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Macrocyclic Complexes of Lead(II): Crystal Structures of LPb(ClO_4)$_2$ and LPb(NO_3)$_2$ (L = 1,4,7-Triazacyclononane)

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The reactions of Pb(ClO_4)$_2$ and Pb(NO_3)$_2$ in aqueous solution with equimolar amounts of the cyclic amine 1,4,7-triazacyclononane ($C_6H_{15}N_3$ = L) yielded colorless crystals of LPb(ClO_4)$_2$ (**1**) and LPb(NO_3)$_2$ (**2**), respectively. Their structures were determined by X-ray crystallography. Crystal data: **1**, monoclinic, $P2_1/c$, a = 7.963 (3) Å, b = 14.534 (7) Å, c = 11.699 (4) Å, β = 91.06 (3)°, Z = 4, Mo Kα, 1540 observed ($I > 2.5\sigma(I)$) data (−75 °C), R = 0.033; **2**, orthorhombic, $Pcab$, a = 11.467 (4) Å, b = 13.479 (7) Å, c = 15.793 (8) Å, Z = 8, Mo Kα, 1859 observed ($I > 2.5\sigma(I)$) data (22 °C), R = 0.057. Both crystals contain LPb^{2+} cations with an average Pb–N bond length of 2.44 Å and N–Pb–N angle of 71°. The coordination spheres of Pb(II) are completed by three oxygen atoms at close contact (≤3.0 Å) in **1** and **2**, respectively, to give highly irregular polyhedra. The inert valence electron pair of Pb^{2+} appears to be stereochemically active.

Introduction

The coordination chemistry of lead(II) with macrocylic ligands has been investigated in the past decade, although not extensively. A number of single-crystal X-ray determinations have been reported of such complexes with saturated 14-membered and 16-membered tetraaza macrocyclic ligands[2,3] and some large cryptates.[4,5] In general, the stability constants of such complexes of lead(II) are rather large in aqueous or methanolic solution due to large cavities created by these ligands, which are suitable for coordinating large lead(II) cations. The coordination number of the Pb^{2+} centers usually exceeds 6 and coordination numbers of 8, 9, and 10 with very irregular coordination polyhedra appear to be quite common. The Pb–N and Pb–O bond lengths are rather long, exceeding in some cases the sum of the ionic radii, and are only slightly covalent.

We here wish to report the preparation and X-ray structures of two complexes of lead(II) containing the small tridentate cyclic amine 1,4,7-triazacyclononane (L), namely PbL(ClO_4)$_2$ (**1**) and PbL(NO_3)$_2$ (**2**). This ligand is known to form very stable 1:1 and 2:1 complexes with many transition metals. The stability constant for the formation of a 1:1 complex of this ligand with lead(II) has been measured in aqueous solution (log K = 10.3 at 25 °C).[6]

Experimental Section

The ligand 1,4,7-triazacyclononane (L) was prepared as described in the literature.[7]

Preparation of PbL(ClO_4)$_2$ (1) and PbL(NO_3)$_2$ (2). An aqueous solution (50 mL) of 1,4,7-triazacyclononane (1 mmol), Pb(NO_3)$_2$ (1 mmol), and 8 g of sodium perchlorate (sodium nitrate, respectively) was heated with stirring to 60 °C. Sodium hydroxide (2 M) was added dropwise until a clear, colorless solution was obtained. After the mixture was allowed to stand for 2–3 days in the refrigerator, colorless crystals of the desired product precipitated, which were filtered off, and washed with ethanol and ether, and air-dried (yield 80–90%).

Anal. Calcd for $C_6H_{15}N_3O_8Cl_2Pb$ (**1**): C, 13.46; H, 2.82; N, 7.85; ClO_4, 37.16. Found: C, 13.7; H, 2.8; N, 7.8; ClO_4, 37.0. Calcd for $C_6H_{15}N_5O_6Pb$ (**2**): C, 15.65; H, 3.28; N, 15.21. Found: C, 15.6; H, 3.4; N, 15.1.

X-ray Structural Determinations. A colorless crystal of **1** and **2**, respectively, was attached to the end of a glass fiber and mounted on a Syntex diffractometer. Unit cell dimensions of **1** at −75 °C and **2** at 22 °C were obtained by least-squares fits of the setting angles of 30 reflections, respectively. The data are summarized in Table I. Intensity data were corrected for Lorentz and polarization effects in the usual manner; an empirical absorption correction was carried out in both cases.[8]

Table I. Crystallographic Data

formula	Pb($C_6H_9N_3$)(ClO_4)$_2$ (**1**)	Pb($C_6H_9N_3$)(NO_3)$_2$ (**2**)
fw	535.3	460.4
space group	$P2_1/c$	$Pcab$
a, Å	7.963 (3)	11.467 (4)
b, Å	14.534 (7)	13.479 (7)
c, Å	11.699 (4)	15.793 (8)
β, deg	91.06 (3)	90.00
V, Å^3	1353.6	2441.0
Z	4	8
d_{calcd}, g/cm^3	2.63	2.51
cryst size, mm^3	0.2 × 0.33 × 0.42	0.3 × 0.4 × 0.4
μ(Mo Kα), cm^{-1}	127.2	133.2
range of transmission factors	0.18–0.42	0.25–0.57
data collcn instrum	Syntex R3	Syntex R3
radiation (graphite monochromated)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
temp, °C	−75	22
scan method	ω	θ–2θ
data collcn range (2θ), deg	1–45	3–70
no. of reflcns measd	1773	1876
no. of unique data ($I > 2.5\sigma(I)$)	1540	1859
octant	$\pm h,k,l$	h,k,l
no. of params refined	151	163
R	0.033	0.057
R_w	0.043	0.049

Table II. Atomic Coordinates for LPb(ClO_4)$_2$

atom	x/a	y/b	z/c
Pb1	0.04683 (6)	0.86588 (3)	0.24187 (4)
Cl1	0.2065 (4)	0.5709 (2)	0.2941 (3)
Cl2	0.1313 (4)	0.2266 (2)	0.5025 (3)
O1	0.096 (1)	0.6398 (7)	0.2470 (9)
O2	0.270 (1)	0.5161 (8)	0.2050 (9)
O3	0.116 (1)	0.5132 (7)	0.3716 (8)
O4	0.341 (1)	0.6135 (6)	0.3576 (8)
O5	0.229 (1)	0.2594 (8)	0.598 (1)
O6	0.082 (1)	0.1334 (7)	0.5233 (8)
O7	−0.017 (2)	0.2812 (8)	0.488 (1)
O8	0.229 (1)	0.2296 (8)	0.4029 (9)
N1	0.191 (1)	0.9969 (8)	0.3260 (9)
C1	0.289 (2)	0.961 (1)	0.426 (1)
C2	0.389 (2)	0.882 (1)	0.403 (2)
N2	0.315 (1)	0.8139 (7)	0.323 (1)
C3	0.422 (2)	0.796 (1)	0.222 (1)
C4	0.428 (2)	0.870 (1)	0.135 (2)
N3	0.266 (1)	0.9130 (8)	0.1154 (9)
C5	0.283 (2)	1.016 (1)	0.127 (2)
C6	0.292 (2)	1.048 (1)	0.243 (1)

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Table III. Selected Bond Distances (Å) and Angles (deg) of $LPb(ClO_4)_2$

Pb–N1	2.42 (1)	N1–C1	1.49 (2)
Pb–N2	2.44 (1)	N1–C6	1.48 (2)
Pb–N3	2.41 (1)	C1–C2	1.43 (2)
N3–C4	1.45 (1)	N2–C2	1.48 (2)
N3–C5	1.51 (2)	N2–C3	1.49 (2)
C5–C6	1.43 (2)	C3–C4	1.48 (3)
Pb–O3′	2.82 (1)	Pb–O1	3.31 (1)
Pb–O6′	2.95 (1)	Pb–O2′	3.40 (1)
Pb–O7′	2.96 (1)	Pb–O5′	3.44 (1)
Pb–O8′	3.37 (2)		
N1–Pb–O3′	78.8 (4)	N2–Pb–O3′	144.1 (6)
N1–Pb–O6′	77.9 (4)	N2–Pb–O6′	87.4 (4)
N1–Pb–O7′	136.4 (6)	N2–Pb–O7′	106.3 (6)
N3–Pb–O6′	147.1 (6)	O6′–Pb–O3′	105.7 (6)
N3–Pb–O3′	80.1 (4)	O6′–Pb–O7′	145.3 (7)
N3–Pb–O7′	66.9 (4)	O3′–Pb–O7′	82.0 (4)
N1–Pb–N2	71.4 (3)		
N2–Pb–N3	71.8 (3)		
N3–Pb–N1	71.5 (3)		

Table IV. Atomic Coordinates of $LPb(NO_3)_2$

atom	*x*	*y*	*z*
Pb	0.22646 (6)	0.16286 (5)	0.03486 (4)
N11	0.475 (1)	0.226 (1)	–0.052 (1)
O1	0.414 (1)	0.150 (1)	–0.0642 (9)
O2	0.458 (1)	0.273 (1)	0.0163 (9)
O3	0.549 (1)	0.254 (1)	–0.106 (1)
N1	0.328 (1)	0.013 (1)	0.0740 (9)
N2	0.310 (1)	0.191 (1)	0.1747 (9)
N3	0.105 (1)	0.077 (1)	0.139 (1)
C1	0.425 (2)	0.049 (2)	0.126 (2)
C2	0.395 (2)	0.116 (2)	0.194 (2)
C3	0.212 (2)	0.189 (2)	0.234 (1)
C4	0.133 (2)	0.102 (2)	0.227 (1)
C5	0.130 (2)	–0.028 (2)	0.122 (1)
C6	0.253 (2)	–0.055 (1)	0.122 (1)
N22	0.297 (1)	0.436 (1)	0.112 (1)
O4	0.351 (1)	0.398 (1)	0.173 (1)
O5	0.208 (1)	0.393 (1)	0.079 (1)
O6	0.336 (1)	0.511 (2)	0.084 (1)

The structures were solved via Patterson and Fourier syntheses. Idealized positions of the methylene and amine H atoms were calculated and included in the refinement cycles with a common isotropic thermal parameter (U of **1**, 0.08 Å^2; U of **2**, 0.075 Å^2). The function minimized during least-squares refinements was $\sum w(|F_o| - |Fc|)^2$ with final convergence to $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ = 0.033 (**1**) and 0.057 (**2**) ($w = 1\sigma^2(I)$).

Scattering factors for all atoms were taken from ref 9. The real and imaginary parts of anomalous dispersion for all non-hydrogen atoms were included.

The final atomic parameters are given in Tables II (**1**) and IV (**2**) and selected bond distances and angles in Tables III (**1**) and V (**2**). Tables of anisotropic thermal parameters, coordinates of H atoms, and bond distances and angles for (**1**) and (**2**), respectively, are available as supplementary material.

Table V. Selected Bond Distances (Å) and Angles (deg) of $LPb(NO_3)_2$

Pb–O1	2.665 (15)	Pb–O2′	3.21 (1)
Pb–O2	3.055 (15)	Pb–O5	3.18 (1)
Pb–N1	2.41 (1)	Pb–O3′	3.22 (1)
Pb–N2	2.44 (1)		
Pb–N3	2.445 (16)		
Pb–O6″	2.86 (1)		
O1–Pb–O2	43.5 (3)	N1–Pb–O2	90.7 (4)
O1–Pb–N1	72.9 (4)	N2–Pb–O2	70.7 (3)
O1–Pb–N2	103.0 (5)	N3–Pb–O2	142.2 (4)
O1–Pb–N3	145.5 (5)	O5–Pb–O2	66.8 (3)
O1–Pb–O5	104.2 (4)	O6″–Pb–O2	120.0 (5)
O1–Pb–O6″	76.7 (3)	O2′–Pb–O2	133.9 (5)
O1–Pb–O2′	137.5 (5)	O3′–Pb–O2	108.4 (4)
O1–Pb–O3′	97.4 (4)	N1–Pb–N2	73.1 (3)
N2–Pb–N3	72.0 (3)	N1–Pb–N3	73.0 (2)
N2–Pb–O5	71.2 (3)	N1–Pb–O5	142.4 (5)
N2–Pb–O6″	143.3 (4)	N1–Pb–O6″	71.9 (3)
N2–Pb–O2′	114.8 (4)	N1–Pb–O2′	135.4 (5)
N2–Pb–O3′	145.1 (5)	N1–Pb–O3′	140.8 (5)
O5–Pb–O6″	145.3 (5)	N3–Pb–O5	106.0 (4)
O5–Pb–O2′	72.2 (3)	N3–Pb–O6″	87.6 (3)
O5–Pb–O3′	76.6 (3)	N3–Pb–O2′	69.0 (3)
O6″–Pb–O2′	83.9 (3)	N3–Pb–O3′	105.5 (4)
O6″–Pb–O3′	68.9 (3)	O2′–Pb–O3′	40.1 (3)

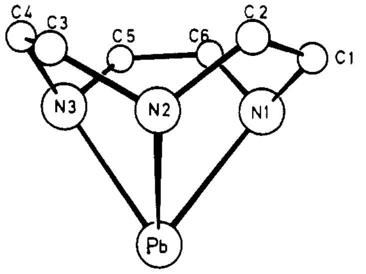

Figure 1. Perspective view and atomic labeling of the LPb^{2+} moiety in **1** omitting the hydrogen atoms for the sake of clarity. The same structure of LPb^{2+} is observed in crystals of **2**.

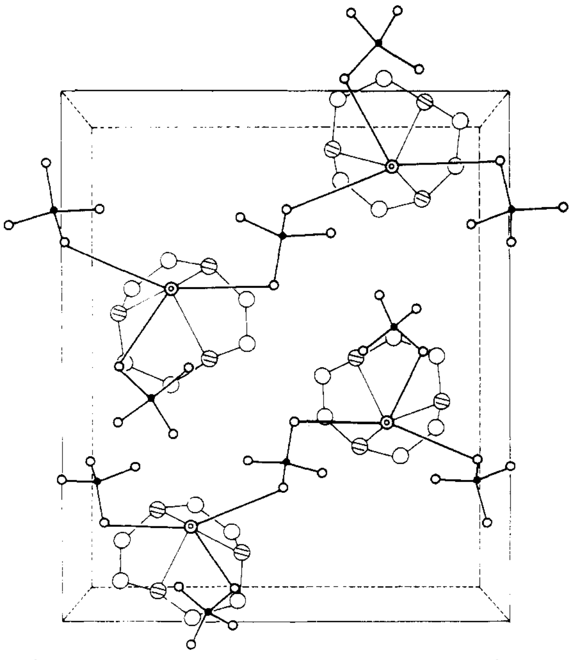

Figure 2. View of the packing of **1**. The three short Pb–O distances are drawn only to demonstrate the chain structure of $(ClO_4)LPb(ClO_4)LPb...$ in **1**.

Results and Discussion

The reaction of the cyclic triamine L with $Pb(ClO_4)_2$ and $Pb(NO_3)_2$ in aqueous solution (1:1) at room temperature in the presence of a large excess of the respective anion was found to produce colorless crystals of **1** and **2**, respectively. These salts dissolve readily in water, and the resulting solutions have a pH of approximately 7, indicating that the ligand L remains coordinated to lead(II) in solution. The infrared spectra of **1** and **2** clearly show that in the solid state the perchlorate and nitrate anions, respectively, are also coordinated. Thus, ν(Cl–O) stretching frequencies are observed for **1** at 1130 (s), 1110 (s), 1090 (w), 1080 (s), and 900 (w) cm^{-1}, indicating monodentate

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(8) Computations were carried out by using the SHELXTL program package (revision 3.0; July 1981) by G. M. Sheldrick, Universität Göttingen.

(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

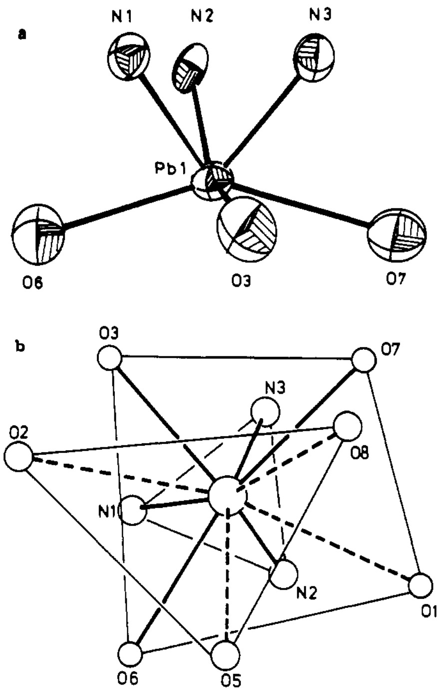


Figure 3. (a) Structure of the PbN_3O_3 polyhedron in **1**. (b) Schematic representation of the complete environment of the Pb^{2+} ion in **1**. Strong lines between Pb and O or N atoms represent short bonds, broken lines represent relatively weak Pb...O interactions. The lone pair of valence electrons of Pb^{2+} is directed from the lead center perpendicular above the paper plane.

and/or bidentate ClO_4^-.[10] The ν(N–O) stretching frequency of **2** was observed as a very strong, broad band centered at 1380 cm^{-1}, and in addition three weak bands at 1765, 1745, and 1735 cm^{-1}, which are assigned nitrate combination frequencies, have been detected in the infrared spectrum. Especially the latter bands are indicative of coordinated nitrate (monodentate and/or bidentate).[11] The crystal structures of **1** and **2** have been determined in order to establish the exact coordination spheres of the lead(II) centers and the mode of coordination of ClO_4^- and NO_3^-.

Description of the Crystal Structure of 1. Crystals of **1** consist of LPb^{2+} units (Figure 1) and perchlorate anions that are weakly bound to the lead(II) centers. Figure 2 shows a crystal-packing diagram clearly showing one bidentate bridging ClO_4^- group between two Pb^{2+} centers (Pb–O6 = 2.95 (1) Å; Pb′–O7 = 2.96 (1) Å) that connects the PbL^{2+} units to linear chains in the crystal. The other two oxygen atoms (O5 and O8) of this ClO_4^- group also point to Pb^{2+} centers, although the Pb–O distances (Pb–O5′ = 3.44 (1) Å and Pb–O8′ = 3.37 Å) are rather long and are certainly not covalent. The second ClO_4^- is coordinated to one PbL^{2+} moiety via one oxygen atom, O3 (Pb–O3 = 2.82 (1) Å) and may best be described as a monodentate ClO_4^- ligand; O2 points to the same lead center (Pb–O2 = 3.40 (1) Å) and O1 points to a second Pb^{2+} center (Pb–O1 = 3.31 (1) Å) connecting the LPb-ClO_4-LPb-ClO_4 chains, forming a layered structure. These latter Pb–O interactions are electrostatic rather than covalent. Thus, a monodentate and a bridging bidentate perchlorate anion is present in **1**. The Cl–O bond lengths do not vary significantly from the usual average value found in anionic ClO_4^- ($1.43^+ - 0.1$ Å), but as mentioned above, in the infrared spectrum five ν(Cl–O) stretching frequencies are observed.

The Pb–N bond lengths in PbL^{2+} are quite short as compared to those found in other N-macrocyclic complexes of lead(II);[2–5] they are considered to be covalent bonds.

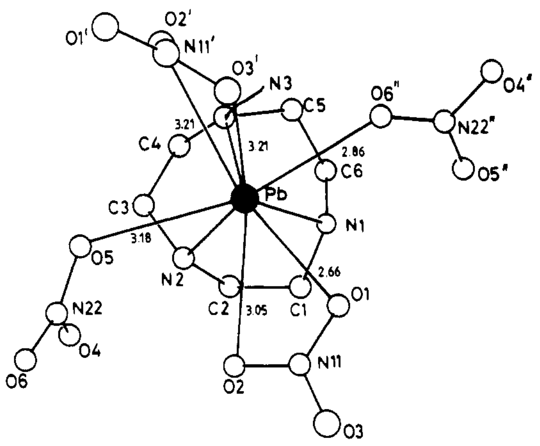
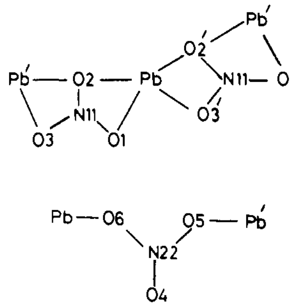


Figure 4. Structure of **2** showing the atomic numbering.

Chart I



Two types of Pb–O interactions are discerned in **1**: three oxygen atoms are bound to Pb^{2+} at distances 2.82–2.96 Å and four oxygens are at distances 3.37–3.44 Å. The former agree with those found in lead nitrate (2.805 Å) and in other macroheterocyclic lead(II) complexes (2.7–2.9 Å).[4,5] The sum of the ionic radius of Pb^{2+} with coordination number 10 and that of O^{2-} with coordination number 2 is 2.75 Å.[13] Thus, the three shorter Pb–O bond lengths in **1** are probably best described as predominantly ionic with only very little covalent bonding. It is noted that in tetragonal PbO the lead–oxygen distance is found to be 2.30 Å—a covalent Pb–O bond. This leads to a Pb^{2+} center with six-coordination (N_3O_3) (Figure 3a). Taking into account the four further, much weaker Pb–O interactions, the coordination number increases to 10 (6 + 4). Interestingly, the polyhedra formed in either environment (coordination number 6 or 10) is highly irregular.

In Figure 3b the effect of the stereochemically active lone valence-electron pair can be nicely seen: Considering the Pb^{2+} center in the paper plane, the N1, N2, and N3 nitrogen atoms form a plane below, the oxygens O3, O7, O6, and O1 form a second plane above (O3, O6, O7 form the short Pb–O distances), and finally oxygens O2, O5, and O8 form a third plane still further above the paper plane. (These Pb–O distances are very long.) The lone valence-electron pair then points perpendicular above the paper plane. If one so assigns a stereochemical position to the lone pair of electrons on lead(II), it attains the coordination number 11.

Description of the Crystal Structure of 2. Crystals of **2** consist of LPb^{2+} units as shown in Figure 1 and nitrate anions coordinated to lead(II) in the following fashion. One NO_3^- is asymmetrically bidentate to two different Pb^{2+} ions whereas the second NO_3^- group is asymmetrically bidentate, bridging two LPb^{2+} moieties (Chart I). Thus, with the exception of one oxygen atom (O4), all oxygens of the nitrate groups are interacting with lead(II) centers, generating a layered structure. The average N–O bond

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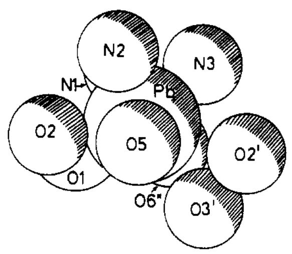


Figure 5. Perspective view of the PbN_3O_6 polyhedron of **2** emphasizing the spatial requirements of the atoms.

length of the nitrate groups of 1.252 Å corresponds to that found in many simple ionic nitrate salts.

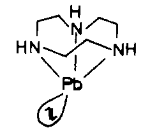
The Pb–O distances range from 2.66 to 3.21 Å. There are three short Pb–O bond lengths (2.66, 2.86, 3.05 Å) and three longer ionic interactions at 3.18, 3.21, and 3.21 Å (Figure 4). These values can be compared to the lead–oxygen distances of 2.805 Å in lead nitrate[12] and to those in other N-macrocyclic lead nitrate complexes (2.56–2.87 Å,[14] 2.74–3.17 Å,[3] 2.88–3.31 Å[2]). The sum of the ionic radius of Pb^{2+} and the van der Waals radius of oxygen is 2.67 Å. Therefore, we conclude that the Pb–O bonds in **2** display very little covalency.

The lead centers in **2** attain a coordination number of 6 (three short Pb–N and Pb–O interactions, respectively) or 9 (6 + 3) if the three long Pb–O distances are also taken into consideration. Both polyhedra are quite irregular, but it is interesting to note that the geometries of the PbN_3O_3 polyhedra in **1** and **2** are quite similar (Figure 3b).

This is a clear indication that the lone pair of valence electrons of the LPb^{2+} unit is stereochemically active in the same fashion in compounds **1** and **2**. Figure 5 displays a perspective view of the PbN_3O_6 polyhedron, emphasizing the spatial requirements of the atoms. The lead(II) center is surrounded by three nitrogen atoms, which define a plane above Pb^{2+}; a second nearly parallel plane is then defined by five oxygen atoms below Pb^{2+} (O1, O2, O6″, O2′, O5). It is then clearly seen that the lone pair of electrons of LPb^{2+} points below the latter plane.

Conclusion

We have shown in this work that the small tridentate macrocyclic ligand, 1,4,7-triazacyclononane binds strongly in aqueous solution to lead(II), forming a 1:1 complex with three covalent lead–nitrogen bonds. The LPb^{2+} moiety forms in the solid state three further bonds of highly ionic character to oxygen atoms as in **1** and **2**. The lead(II) centers are then in an environment of six donor atoms forming a highly irregular polyhedron, the shape of which is very similar in both cases. The lone pair of valence electrons of the LPb^{2+} unit appears to be stereochemically active in the same fashion in the two crystal structures under investigation:



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Supplementary Material Available: Tables of refined thermal parameters, atomic coordinates of hydrogen atoms, and bond distances and angles for **1** and **2** (5 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (29 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Crystal Structure of Bis[bis(1,4,7-triazacyclononane)nickel(III)] Dithionate Heptahydrate and Its Single-Crystal EPR Spectrum

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The structure of bis[bis(1,4,7-triazacyclononane)nickel(III)] dithionate heptahydrate, $[Ni(C_6H_{15}N_3)_2]_2(S_2O_6)_3{\cdot}7H_2O$, has been determined. The nickel(III) complex crystallized in the monoclinic system, space group $P2_1/n$, with $a = 8.669$ (7) Å, $b = 28.91$ (2) Å, $c = 9.579$ (7) Å, $\beta = 91.28$ (5)°, and $Z = 2$. The structure was refined to a final R value of 0.061 for 3360 unique reflections. The coordination sphere at the Ni(III) centers consists of six nitrogen atoms of two facially coordinated 1,4,7-triazacyclononane rings in a tetragonally distorted octahedral arrangement. The six nickel–nitrogen bonds form two sets with two longer axial bonds, 2.107 (5) and 2.111 (5) Å, and four shorter equatorial bonds, 1.964 (5), 1.985 (5), 1.970 (5), and 1.965 (5) Å. From the EPR powder and single-crystal spectra an axial $\mathbf{g}$ tensor ($g_\| = 2.03_2$, $g_\perp = 2.12_9$ at 298 K) was deduced. The sequence $g_\perp > g_\| \geq g_0$ ($g_0 = 2.00_2$) is compatible only with a $^2A_{1g}$ (d_{z^2}) ground state and a tetragonally elongated NiN_6 octahedron. The first excited high-spin state is estimated to have an energy of about 4000 cm^{-1} with respect to that of the low-spin ground state.

Introduction

Structural information on complexes of nickel in the oxidation state +III are rather scarce. Only a limited number of such complexes have been characterized to date by X-ray determinations due to their generally strong oxidative capabilities. Kinetically stable complexes of Ni(III) containing tetraaza macrocycles and two axially coordinated monodentate ligands have been prepared, and their structures have been determined by X-ray crystallography: *trans*-[dichloro(1,4,8,11-tetraazacyclotetradecane)nickel(III)] perchlorate,[2] $[Ni([14]aneN_4)Cl_2]ClO_4$, and *trans*-[bis(dihydrogen phosphato)(*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(III)] perchlorate,[3] $[Ni(meso\text{-}Me_6[14]aneN_4)(H_2PO_4)_2]ClO_4$. Recently, the structures of (1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetato)nickel(III)[4] and of an adduct of tris(2,2′-bipyridine)nickel(III) perchlorate,[5]

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