Lanthanide Tetramethoxyborate Complexes Isolated from Reductive Amination of 2,6-Diformyl-*p*-cresol

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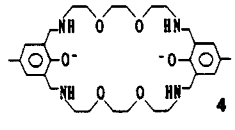
Treatment of a hot methanolic solution of 2,6-diformyl-*p*-cresol (1 mmol), 3,6-dioxa-1,8-octanediamine (2 mmol), and a lanthanide(III) nitrate (1 mmol) with sodium cyanotrihydroborate (1.5 mmol) unexpectedly yields a mixture of isostructural but totally different compounds, $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$, and an asymmetric Schiff base complex, $Ln_2\mathbf{5}(NO_3)_4 \cdot 1.2CH_3OH$. The lanthanum complex of the $B(OCH_3)_4^-$ anion crystallizes in the monoclinic system, *C*2/*c*, with $a = 16.50(6)$ Å, $b = 6.5(2)$ Å, $c = 15.84(6)$ Å, $\beta = 106.8(1)°$, $V = 1621(2)$ Å^3, and $Z = 4$. With 1566 unique and 1374 observed ($I > 3\sigma(I)$) data and 101 variables, $R = 0.017$ and $R_w = 0.025$. The structure features an assembly of $[La(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]_n$ chains in which La^{3+} ions are bridged by bidentate $B(OCH_3)_4^-$ anions which are distorted noticeably from T_d symmetry. The shortest La–O distances in the C_{2v} 10-fold 4A,6B-extended dodecahedral coordination polyhedron (two bidentate NO_3^-, two methanol molecules, and two bidentate $B(OCH_3)_4^-$) involve the two $B(OCH_3)_4^-$ anions. The $B(OCH_3)_4^-$ anions form strong bonds with Ln^{3+} cations and can achieve the geometrical distortions required for constituting the irregular Ln^{3+} coordination polyhedra. As good competitors for Ln^{3+} cations, $B(OCH_3)_4^-$ anions can be expected to have destabilizing effects on Schiff base chelates which depend on coordination to Ln^{3+} cations to achieve stability. The structure of the $Pr_2\mathbf{5}(NO_3)_4 \cdot 1.2CH_3OH$ complex is reported elsewhere.

Introduction

Dinuclear Schiff base lanthanide(III) (Ln^{3+}) complexes $Ln_2X(NO_3)_4 \cdot nH_2O$ (X = **1**,[1] **2**,[2] **3**[3]) are readily precipitated from boiling methanolic solutions of lanthanide nitrates and suitable polyamine and diformylphenolic precursors. Although these dinuclear complexes have interesting spectroscopic properties,[4–6] their utility in further syntheses, solution studies,[7,8] and potential applications in extractive metallurgy,[9,10] as well as luminescent[11] and paramagnetic[12,13] diagnostics, is severely limited by the lability of the C═N bond. Reduction of organic imine functionalities with sodium cyanotrihydroborate or tetrahydroborate is quite easily achieved;[14] however, when the imine is complexed to metal ions, the process is very complicated.[15,16]

1. Y = O, Z = CH_3
2. Y = NH, Z = CH_3
3. Y = O, Z = Cl

An interesting display of this complexity is revealed in the reductive amination of 3,6-dioxa-1,8-octanediamine and 2,6-diformyl-*p*-cresol with sodium cyanotrihydroborate in the presence of lanthanide(III) nitrates. The products are either pure dinuclear complexes of the tetraazamacrocycle **4** ($Ln_2\mathbf{4}(NO_3)_4$) or an unexpected mixture of interesting lanthanide(III) complexes of tetramethoxyborate anions ($B(OCH_3)_4^-$), $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$, and an asymmetric Schiff base macrocycle **5**, $Ln_2\mathbf{5}(NO_3)_4 \cdot 1.2CH_3OH$.



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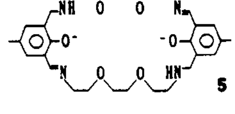

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The crystal morphologies of the complexes of **4**, **5**, and $B(OCH_3)_4^-$ are similar, but those of $[Ln_2(B(OCH_3)_4(NO_3)_2(CH_3OH)_2]$ are better formed and were frequently selected from their

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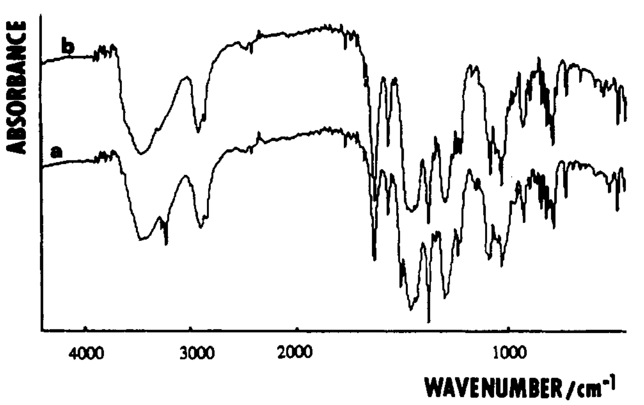

Figure 1. Similarity between the FT-IR spectra of (a) the sample from which the crystal of $Pr(B(OCH_3)_4(NO_3)_2(CH_3OH)_2$ was obtained and (b) pure crystalline Pr_2**5**$(NO_3)_4 \cdot 1.2CH_3OH$ parallelopipeda (see text).

mixture with Ln_2**5**$(NO_3)_4 \cdot 1.2CH_3OH$ for single-crystal X-ray diffraction studies. The synthesis of pure well-formed crystals of Ln_2**5**$(NO_3)_4 \cdot 1.2CH_3OH$ was subsequently accomplished by a different procedure,[17] and it was found that both Ln_2**5**$(NO_3)_4 \cdot 1.2CH_3OH$ and $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ crystallize in the monoclinic system, space group $C2/c$. The BO_4 group in $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$, which is part of the 10-fold coordination polyhedron of the La^{3+} ion, shows large distortions from T_d geometry. The ability to undergo such distortions underscores the increasing importance of boron as a versatile building block of novel ligands incorporating coordination features of potential significance to the ceramic precursor industry,[18] electron-transfer studies,[19] pharmaceuticals,[20] sensitized luminophores,[21] and other areas.[22]

We report herein the preparation of the mixture of Ln_2**5**$(NO_3)_4 \cdot 1.2CH_3OH$ with $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ and the crystal structure of the $[La(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ complex, which reveal the diversity of possibile metal ion mediated reactions in reductive amination processes. Spectroscopic and structural details of complexes of **4** and **5** are given in a separate report.[17]

Experimental Details

Materials. 2,6-Diformyl-*p*-cresol was prepared as described previously;[1,2] 3,6-dioxa-1,8-octanediamine was a gift from Texaco Chemicals Co.; lanthanide nitrates were obtained by neutralizing 99.9% or 99.99% pure lanthanide sesquioxides from Aldrich, followed by evaporation of water to near dryness; and sodium cyanotrihydroborate was of 95% purity from Aldrich.

Synthesis. The crystalline mixture from which crystals of $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ suitable for X-ray diffraction were isolated was obtained in the following reductive amination process. The imine selective reductant, sodium cyanotrihydroborate, was slowly introduced into a warm methanolic solution into which 1 mmol of lanthanide(III) nitrate, 1 mmol of 2,6-diformyl-*p*-cresol, and 2 mmol of 3,6-dioxa-1,8-octanediamine had been dissolved in that order. These mole ratios represent optimal conditions for the formation of Schiff bases[2] **1**–**3**. The resulting solution was refluxed overnight, and the crystalline product was filtered hot. Crystals of the praseodymium(III) and neodymium(III) complexes were obtained in a similar procedure. Although optical microscopy shows crystals of uniform morphology, carbon–hydrogen–nitrogen analyses of several samples suggest that these products are mixtures. This is confirmed by infrared spectroscopy of one of those mixtures which shows the presence of secondary N–H, C=N, and phenolic C–O absorptions like those of the pure isostructural Ln_2**5**$(NO_3)_4 \cdot 1.2CH_3OH$ crystals (Figure 1). The synthesis of Ln_2**5**$(NO_3)_4 \cdot 1.2CH_3OH$ in pure form was accomplished by a different procedure.[17] Attempts to prepare pure $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ complexes from methanolic solutions of sodium cyanotrihydroborate or sodium tetrahydroborate with lanthanide(III) nitrates were not successful. Further when the reductive amination procedure yielded Ln_2**4**$(NO_3)_4$ complexes, the tetramethoxyborate complex was not obtained.

Table I. Crystallographic Data for the $[La(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ Complex

formula	$BC_6H_{20}N_2O_{12}La$	D_{obs}/D_{calc}, g·cm^{-3}	1.93/2.07
cryst system	monoclinic	no. of unique data	1566
space group	$C2/c$	no. of obsd data ($I \geq 3\sigma(I)$)	1374
a, Å	16.50(6)	final shift/esd in final cycle	0.09
b, Å	6.5(2)	no. of variables	101
c, Å	15.84(6)	R^a	0.017
β, deg	106.8(1)	$R_w{}^b$	0.025
V, Å^3	1621(2)	GOF^c	0.99
Z	4		

[a] $R = \sum|F_o - |F_c|| / \sum F_o$. [b] $R_w = [\sum w(F_o - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ with $w = 1/(\sigma_F)^2$, where $\sigma_F = \sigma(F^2)/2F$; $\sigma(F^2) = [(\sigma_1)^2 + (0.04F^2)^2]^{1/2}$. [c] GOF $= [\sum w(F_o - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o and N_v are, respectively, the number of observations and variables.

Table II. Positional Parameters (Esd's) for $La(NO_3)_2(B(OCH_3)_4)(CH_3OH)_2$

atom	x	y	z	B_{eq} (Å^2)^a
La	0.000	0.47360(3)	0.250	1.501(4)
O(1)	0.06811(9)	0.1223(3)	0.2540(1)	2.34(3)
O(2)	0.1297(1)	0.4627(3)	0.3912(1)	3.09(5)
O(3)	0.0347(1)	0.4251(4)	0.0993(1)	2.86(4)
O(4)	0.1523(2)	0.5069(4)	0.0742(2)	5.97(9)
O(5)	0.1391(1)	0.5351(3)	0.2050(1)	2.86(4)
O(6)	0.0170(1)	0.8288(3)	0.3231(1)	2.42(3)
N(1)	0.1095(2)	0.4895(3)	0.1248(2)	2.73(5)
C(1)	0.1497(2)	0.0440(5)	0.2594(4)	5.9(1)
C(2)	0.2171(3)	0.4973(6)	0.4082(3)	4.9(1)
C(3)	0.0345(3)	0.9101(6)	0.4096(2)	4.93(8)
B	0.000	−0.0247(5)	0.250	2.03(8)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

It is therefore concluded that the products as synthesized are mixtures of two different but isostructural complexes, Ln_2**5**$(NO_3)_4 \cdot 1.2CH_3OH$ and $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ (Ln = La, Pr, Nd) and the formation of the tetramethoxyborate complex appears to be dependent on the simultaneous formation of the complex of **5**. Preparation of similar complexes of **5** and $B(OCH_3)_4^-$ with the smaller lanthanide(III) ions, Eu^{3+} and Sm^{3+}, was attempted but without success.

Crystal Structure Determination. A colorless crystal of the $[La(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ complex, measuring 0.15 × 0.20 × 0.25 mm, was picked from a crystalline sample obtained from the above preparation and mounted on a thin glass fiber and coated with epoxy cement. Details of unit cell determination, crystal orientation, and data collection on the CAD4 diffractometer were reported previously.[22] Those special to this determination are in Table S1 (supplementary material). Data were corrected for Lorentz and polarization effects and for absorption using ψ scans on several reflections near $\chi = 90$. Only statistical variations in the intensities of three monitored reflections were observed. Complex neutral-atom scattering factors were used.[23] The position of the La atom was located from an origin-removed Patterson function. Remaining non-hydrogen atoms were located from successive cycles of full-matrix least-

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Table III. Selected Bond Distances (Å) and Interbond Angles (deg) with Esd's in Parentheses

La–O(1)	2.431(2)	O(2)–C(2)	1.406(5)
La–O(2)	2.611(2)	O(3)–N(1)	1.254(4)
La–O(3)	2.631(2)	O(4)–N(1)	1.218(4)
La–O(5)	2.622(2)	O(5)–N(1)	1.257(4)
La–O(6)	2.556(2)	O(6)–C(3)	1.418(3)
O(1)–C(1)	1.418(4)	O(6)–B	1.461(3)
O(1)–B	1.461(3)		

O(1)–La–O(1)′	51.85(7)	O(3)–La–O(6)′	73.76(6)
O(1)–La–O(2)	72.94(6)	O(5)–La–O(5)′	162.51(9)
O(1)–La–O(2)′	104.16(6)	O(5)–La–O(6)	89.80(6)
O(1)–La–O(3)	72.75(6)	O(5)–La–O(6)′	74.31(6)
O(1)–La–O(3)′	94.67(6)	O(6)–La–O(6)′	51.50(7)
O(1)–La–O(5)	74.14(6)	La–O(1)–C(1)	136.9(2)
O(1)–La–O(5)′	123.15(6)	La–O(1)–B	104.8(1)
O(1)–La–O(6)	144.01(5)	C(1)–O(1)–B	118.3(2)
O(1)–La–O(6)′	144.19(5)	La–O(2)–C(2)	134.4(2)
O(1)–La–O(2)′	176.89(9)	La–O(3)–N(1)	96.9(2)
O(2)–La–O(3)	115.80(7)	La–O(5)–N(1)	97.2(2)
O(2)–La–O(3)′	63.79(7)	La–O(6)–C(3)	137.5(2)
O(2)–La–O(5)	70.92(7)	La–O(6)–B	104.8(1)
O(2)–La–O(5)′	109.58(7)	C(3)–O(6)–B	117.6(2)
O(2)–La–O(6)	71.38(6)	O(3)–N(1)–O(4)	121.5(3)
O(2)–La–O(6)′	111.59(6)	O(3)–N(1)–O(5)	117.5(3)
O(3)–La–O(3)′	166.3(1)	O(4)–N(1)–O(5)	121.0(3)
O(3)–La–O(5)	48.24(7)	O(1)–B–O(1)′	98.5(3)
O(3)–La–O(5)′	134.62(7)	O(1)–B–O(6)	114.9(1)
O(3)–La–O(6)	119.67(6)	O(1)–B–O(6)′	115.3(1)

squares refinement and difference Fourier syntheses. At the end of the refinement reasonable positions were seen for the H atoms, and these were included as fixed contributions in idealized positions with isotropic thermal parameters 1.2 times those of the attached carbon atoms and updated periodically. The final difference map was essentially featureless. Final positional parameters for the non-hydrogen atoms are given in Table II. Additional crystallographic data are provided as supplementary material (Tables S1–S5).

The preparation of the mixture of $Pr_2\mathbf{5}(NO_3)_4\cdot 1.2CH_3OH$ and $[Pr(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]$ was also indicated by IR studies and an X-ray diffraction investigation in which a crystal pulled from the mixture, like the lanthanum complex described above, was found to be monoclinic with $\beta \approx 107°$.

Results and Discussion

The formation of the $Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2$ complexes was confirmed by single-crystal X-ray crystallography. Vital crystal data are given in Table I, and selected bond distances and angles are given in Table III. Figure 2 depicts the coordination around one La atom, while Figure 3 shows the polymeric chain nature of the representative $[La(B(OCH_3)_2)(NO_3)_4(CH_3OH)_2]_n$ assembly which is parallel to the *b*-axis of the monoclinic cell.

The 10-fold coordination of the La^{3+} cation is constituted by two bidentate NO_3^- and two $B(OCH_3)_4^-$ anions, which are also bidentate, and two methanol molecules. The LaO_{10} polyhedron is of low symmetry and is best described as a distorted 4A,6B-extended dodecahedron of nearly C_{2v} symmetry.[26] The *a* and *a*′ edges[26] are constituted by O(1) and O(1)′ and O(6) and O(6)′, respectively. The 2-fold axis bisects *a* and *a*′, while the vertical planes are along these edges. The La–O distances are in the range[26] usually observed for decacoordinated La^{3+}. The shortest La–O contacts involve the O(1) and O(6) atoms of $B(OCH_3)_4^-$ anions, which suggests that interactions between the La^{3+} cations and the $B(OCH_3)_4^-$ anions are strong. Although B–O bond distances are normal and equivalent, bond angles within the BO_4 unit (Table III) show a noticeable deviation from tetrahedral geometry.[27] Such distortions are generally essential to accommodate the large and often irregular Ln^{3+} coordination polyhedra.[26] The $B(OCH_3)_4^-$ anion is thus a good competitor for Ln^{3+} cations and might also be able to form complexes with higher $B(OCH_3)_4^-$ to Ln^{3+} ratios. When the stability of the Schiff base chelate is dependent on coordination to the Ln^{3+} cations,[28] abstraction of the Ln^{3+} species by $B(OCH_3)_4^-$ anions could trigger disintegration or polymerization processes, thereby leading to undesirable final reduction products. The linear chain structure of $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2]_n$ (Figure 3) is interesting in terms of the migration and transfer of electronic excitation energy.[29]

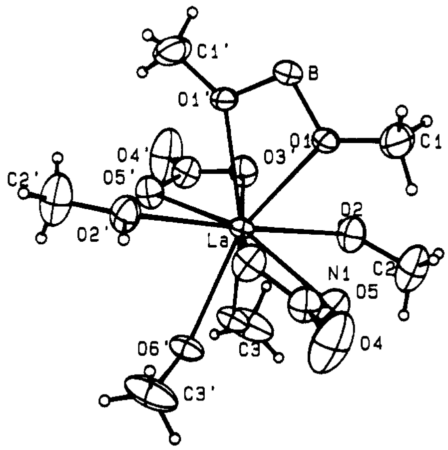

Figure 2. Perspective view of the coordination about La in $La(B(OCH_3)_4(NO_3)_2(CH_3OH)_2$. Thermal ellipsoids are drawn at the 50% probability level with those for hydrogen set arbitrarily small for clarity. The primed atoms are related to the unprimed atoms by the crystallographic 2-fold axis.

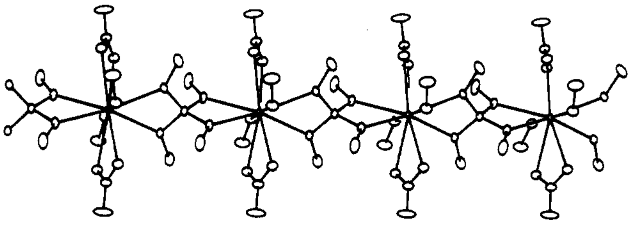

Figure 3. View of a portion of one of the $[La(B(OCH_3)_4(NO_3)_2(CH_3OH)_2]_n$ chains showing the bridging nature of the $B(OCH_3)_4^-$ anions.

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Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, root-mean-square amplitude displacement values, and calculated hydrogen positions (5 pages). Ordering information is given on any current masthead page.

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