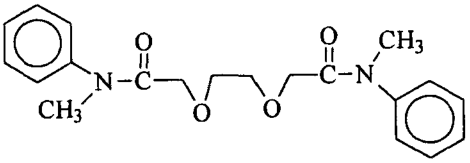
separation factor in five derivatives of glycol-*O*,*O*′-diacetamides, and both the factor and distribution ratio of lighter lanthanide ion for TDD are larger than those for dicyclohexyl-18-crown-6 ether,[6] if picrate is used as accompanying ion. In order to further investigate the effect of terminal group on the properties and structures, we have changed the terminal group (*N*,*N*′-diphenyl) of TDD to (*N*,*N*′-dimethyl), *i.e.*, *N*,*N*′-dimethyl-*N*,*N*′-diphenyl-3,6-dioxaoctanediamide (DDD). DDD was used as an active carrier for a calcium selective electrode,[7] and complexes of lanthanide picrates with DDD have never been reported. We report the synthesis, characterization and structure of complexes of lanthanide picrate with DDD. To our knowledge, most of the acyclic polyether complexes usually have weak luminescence, but the DDD complex of Eu(III) is observed to have strong emission in solid state.



N,*N*′-dimethyl-*N*,*N*′-diphenyl-3,6-dioxaoctanediamide (DDD).

EXPERIMENTAL

Reagents

The lanthanide picrates[8] and DDD[9] were prepared according to literature methods. All solvents used were purified by standard methods.

Chemical and Physical Measurements

The metal ion was determined by EDTA titration using xylenol orange as an indicator. C, N and H were determined using an Elementar vario EL. IR spectra were recorded on a Nicolet 170SX FT – IR instrument using KBr discs in the 220–4000 cm^{-1} region. Conductivity measurements were carried out with a DDS-11A conductivity bridge using 10^{-3} mol dm^{-3} solution in MeCN at 25°C. ^{1}H NMR spectra were measured on a Brucker AC 80 spectrometer in CD_3COCD_3 solutions with TMS as internal standard. Fluorescence spectra were obtained on a Hitachi M-850 fluorescence spectrophotometer.

Synthesis of [Ln(Pic)$_3$(DDD)]

A solution of 0.1 mmol DDD in 10 cm^3 of anhydrous ethanol was added dropwise to a solution of 0.1 mmol lanthanide picrates in 8 cm^3 of anhydrous ethanol. The mixture was stirred at room temperature for 4 h. The precipitated solid complex was filtered, washed with anhydrous ethanol and dried *in vacuo* over P_4O_{10} for 48 h. All the complexes were obtained as yellow powders. Analytical data and molar conductance values of the complexes in MeCN are given in Table I. The solid Sm(III) complex was recrystallized from MeCN by slow evaporation to give transparent yellow crystals of [Sm(Pic)$_3$(DDD)] $\cdot \frac{1}{2}H_2O$.

X-ray Structure Determination of [Sm(Pic)$_3$(DDD)] $\cdot \frac{1}{2}H_2O$

Crystal data: $C_{38}H_{31}N_{11}O_{25.5}Sm$, $Mr = 1200.09$, triclinic, space group $P1$, $a = 12.421(1)$ Å, $b = 13.081(2)$ Å, $c = 14.609(1)$ Å, $\alpha = 82.61(1)°$, $\beta = 86.67(1)°$, $\gamma = 86.83(1)°$, $U = 2347.2(4)$ Å^3, $Z = 2$, $D_c = 1.698$ g $\cdot$ cm^{-3}, $\lambda(\text{Mo}K\alpha) = 0.71073$ Å, $F(000) = 1204$, $\mu(\text{Mo}K\alpha) = 13.55$ cm^{-1}. Intensity data for a crystal $0.44 \times 0.34 \times 0.34$ mm were measured at 22°C on a P_4 four-circle diffractometer with graphite monochromatized Mo$K\alpha$ radiation, using a $\omega/2\theta$ scan. Lorentz and polarization corrections were applied, but no absorption correction was made.

The structure was solved by the Patterson method and subsequent difference Fourier techniques, and refined by block-matrix least-squares procedures. Non-hydrogen atoms were refined anisotropically. The weighting scheme was $\omega = 1/\{\sigma^2(F_0^2) + [0.0462(\max(F_0^2, 0) + 2F_0^2/3)]^2\}$, final $WR = 0.081$, $R = 0.035$. The highest peak in the final difference Fourier was 1.240 e Å^{-3}. All calculations were performed on an Eclipse/S 140 computer with the SHELXTL program. Final atomic coordinates are given in Table II. Tables of anisotropic thermal parameters, hydrogen atom

TABLE I Analytical data for the complexes

Complex	*Analysis* (%)^a				Λ_m (S cm^2 mol^{-1})
	C	*H*	*N*	*Ln*	
[La(Pic)$_3$(DDD)]	38.55(38.69)	2.49(2.56)	12.78(13.06)	11.86(11.77)	15.25
[Pr(Pic)$_3$(DDD)]	38.36(38.62)	2.25(2.56)	12.85(13.04)	11.84(11.92)	31.50
[Sm(Pic)$_3$(DDD)]	38.22(38.31)	2.50(2.54)	12.53(12.94)	12.69(12.63)	24.20
[Eu(Pic)$_3$(DDD)]	38.28(38.26)	2.53(2.54)	13.07(12.92)	12.70(12.74)	24.04
[Er(Pic)$_3$(DDD)]	37.73(37.78)	2.48(2.50)	12.65(12.76)	13.60(13.85)	32.59
[Y(Pic)$_3$(DDD)]	40.42(40.40)	2.70(2.68)	13.58(13.64)	7.61(7.87)	24.34

^{a}Calculated values in parentheses.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the complex. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq} ($Å^2$)	*Atom*	*x/a*	*y/b*	*z/c*	U_{eq} ($Å^2$)
Sm	2536(1)	2216(1)	1821(1)	34(1)	O26W	2846(13)	−1895(13)	−1034(12)	239(8)
O1	3525(2)	1438(2)	585(2)	46(1)	N1	4436(3)	1483(3)	−799(2)	50(1)
O2	3985(2)	3267(2)	859(2)	43(1)	N2	1791(3)	3226(3)	4655(2)	46(1)
O3	3483(2)	3572(2)	2583(2)	40(1)	N3	756(3)	3043(2)	78(2)	44(1)
O4	2056(2)	2383(2)	3401(2)	46(1)	N4	−2699(3)	4773(3)	747(3)	58(1)
O5	1532(2)	3833(2)	1678(2)	42(1)	N5	389(3)	5490(3)	2412(3)	52(1)
O6	1728(2)	2851(2)	199(2)	51(1)	N6	1045(3)	−120(3)	809(3)	55(1)
O7	317(3)	2750(3)	−561(2)	74(1)	N7	−2053(3)	−1484(3)	2643(3)	55(1)
O8	−3052(3)	4371(3)	122(3)	80(1)	N8	−904(3)	1873(3)	3134(3)	62(1)
O9	−3250(2)	5325(3)	1222(3)	80(1)	N9	4924(3)	904(3)	2847(2)	48(1)
O10	−182(3)	5754(4)	3045(3)	100(1)	N10	4953(3)	−2051(3)	5206(3)	61(1)
O11	1305(3)	5756(3)	2251(3)	83(1)	N11	1525(3)	−828(3)	3875(3)	64(1)
O12	820(2)	1658(2)	1791(2)	46(1)	C1	4797(4)	2584(4)	−2247(3)	60(1)
O13	1504(5)	571(4)	433(4)	168(3)	C2	5520(5)	3062(5)	−2899(4)	69(2)
O14	1240(4)	−947(3)	587(3)	120(2)	C3	6597(5)	2949(4)	−2784(4)	73(2)
O15	−1926(3)	−2247(3)	2248(3)	91(1)	C4	6968(5)	2355(5)	−2034(5)	82(2)
O16	−2792(2)	−1362(2)	3212(2)	69(1)	C5	6275(4)	1863(5)	−1370(4)	71(1)
O17	−1299(3)	1740(3)	3927(3)	93(1)	C6	5179(4)	1990(3)	−1486(3)	52(1)
O18	−626(4)	2696(3)	2801(3)	126(2)	C7	4002(6)	499(4)	−970(4)	70(2)
O19	2650(2)	544(2)	2626(2)	47(1)	C8	4136(3)	1880(3)	−30(3)	40(1)
O20	4460(2)	1580(2)	2321(2)	54(1)	C9	4577(4)	2887(3)	105(3)	50(1)
O21	5891(2)	896(3)	2931(3)	82(1)	C10	4609(4)	3973(4)	1265(3)	57(1)
O22	5894(3)	−1898(3)	5302(2)	72(1)	C11	3942(4)	4412(4)	1984(3)	59(1)
O23	4491(3)	−2789(3)	5605(3)	112(2)	C12	3007(3)	3919(3)	3401(3)	44(1)
O24	1199(3)	−1651(4)	3757(3)	101(1)	C13	2241(3)	3106(3)	3822(2)	39(1)
O25	949(3)	−83(3)	3987(4)	112(2)	C14	1034(5)	2459(5)	5107(4)	70(2)
C15	2026(3)	4070(3)	5139(3)	45(1)	C27	157(3)	946(3)	1966(2)	36(1)
C16	1515(4)	5031(4)	4919(3)	61(1)	C28	220(3)	18(3)	1538(3)	39(1)
C17	1762(5)	5836(4)	5385(4)	75(2)	C29	−479(3)	−771(3)	1759(3)	44(1)
C18	2473(5)	5678(4)	6066(4)	74(2)	C30	−1299(3)	−666(3)	2422(3)	42(1)
C19	2956(4)	4727(4)	6299(4)	68(1)	C31	−1432(3)	198(3)	2868(3)	44(1)
C20	2740(4)	3917(4)	5827(3)	54(1)	C32	−731(3)	980(3)	2631(3)	41(1)
C21	615(3)	4113(3)	1380(2)	36(1)	C33	3190(3)	32(3)	3258(3)	40(1)
C22	121(3)	3697(3)	659(2)	38(1)	C34	4309(3)	99(3)	3384(3)	41(1)
C23	−945(3)	3908(3)	456(3)	44(1)	C35	4877(3)	−565(3)	4021(3)	45(1)
C24	−1564(3)	4575(3)	936(3)	44(1)	C36	4342(3)	−1321(3)	4570(3)	47(1)
C25	−1127(3)	5086(3)	1592(3)	43(1)	C37	3235(4)	−1411(3)	4524(3)	50(1)
C26	−69(3)	4890(3)	1768(2)	37(1)	C38	2696(3)	−746(3)	3906(3)	45(1)

coordinates and structure factors are available as supplementary data from W.L. upon request.

RESULTS AND DISCUSSION

Analytical data for the complexes conform to a 1 : 3 : 1 metal to picrate to DDD stoichiometry, Ln(Pic)$_3$(DDD) (see Table I). All complexes are soluble in DMSO, DMF, MeCN, acetone and THF, slightly soluble in MeOH and AcOEt, and sparingly soluble in benzene, Et_2O and cyclohexane. The molar conductance values of the complexes in MeCN (Table I) indicate that all complexes act as non-electrolytes,[10] implying that all the picrate groups are in the coordination sphere.

IR Spectra

The IR spectrum of free DDD shows bands at 1679 and 1104 cm^{-1} which may be assigned to ν(C=O) and ν(C–O–C), respectively. In the IR spectra of La(III), Eu(III) and Er(III) complexes, the two bands shift by *ca* 55 and 20 cm^{-1} towards lower wave numbers, thus indicating that all the C=O and ether O atoms take part in coordination to the metal ions. The larger shift for ν(C=O) in the spectra of the complexes suggests that the Ln–O(carbonyl) bond is stronger than Ln–O(ether).[11] These results are consistent with the ^{1}H NMR and the crystal structure determination.

The OH out-of-plane bending vibration of free Hpic at 1151 cm^{-1} disappears in the spectra of the complexes,[11] indicating that the H-atom of the OH group is replaced by Ln(III). The ν(C–O) vibration at 1265 cm^{-1} is shifted towards higher frequency by *ca* 8 cm^{-1} in the complexes. This is due to the following two effects. First, the hydrogen atom of the OH group is replaced by Ln(III), increasing the π-bond character of the C–O bond. Secondly, coordination of the oxygen atom of O–C (Pic^-) to Ln(III) causes the π-character to be weakened. Free Hpic has $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ at 1555 and 1342 cm^{-1}, respectively, which splits into two bands at *ca* 1588, 1540 cm^{-1}, and *ca* 1360, 1326 cm^{-1}, respectively, in the complexes. This indicates that some of the nitronyl O atoms take part in coordination.[12]

^{1}H NMR Spectra

The spectrum of the ligand exhibits an unresolved multiplet at 7.39 ppm and three singlets at 3.66, 3.48 and 3.20 ppm assigned to Ph, $-C(O)CH_2-$, $-C_2H_4-$, and $-CH_3$ protons, respectively. In the ^{1}H NMR of the $La(Pic)_3(DDD)$ and $Y(Pic)_3(DDD)$, the proton signals move to lower field; the signals of the $-C(O)CH_2-$, $-C_2H_4-$ and $-CH_3$ protons shift by 0.8, 0.5 and 0.2 ppm, respectively. The larger shift for $-C(O)CH_2-$ protons than $-C_2H_4-$ indicates the Ln–O (C=O) bond to be stronger than the Ln–O (C–O–C) one.[11]

The ^{1}H signal of OH group in free Hpic disappears in the complexes, indicating that the H atom of the OH group is replaced by Ln(III). The benzene ring protons of the free Hpic exhibit a singlet at 9.12 ppm. Upon coordination, the signal moves to higher field. Only one singlet is observed for the benzene ring protons of the three coordinated picrate groups, indicating fast exchange among the groups in solution.[13]

Electronic Fluorescence

Only the Eu(III) complex shows strong emission when excited with 433 nm radiation in the solid state. The emission spectrum data for the complex are reported in Table III. Fluorescence arises from ligand-to-cation energy transfer, mainly from the lowest resonance level. The most intense transition is $^5D_0 \rightarrow {}^7F_2$ at 615 nm, followed by $^5D_0 \rightarrow {}^7F_4$ at 698 nm, then is $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_3$. A weak line appears at 579 nm arising from the $^5D_0 \rightarrow {}^7F_0$. The intensity ratio value $\eta(^5D_0 \rightarrow {}^7F_2/^5D_0 \rightarrow {}^7F_1)$ is 16.8, indicating a rather low symmetry for the electrostatic field surrounding Eu(III).[14] This conclusion corresponds with the crystal structure of the Sm(III) complex.

Crystal Structure of [Sm(Pic)$_3$(DDD)]$\cdot\frac{1}{2}H_2O$

The structure of [Sm(Pic)$_3$(DDD)]$\cdot\frac{1}{2}H_2O$ is shown in Figure 1. Figure 2 shows the molecular packing arrangement in the unit cell. Selected bond distances and angles are given in Table IV.

The crystal structure is composed of [Sm(Pic)$_3$(DDD)] and one half of a H_2O molecule linked by weak van der Waals' forces. The Sm(III) ion is 9-coordinated by four oxygen atoms of DDD and five oxygen atoms of two bidentate and one unidentate picrates. The coordination polyhedron is a tricapped trigonal prism. The DDD molecule wraps around the metal ion with its oxygen atoms and forms a ring-like coordination structure together with the bidentate picrate [O(19)] situated at the open side of the DDD chain (Figure 3). The four oxygen atoms of DDD [O(1), O(2), O(3), O(4)] are not quite coplanar, their deviation from the mean plane being the range 0.1–0.2 Å. The mean absolute deviation is 0.154 Å. The Sm atom lies out

TABLE III Electronic fluorescence data for the Eu(III) complex

Electron transition	*Peak* (nm)	*Relative intensity*
$^5D_0 \rightarrow {}^7F_0$	579	1.086
$^5D_0 \rightarrow {}^7F_1$	590	3.712
$^5D_0 \rightarrow {}^7F_2$	615	62.28
$^5D_0 \rightarrow {}^7F_3$	653	2.364
$^5D_0 \rightarrow {}^7F_4$	698	7.785

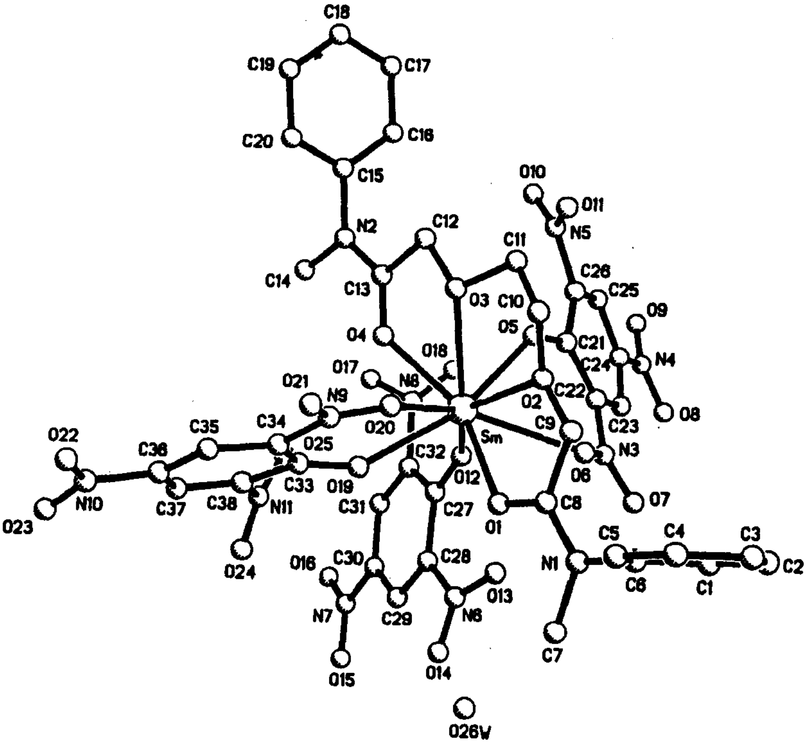


FIGURE 1 Molecular structure of $[Sm(Pic)_3(DDD)]\cdot\frac{1}{2}H_2O$, showing the atom labelling scheme.

of this plane by 0.512 Å. Obviously DDD is distorted to some extent in order to maintain the Sm–O distances at suitable lengths for coordination.

The average distance between the samarium atom and the coordinated oxygen atom is 2.470 Å, where Sm–O(12) is the shortest, probably due to the higher electron density on the oxygen anion of the picrate. Sm–O [phenolic, O(19,5)] distances are shorter than Sm–O [nitro, O(20,6)] in the bidentate picrate. Sm–O (C=O) distances (mean 2.405 Å) are significantly shorter than Sm–O (C–O–C) (mean 2.574 Å). This suggests that the Sm–O (C=O) bond is stronger than Sm–O (C–O–C), in agreement with the IR data.

The structural results show that DDD acts as a multidentate ligand forming a ring-like coordination structure. Because of its superior flexibility, DDD exhibits a stable conformation that provides a cavity. The internal cavity formed by the coordinating oxygen atoms is suited for the uptake of a cation, while the nonpolar groups (CH_2 groups, aliphatic rings) form a lipophilic shell around the coordination sphere. The DDD molecule therefore

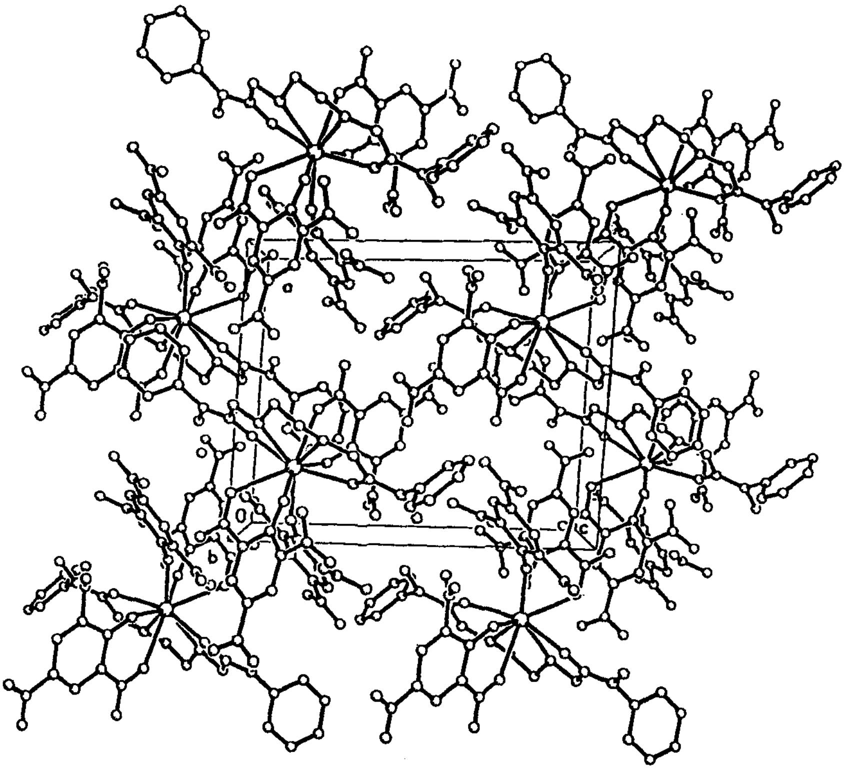


FIGURE 2 Unit cell contents for $[Sm(Pic)_3(DDD)]\cdot\frac{1}{2}H_2O$.

TABLE IV Selected bond lengths (Å) and angles (deg) for $[Sm(Pic)_3(DDD)]\cdot\frac{1}{2}H_2O$

Sm–O1	2.425(3)	Sm–O6	2.643(3)
Sm–O2	2.567(2)	Sm–O12	2.295(2)
Sm–O3	2.581(2)	Sm–O19	2.347(2)
Sm–O4	2.385(2)	Sm–O20	2.602(3)
Sm–O5	2.387(2)		
Mean lengths			
Sm–O (C–O,Pic)	2.343	Sm–O (NO_2,Pic)	2.623
Sm–O (C=O,DDD)	2.405	Sm–O (C–O–C,DDD)	2.574
O1–Sm–O2	62.06(8)	O2–Sm–O3	61.55(7)
O3–Sm–O4	61.98(8)	O4–Sm–O5	78.83(9)
O1–Sm–O5	126.47(9)		

shows high coordination ability and lipophilicity, both of which make it a useful component sensor for Ca^{2+}. Furthermore, it can be shown experimentally that the structures and properties of the open-chain crown ethers complexes are closely related to the counter anion, the number of

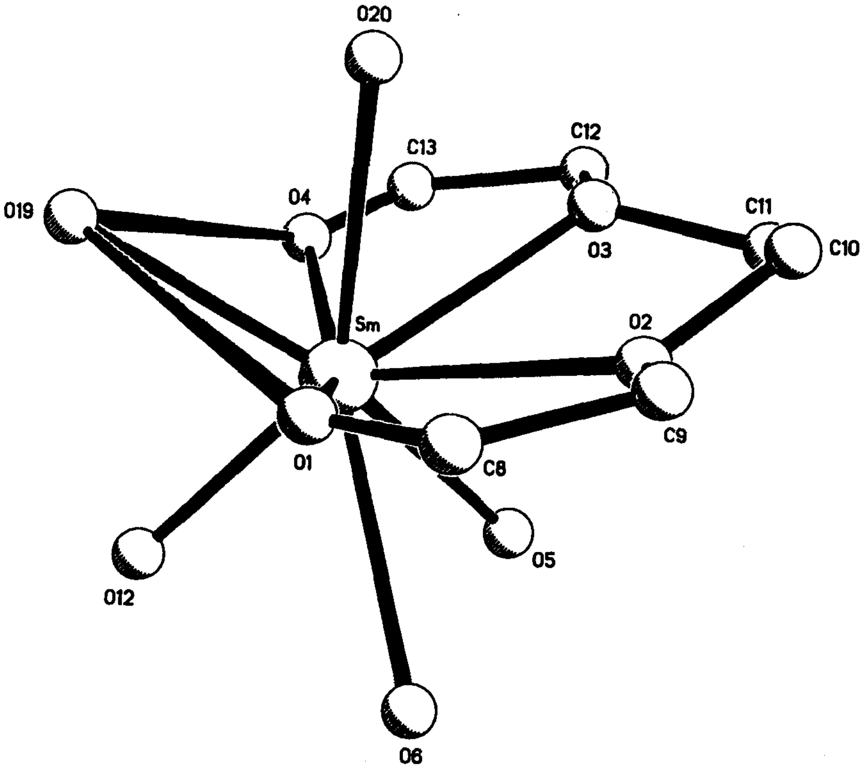


FIGURE 3 The ring-like coordination structure of [Sm(Pic)$_3$DDD]$\cdot\frac{1}{2}$H$_2$O.

(–CH$_2$–O–CH$_2$–) units and terminal group effects.[15,16] A further study concerned with these will be reported in following communications.

Acknowledgments

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