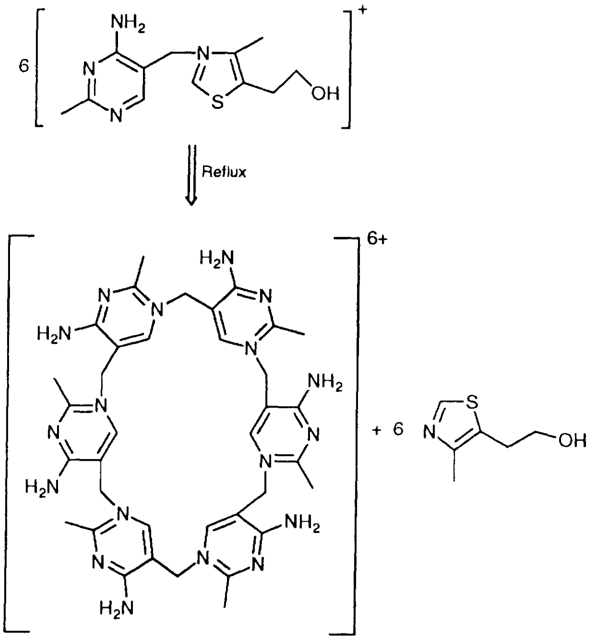
# Crystal Structures of [Pb(NO$_3$)$_6$]$^{4-}$ and [Ba(NO$_3$)$_6$]$^{4-}$ Salts of 24-Pyrimidinium Crown 6 {5,12,19,26,33,40-Hexaamino-3,10,17,24,31,38-hexamethyl[1.$_6$](1,5)pyrimidiniophane}†

**Roger E. Cramer,* Kathryn A. Mitchell, Anne Y. Hirazumi and Susan L. Smith**
*Department of Chemistry, University of Hawaii at Manoa, Honolulu 96822, USA*

Reflux of thiamin [3-(4-amino-2-methylpyrimidin-5-ylmethyl)-5-(2-hydroxyethyl)-4-methylthiazolium] mononitrate in methanol for 2 h, followed by recrystallization from water, produced single crystals of [L][NO$_3$]$_6$ {L = 5,12,19,26,33,40-hexaamino-3,10,17,24,31,38-hexamethyl[1.$_6$](1,5)-pyrimidiniophane or 24-pyrimidinium crown 6}. Addition of a saturated aqueous solution of M(NO$_3$)$_2$ (M = Ba or Pb) to a saturated aqueous solution of [L][NO$_3$]$_6$ yielded single crystals of [L][Ba(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O and [L][Pb(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O respectively. Both compounds crystallize in the trigonal space group $R\bar{3}$: Ba, $a = b = 14.265(3)$, $c = 25.206(9)$ Å, $Z = 3$, $R = 0.0435$, $R' = 0.0586$, 1169 independent reflections with $F > 6.0\sigma(F)$; Pb, $a = b = 14.228(5)$, $c = 25.24(1)$ Å, $Z = 3$, $R = 0.0343$, $R' = 0.0354$, 1263 independent reflections with $F > 1.0\sigma(F)$. The M$^{2+}$ ions in these isomorphous structures lie on a three-fold axis and are co-ordinated to 12 nitrate oxygen atoms, with a co-ordination polyhedron resembling a distorted cuboctahedron.

The rapid destruction of thiamin [3-(4-amino-2-methylpyrimidin-5-ylmethyl)-5-(2-hydroxyethyl)-4-methylthiazolium] (vitamin B$_1$) by sulfite ion in aqueous solution was first reported by Williams,[1] who observed cleavage of the biomolecule into two fragments; the soluble thiazole and the insoluble pyrimidinesulfonate ion. In 1974, Shimahara *et al.*[2] reported a pyrimidinium oligomerization resulting from thiazole displacement of one thiamin molecule by the pyrimidine nucleophile of a second thiamin upon reflux in alcohols. Based on chemical analysis and mass spectrometry, they inferred a pentameric structure. Upon studying the mechanism of this reaction, Zoltewicz *et al.*[3] reported that the oligomerization reaction proceeds *via* a second-order nucleophilic displacement. Following the procedure reported by Shimahara *et al.*, a solid oligomer was isolated and recrystallized by Evangelista.[4] X-Ray crystallographic studies[5] have shown it to be the cyclic, hexameric 24-pyrimidinium crown 6 {5,12,19,26,33,40-hexaamino-3,10,17,24,31,38-hexamethyl[1.$_6$](1,5)pyrimidiniophane} salt [L][NO$_3$]$_6$ shown in Scheme 1.

We have recently reported the structure of [L][HgI$_3$(dmso)][HgI$_4$][Hg$_2$I$_7$]·11dmso·2H$_2$O (dmso = dimethyl sulfoxide) in which the novel [Hg$_2$I$_7$]$^{3-}$ anion occurs.[6] We postulated that the high positive charge and large size of 24-pyrimidinium crown 6 induced the formation of the large polynegative [Hg$_2$I$_7$]$^{3-}$ anion. There is little information available on the large tetranegative anions [Ba(NO$_3$)$_6$]$^{4-}$ and [Pb(NO$_3$)$_6$]$^{4-}$. About 40 years ago compounds such as (NH$_4$)$_4$Ba(NO$_3$)$_6$ and Li$_4$Ba(NO$_3$)$_6$[7] or K$_4$Pb(NO$_3$)$_6$[8] were proposed based on measurements such as solution viscosity or electrical conductance. However in 1969 the Raman spectrum of a solution of stoichiometry K$_4$Pb(NO$_3$)$_6$ was reported to be inconsistent with co-ordinated nitrate ions.[9] Here we report the characterization and crystal structure of two isomorphous complexes, [L][Ba(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O and [L][Pb(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O, which firmly establish the existence of [Pb(NO$_3$)$_6$]$^{4-}$ and [Ba(NO$_3$)$_6$]$^{4-}$.



L

Scheme 1

## Experimental

*Synthesis.*—[L][NO$_3$]$_6$. Crystals of [L][NO$_3$]$_6$ were synthesised using a modification of the procedure reported by Shimahara *et al.*[2] wherein thiamin mononitrate (3.3 g, 0.01 mol) was refluxed in absolute methanol (100 cm$^3$) for 1.5 h. The product, a white precipitate, was allowed to cool and then collected on a glass frit, rinsed with cold methanol (5 cm$^3$) and subsequently recrystallized from hot distilled water yielding 0.69 g of [L][NO$_3$]$_6$ in 34% yield.

[L][Pb(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O. The salt [L][NO$_3$]$_6$ (0.1329 g) was dissolved in distilled water (5 cm$^3$) upon heating and

---

† *Supplementary data available* (No. SUP 56978, 3 pp.) IR data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii xxviii.

allowed to cool. Lead(II) nitrate (0.2385 g) was then dissolved in distilled water (5 cm$^3$) and added to the aqueous solution of [L][NO$_3$]$_6$ which was allowed to stand unperturbed for 48 h, yielding 0.1856 g of [L][Pb(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O as single clear prismatic crystals in 99% yield (Found: C, 27.95; H, 3.15; N, 23.35; Pb, 13.15. Calc. for $C_{36}H_{60}N_{26}O_{30}Pb$: C, 28.00 H, 3.90; N, 23.60; Pb, 13.40%). NMR [(CD$_3$)$_2$SO]: $^1$H (300 MHz) (all singlets), δ 2.63 (3 H, Me), 5.21 (2 H, CH$_2$ bridge), 7.84 (1 H, aromatic CH), 8.82 (1 H, NH$_2$), and 9.44 (1 H, NH$_2$); $^{13}$C (125 MHz), δ 21.8 [C(21)], 50.0 [C(35)], 105.9 [C(5)], 147.4 [C(6)], 161.0 [C(4)] and 163.1 [C(2)].

[L][Ba(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O. The salt Ba(NO$_3$)$_2$ (0.1882 g) was used instead of Pb(NO$_3$)$_2$ in the aforementioned synthesis. The reaction afforded 0.1772 g of [L][Ba(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O as single clear prismatic crystals in 95% yield (Found: C, 30.00; H, 3.70, Ba, 9.25; N, 24.20. Calc. for $C_{36}H_{60}BaN_{26}O_{30}$: C, 29.30; H, 4.10; Ba, 9.30; N, 24.70%). NMR[(CD$_3$)$_2$SO]: $^1$H (300 MHz) (all singlets), δ 2.65 (3 H, Me), 5.21 (2 H, CH$_2$ bridge), 7.84 (1 H, aromatic H), 8.82 (1 H, NH$_2$) and 9.45 (1 H, NH$_2$); $^{13}$C (125 MHz), δ 22.0 [C(21)], 50.1 [C(35)], 106.3 [C(5)], 147.5 [C(6)], 161.2 [C(4)], and 163.3 [C(2)]. Elemental analyses were by Oneida Research Services, Whitesboro, NY.

*UV/VIS Spectroscopy.*—A Beckman DU-7 UV/VIS spectrophotometer was used to determine the ultraviolet absorptions of $2.27 \times 10^{-5}$ mol dm$^{-3}$ [L][Ba(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O and $4.74 \times 10^{-5}$ mol dm$^{-3}$ [L][Pb(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O solutions in a 1 cm cell: $\lambda_{max}$ at 259.5(1) (5.11) and 218.5(1) nm (log ε 5.02) for the barium salt, 256.5(1) (4.67) and 216.5(1) nm (log ε 4.70) for the lead salt. The peak in the 250 nm region is due to the pyrimidine chromophore,[10] while that in the 220 nm region corresponds to the nitrate.[11] These wavelengths and absorption coefficients are similar to those reported for [L][NO$_3$]$_6$.[5]

*IR Spectroscopy.*—A Perkin Elmer 1430 ratio recording spectrophotometer was used to record spectra of KBr-pelleted samples of [L][NO$_3$]$_6$, [L][Pb(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O and [L][Ba(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O. The absorption maxima and possible peak assignments are listed in SUP 56978.

The infrared absorption spectrum of the [L]$^{6+}$ portion of the compounds is complex, yet remains similar for all three salts. The only significant differences between the spectra are bands associated with the N–O vibrations of the nitrate. The [L][NO$_3$]$_6$ salt exhibits only the nitrate bands which can be assigned to the free ion, at 1384, 825 and 724 cm$^{-1}$. The metal hexanitrate salts, however, contain both free nitrates and those bound in the [M(NO$_3$)$_6$]$^{4-}$ anion. Co-ordination of the nitrate to a metal ion allows the degenerate $\nu_3$ and $\nu_4$ bands to split, while the $\nu_1$ (symmetric stretch) becomes IR active.[12-14] The $\nu_2$ band at 825 cm$^{-1}$, for both bound and unbound nitrates, remains strong and sharp for the [M(NO$_3$)$_6$]$^{4-}$ compounds. The $\nu_3$ band does not split, but is observed as a broad peak at 1384 cm$^{-1}$ for both the lead and barium salts. The $\nu_4$ band splits and is observed as two single strong broad bands at approximately 770 and 717 cm$^{-1}$ for both these salts. The $\nu_1$ band is IR active and occurs at approximately 1006 cm$^{-1}$.

As mentioned in the Introduction, Saraf and Prasad[9] reported a Raman study of a solution of stoichiometry K$_4$Pb(NO$_3$)$_6$. They found the $\nu_1$ band at 1064.4 compared to 1055.5 cm$^{-1}$ for a solution of Pb(NO$_3$)$_2$ and concluded this did not support the existence of [Pb(NO$_3$)$_6$]$^{4-}$. The decrease in the $\nu_1$ wavenumber to 1006 cm$^{-1}$ which we report here is in the direction expected upon co-ordination of the NO$_3$$^-$ anion. Presumably [Pb(NO$_3$)$_6$]$^{4-}$ occurs in solution in only trace amounts, and was detected by the earlier transport-number experiments,[7,8] but not by the Raman measurements,[9] which instead see the bulk of nitrate anions which are not bound to Pb$^{2+}$.

*NMR Spectroscopy.*—A GE QE-300 FT spectrophotometer was used to obtain $^1$H NMR spectra of [L][Pb(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O and [L][Ba(NO$_3$)$_6$][NO$_3$]$_2$·6H$_2$O in (CD$_3$)$_2$SO. An Omega 500 MHz FT spectrophotometer was used to obtain proton-decoupled $^{13}$C NMR spectra of both compounds in (CD$_3$)$_2$SO.

*X-Ray Data Collection and Reduction.*—Crystals prepared as described above were glued to glass fibres. A Nicolet R3mv diffractometer was used to determine the unit-cell parameters and for data collection. The SHELXTL autoindexing routine[15] indicated a rhombohedral unit cell based on 15 reflections with 2θ values between 3.66 and 17.64° for the lead salt and 22 reflections between 15.63 and 30.21° for the barium salt. Rotation photographs and systematic absences were consistent with the space group $R\bar{3}$ which was confirmed by successful solution and refinement of the structures. A total of 4455 reflections for which $-15 < h < 0$, $-7 < k < 15$ and $-27 < l < 27$ were collected for the lead salt. A portion of this data set was collected in a primitive unit cell to confirm the systematic absences due to the *R* cell. These were averaged to produce 1294 unique reflections, yielding a merging *R* value of 0.0205. For the barium structure only those 3432 reflections which were allowed by the *R* condition, and which fell in the same *h*, *k*, *l* ranges, were collected and averaged to yield 1302 unique reflections with a merging *R* value of 0.085. During data collection the intensities of the three check reflections monitored periodically showed no decrease. The data were corrected for Lorentz and polarization effects using the SHELXTL system. An absorption correction was applied using four ψ scans for each data set. A summary of the data collection and crystal parameters is given in Table 1.

*Structure solution and refinement.* The structure of the lead salt was solved by Patterson methods, which located the metal ion. The remaining atoms were located from a series of Fourier difference maps. Using those data for which $F > \sigma(F)$, the structure was refined with anisotropic thermal parameters for all atoms except H and those of the disordered, unco-ordinated nitrate group. Hydrogen atoms were included and refined using a fixed thermal parameter of 0.08 Å$^2$. After the final cycle of refinement in which the largest parameter shift was 0.39σ, the largest remaining peak in the Fourier difference map was 0.4 e Å$^{-3}$ in the vicinity of the disordered nitrate. Since the barium structure is isomorphous, its refinement was initiated using the atomic coordinates of the lead structure and the 1169 data for which $F > 6\sigma(F)$. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included at calculated positions, except for water hydrogens the positions of which were refined along with a common thermal parameter for both water hydrogens while another common thermal parameter was refined for the remaining hydrogens. After the final cycle of refinement in which the largest parameter shift was 0.03σ, the largest remaining peak in the final Fourier difference map was 0.4 e Å$^{-3}$ in the vicinity of the barium ion.

Final atomic coordinates are listed in Table 2, bond distances in Table 3 and angles in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

## Results and Discussion

*The Crystal Structures.*—The asymmetric unit consists of a pyrimidine ring with its substituents, a lead or barium ion, a nitrate co-ordinated to the metal ion, a water molecule and one O and one N atom of the disordered, unco-ordinated nitrate ion. The $R\bar{3}$ symmetry operations generate a unit cell containing three [L]$^{6+}$ cations, three [M(NO$_3$)$_6$]$^{4-}$ anions, 18 water molecules and six disordered unco-ordinated nitrate ions. Fig. 1 shows one 24-pyridinium crown 6 cation, a [Ba(NO$_3$)$_6$]$^{4-}$ anion, and the disordered nitrate associated with the macrocycle. The lead structure is isomorphous.

The centre of the hexameric 24-pyrimidinium crown 6 macrocycle is located at Wyckoff position *b* ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{6}$) which requires that the cation belong to the $S_6$ point group. The

**Table 1** Crystal data and details of data collection and refinement procedures[a]

| | $[L][Pb(NO_3)_6][NO_3]_2{\cdot}6H_2O$ | $[L][Ba(NO_3)_6][NO_3]_2{\cdot}6H_2O$ |
|---|---|---|
| Formula | $C_{36}H_{60}N_{26}O_{30}Pb$ | $C_{36}H_{60}BaN_{26}O_{30}$ |
| *M* | 1544.23 | 1474.40 |
| *F*(000) | 2340 | 2262 |
| $a = b$/Å | 14.228(5) | 14.265(3) |
| *c*/Å | 25.24(1) | 25.206(9) |
| *U*/Å | 4435(4) | 4442(2) |
| Crystal dimensions/mm | 0.26 × 0.18 × 0.13 | 0.25 × 0.25 × 0.30 |
| $D_c$/g cm$^{-3}$ | 1.734 | 1.654 |
| μ/cm$^{-1}$ | 29.8 | 7.8 |
| Absorption coefficient | 0.421–0.519 | 0.850–0.899 |
| Number of parameters | 164 | 158 |
| $R^b$ | 0.0343 | 0.0435 |
| $R'^c$ | 0.0354 | 0.0586 |

[a] Details in common = trigonal space group $R\bar{3}$, $Z = 3$; colourless; 25 °C; graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å); 2θ–θ scans; range 3.0–45.0°. [b] $\Sigma|F_o - F_c|/\Sigma F_o$. [c] $\Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}F_o$, $w^{-1} = \sigma^2(F)$.

**Table 2** Atomic coordinates ( × 10⁴) for $[L][Ba(NO_3)_6](NO_3)_2{\cdot}6H_2O$ and $[L][Pb(NO_3)_6](NO_3)_2{\cdot}6H_2O$ structures

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| (*a*) $[L][Pb(NO_3)_6][NO_3]_2{\cdot}6H_2O$ | | | |
| Pb | 0 | 0 | 0 |
| O(12) | −37(4) | −1357(4) | 782(2) |
| N(10) | −205(3) | −2173(4) | 516(2) |
| O(11) | −483(3) | −2236(3) | 41(1) |
| O(13) | −64(4) | −2880(4) | 714(2) |
| N(1) | 1567(3) | 3267(3) | 1583(2) |
| C(2) | 953(4) | 2414(4) | 1911(2) |
| C(21) | −214(5) | 1667(6) | 1774(3) |
| N(3) | 1353(3) | 2218(3) | 2332(2) |
| C(4) | 2414(4) | 2867(4) | 2454(2) |
| N(41) | 2767(4) | 2614(5) | 2883(2) |
| C(5) | 3110(4) | 3745(4) | 2114(2) |
| C(6) | 2644(4) | 3915(4) | 1687(2) |
| C(35) | 1110(5) | 3471(5) | 1095(2) |
| N(2) | 1/3 | 2/3 | 983(6) |
| O(22) | 4024(9) | 7697(9) | 862(6) |
| O(23) | 3790(21) | 6273(20) | 1187(15) |
| O(1) | 5059(7) | 2967(5) | 82(3) |
| (b) $[L][Ba(NO_3)_6][NO_3]_2{\cdot}6H_2O$ | | | |
| Ba | 0 | 0 | 0 |
| O(12) | −6(3) | −1426(3) | 809(1) |
| N(10) | −162(3) | −2222(3) | 524(2) |
| O(11) | −439(3) | −2246(3) | 48(1) |
| O(13) | −17(4) | −2936(3) | 702(2) |
| O(1) | 5050(6) | 2962(4) | 83(3) |
| N(2) | 1/3 | 2/3 | 954(4) |
| O(22) | 3969(7) | 7667(6) | 886(5) |
| O(23) | 3787(25) | 6366(29) | 1275(19) |
| N(1) | 1556(3) | 3288(3) | 1579(1) |
| C(2) | 948(4) | 2435(4) | 1894(2) |
| C(21) | −212(4) | 1697(4) | 1766(2) |
| N(3) | 1345(3) | 2219(3) | 2317(2) |
| C(4) | 2401(3) | 2860(3) | 2442(2) |
| N(41) | 2732(4) | 2578(4) | 2867(2) |
| C(5) | 3086(3) | 3741(3) | 2115(2) |
| C(6) | 2624(3) | 3933(3) | 1690(2) |
| C(35) | 1111(4) | 3500(4) | 1095(2) |

structure of this cation is very similar to that reported previously in the $[L][HgI_3(dmso)][HgI_4][Hg_2I_7]{\cdot}11dmso{\cdot}2H_2O$ complex.[6] In particular, the bond distances and angles in the hexameric cation are indistinguishable from those in the earlier report[6] and are quite similar to those of the protonated thiamin cation.[16] The dihedral angles between pyrimidinium planes are 94° in the lead structure and 92° in the barium structure, significantly less than the 105° found in the mercury structure which has an iodo ligand at the centre of the 24-pyrimidinium crown 6 macrocycle.

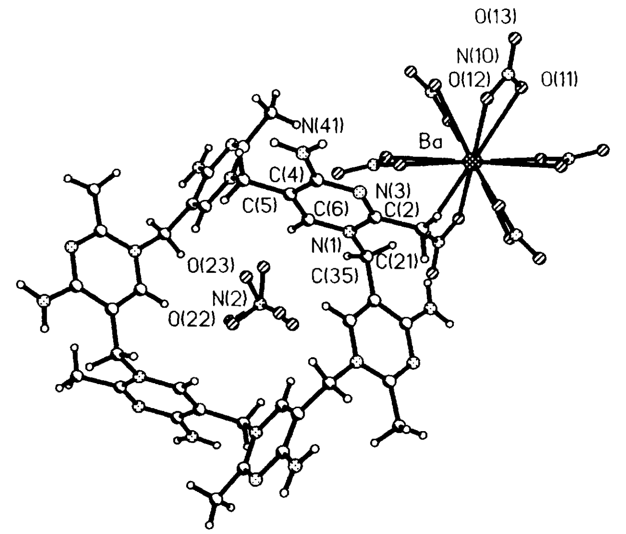


**Fig. 1** Perspective view of $[L][Ba(NO_3)_6][NO_3]_2$, with labels only for the atoms of the asymmetric unit. The six symmetry-equivalent water molecules are not shown. The oxygen atoms of the N(2) nitrate are disordered, with occupancies of 75% for O(22) and 25% for O(23). The second N(2) nitrate, located below the macrocycle and related by inversion to the one shown, has been omitted. The structure of the lead(II) salt is isomorphous

The metal ions occupy Wyckoff position *a* and are co-ordinated to six bidentate nitrate ions to generate a $[M(NO_3)_6]^{4-}$ anion, Fig. 2, which also transforms according to the $S_6$ point group. The $[M(NO_3)_6]^{4-}$ anions interact with the 24-pyrimidinium crown 6 cation *via* a hydrogen bond from the exocyclic N(41) amino group of the pyrimidinium ring to the co-ordinated O(11) atom of the nitrate. This generates a structure which consists of alternating layers of 24-pyrimidinium crown 6 cations and $[M(NO_3)_6]^{4-}$ anions with each cation hydrogen bonded to three anions in the layer above it and three anions in the layer beneath. Each anion is surrounded by six cations in an analogous fashion.

Each 24-pyrimidinium crown 6 cation is associated with two inversion-related unco-ordinated nitrate ions. The nitrogen atom N(2) is located on the three-fold axis at Wyckoff position *c*. The oxygen atom of this nitrate is disordered over two positions, with the O(22) position refining to an occupancy of about 75% and O(23) to 25%. While these nitrate ions do not occupy the centre of the macrocyclic cavity, they are clearly closely associated with it. The N(2) atom is positioned 1.73 Å

**Table 3** Bond distances (Å)

| | $[\mathrm{L}][\mathrm{Pb(NO_3)_6}][\mathrm{NO_3}]_2\cdot 6\mathrm{H_2O}$ | $[\mathrm{L}][\mathrm{Ba(NO_3)_6}][\mathrm{NO_3}]_2\cdot 6\mathrm{H_2O}$ |
|---|---|---|
| M–O(11) | 2.906(5) | 2.944(4) |
| M–O(12) | 2.744(5) | 2.876(4) |
| N(10)–O(12) | 1.257(7) | 1.266(6) |
| N(10)–O(11) | 1.252(6) | 1.257(5) |
| N(10)–O(13) | 1.227(9) | 1.222(7) |
| N(1)–C(2) | 1.367(6) | 1.344(5) |
| N(1)–C(6) | 1.364(6) | 1.358(5) |
| N(1)–C(35) | 1.488(8) | 1.474(7) |
| C(2)–C(21) | 1.500(7) | 1.487(6) |
| C(2)–N(3) | 1.300(8) | 1.313(7) |
| N(3)–C(4) | 1.355(6) | 1.353(5) |
| C(4)–N(41) | 1.318(9) | 1.311(7) |
| C(4)–C(5) | 1.430(6) | 1.409(6) |
| C(5)–C(6) | 1.349(8) | 1.355(7) |
| C(5)–C(35) | 1.515(8) | 1.512(9) |
| N(2)–O(22) | 1.33(1) | 1.263(7) |
| N(2)–O(23) | 1.17(3) | 1.23(4) |

**Table 4** Co-ordination sphere angles (°) in $[\mathrm{M(NO_3)_6}]^{4-}$ anions

| Angle* | Equivalent position of last atom | M = Pb | M = Ba |
|---|---|---|---|
| O(12)–M–O(11) | $x, y, z$ | 44.9(1) | 43.7(1) |
| O(12)–M–O(12) | $-x, -y, -z$ | 180 | 180 |
| O(12)–M–O(12) | $-y, x-y, z$ | 74.1(1) | 75.3(1) |
| O(12)–M–O(12) | $y, y-x, -z$ | 105.9(1) | 104.7(1) |
| O(12)–M–O(11) | $-x, -y, -z$ | 135.1(1) | 136.3(1) |
| O(12)–M–O(11) | $-y, x-y, -z$ | 102.0(1) | 102.0(1) |
| O(12)–M–O(11) | $y, y-x, -z$ | 78.0(1) | 78.0(1) |
| O(12)–M–O(11) | $y-x, -x, z$ | 115.1(1) | 115.3(1) |
| O(12)–M–O(11) | $x-y, x, -z$ | 64.9(1) | 64.7(1) |
| O(11)–M–O(11) | $-y, x-y, z$ | 120.0(1) | 119.8(1) |
| O(11)–M–O(11) | $y, y-x, -z$ | 60.0(1) | 60.2(1) |

* The first two atoms are in equivalent position $x, y, z$

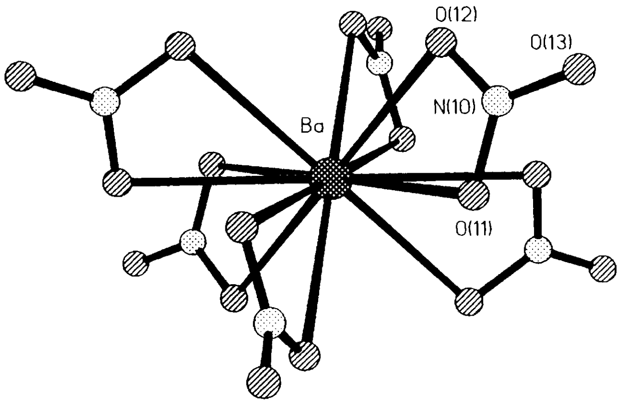


**Fig. 3** Perspective view of the $[\mathrm{Ba(NO_3)_6}]^{4-}$ anion, nearly perpendicular to the three-fold axis

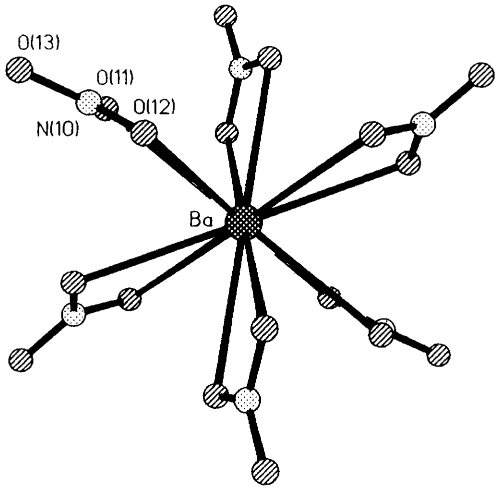


**Fig. 2** Perspective view of the $[\mathrm{Ba(NO_3)_6}]^{4-}$ anion, nearly down the three-fold axis. The $[\mathrm{Pb(NO_3)_6}]^{4-}$ anion is isomorphous

from the centre of the macrocycle along the three-fold axis in the lead structure and in an analogous position, 1.80 Å from the centre, in the barium structure. Each of the three O(22) atoms approaches one of the six H(6) atoms at a distance of 2.2 Å in the lead salt and at 2.4 Å in the barium structure. The O(23) atoms also approach an H(6) atom at a distance of 2.2 Å in the lead structure and 2.3 Å in the barium structure. In both salts, the N(2) and O(22) atoms form a nearly planar nitrate ion with a O(22)–N(2)–O(22) angle of 115.8(8)° in the lead salt and 118.2(5)° in the barium salt. The N(2) and O(23) atoms which are the minor component of this disordered ion, however, are quite clearly not in the same plane. The O(23)–N(2)–O(23) bond angles are 101(2)° in the lead structure and only 82(3)° in the barium structure. This suggests that the O(23) atoms may not represent a nitrate ion at all, but are perhaps oxygen atoms of partially occupied water molecules and/or hydroxide ions. The distance from an O(23) atom above the macrocycle to one of the inversion-related 'nitrate' oxygens below the structure is 2.6 Å in the lead structure and 2.2 Å in the barium structure, possible hydrogen-bonding distances.

The final components of the structure are the water molecules. They form a hydrogen-bonding bridge between the N(41) atom of the exocyclic amino group, the O(22) atom of the unco-ordinated nitrate ion, and the pyrimidinium nitrogen, N(3).

It is clear from Fig. 3 that the 12 oxygen atoms surrounding the metal ion are of two types. The six O(11) atoms define an approximate hexagonal plane around the metal ion with non-planar deviations of ±0.10 Å in the lead structure and ±0.12 Å in the barium structure, while the O(12) atoms are collected in two groups of three, both above and below this plane. One therefore expects greater repulsion between the O(11) than between the O(12) atoms, in accord with the longer distance observed for Pb–O(11) 2.906(5) Å as compared to the Pb–O(12) 2.744(5) Å. For the larger barium ion the distances are both longer yet the difference is less: Ba–O(11) 2.944(4) and Ba–O(12) 2.876(4) Å.

**Table 5** Other bond angles (°)

| | $[L][Pb(NO_3)_6][NO_3]_2\cdot 6H_2O$ | $[L][Ba(NO_3)_6][NO_3]_2\cdot 6H_2O$ |
|---|---|---|
| M–O(12)–N(10) | 101.3(3) | 99.8(3) |
| O(12)–N(10)–O(11) | 119.0(6) | 118.5(5) |
| O(12)–N(10)–O(13) | 120.6(5) | 120.8(4) |
| O(11)–N(10)–O(13) | 120.4(5) | 120.6(4) |
| C(2)–N(1)–C(6) | 119.4(5) | 119.3(4) |
| C(2)–N(1)–C(35) | 121.8(4) | 121.7(3) |
| C(6)–N(1)–C(35) | 118.7(4) | 118.9(3) |
| N(1)–C(2)–C(21) | 118.9(5) | 119.9(5) |
| N(1)–C(2)–N(3) | 122.1(4) | 122.2(4) |
| C(21)–C(2)–N(3) | 119.0(5) | 117.9(4) |
| C(2)–N(3)–C(4) | 119.8(4) | 119.7(4) |
| N(3)–C(4)–N(41) | 116.5(4) | 115.7(4) |
| N(3)–C(4)–C(5) | 120.8(5) | 120.5(4) |
| N(41)–C(4)–C(5) | 122.6(5) | 123.8(4) |
| C(4)–C(5)–C(6) | 116.6(4) | 116.9(4) |
| C(4)–C(5)–C(35) | 120.9(5) | 121.3(4) |
| C(6)–C(5)–C(35) | 122.5(4) | 121.8(3) |
| N(1)–C(6)–C(5) | 121.3(4) | 121.3(4) |
| N(1)–C(35)–C(5) | 112.0(5) | 112.2(4) |
| O(22)–N(2)–O(23) | 135(1) | 106(1) |
| O(22)–N(2)–O(22A) | 115.5(8) | 118.2(5) |
| O(23)–N(2)–O(23A) | 101(2) | 82(3) |

In the binary nitrates $Pb(NO_3)_2$ and $Ba(NO_3)_2$ the co-ordination polyhedra are described as distorted cuboctahedra.[17,18] In the former the Pb–O distances are 2.8688(6) and 2.7482(6) Å,[17] while the isomorphous barium structure[18] exhibits distances of 2.9414(6) and 2.8789(6) Å. Except for Pb–O(11), these distances in the polymeric $M(NO_3)_2$ structures are indistinguishable from those reported here for the $[M(NO_3)_6]^{4-}$ anions. Thus, these anions may be viewed as a section of the infinite metal nitrate array which has been excised from the $M(NO_3)_2$ lattice. It is noteworthy that the removal of this array from an uncharged lattice, to produce a tetranegative anion, has so little effect on the M–O distances. As shown in Table 6 there is however some difference in the N–M–N angles between the $M(NO_3)_2$ structures and the $[M(NO_3)_6]^{4-}$ anions.

While the N–O distances in the $M(NO_3)_2$ structures are all identical by symmetry,[17,18] that is not the case in the $[M(NO_3)_6]^4$ anions. The distances to the two co-ordinated oxygen atoms are equivalent, N(10)–O(11) 1.252(6) and N(10)–O(12) 1.257(7) Å in the lead structure and N(10)–O(11) 1.257(5) and N(10)–O(12) 1.266(6) Å in the barium structure and are longer than the distances to the unco-ordinated oxygen, N(10)–O(13) 1.227(9) and 1.222(7) Å respectively. Comparable distortions of nitrate bond lengths have been reported previously for numerous metal nitrate complexes.[30]

Although a number of hexanitratometal ion complexes are known, to our knowledge this is the first report of such complexes of $Ba^{II}$ or $Pb^{II}$, or any metal ion in the divalent oxidation state. This is also the first report of any polynitrato complex ion of either $Ba^{II}$ or $Pb^{II}$. Isolation of these salts thus lends support to the hypothesis that the 24-pyrimidinium crown 6 cation facilitates the isolation of large, highly charged anions.

We previously reported the $^1H$ NMR spectrum of $[L][HgI_3(dmso)][HgI_4][Hg_2I_7]\cdot 11dmso\cdot 2H_2O$ dissolved in $(CD_3)_2SO$. In that case the proton peak of the C(35) methylene bridge appeared as an AB quartet, which implied that the 24-pyrimidinium crown-6 and $[HgI_4]^{2-}$ ions were closely associated in solution. For the salts reported in this paper the C(35) methylene bridge protons appear as a singlet and none of the $^1H$ or $^{13}C$ NMR chemical shifts shows any effect of ion association. Further, the UV/VIS absorptions show no noticeable shifts and thus provide no evidence for ion association. We therefore have no evidence that the 24-pyrimidinium crown 6 cation and the $[M(NO_3)_6]^{4-}$ anions associate in solution, or that the $[M(NO_3)_6]^{4-}$ anions even exist in any significant quantity in solution.

While the co-ordination polyhedra of most $[M(NO_3)_6]^{x-}$ complexes are reported to be icosahedra, those of $Ba(NO_3)_2$ and $Pb(NO_3)_2$ are described as cuboctahedra.[17,18] This raises a question as to the best description of the $[M(NO_3)_6]^{4-}$ polyhedra reported here. To address this question we have compared certain geometrical parameters of the $[Ba(NO_3)_6]^{4-}$ and $[Pb(NO_3)_6]^{4-}$ structures to those of idealized icosahedra and cuboctahedra, and to those of other $[M(NO_3)_6]^{x-}$ salts. Analysis of parameters based upon the locations of the 12 co-ordinating oxygen atoms did not prove useful due to the large distortions produced by the very short nitrate bite distance. For example the average polyhedra edge distance ($O\cdots O$ distance) in the $[Pb(NO_3)_6]^{4-}$ anion is 2.91 Å while that for $[Ba(NO_3)_6]^{4-}$ is 2.95 Å. However the edges spanned by the two oxygen atoms of a single nitrate ion average only 2.16 and 2.17 Å in the two structures respectively. While analysis of the oxygen positions is confusing, comparison of the *nitrogen* positions is revealing. Thus in Table 6 we present the N–M–N angles for the two ideal polyhedra, as well as for $Ba(NO_3)_2$, $Pb(NO_3)_2$, the two structures reported in this paper, and various structures of hexanitrato complexes found in the literature.

In an icosahedron, formed by six chelating nitrate ligands, the nitrogen atoms define an octahedron. Thus there are three *trans* N–M–N angles of 180° and 12 *cis* N–M–N angles of 90°. In a cuboctahedron the three *trans* angles are retained at 180°, but the *cis* angles are split into a set of six at 109.5° and another set of six at 70.5°. In Table 6 are listed the values of the *cis* and *trans* angles we have calculated for the various reported structures along with the observed range of values for each structure and the number of angles within each group.

Most of the $[M(NO_3)_6]^{x-}$ complexes listed in Table 6 fit the icosahedral description well. This includes those for the metal ions $Nd^{3+}$, $Lu^{3+}$, $Ce^{3+}$ and $Ce^{4+}$. In addition four of five structures for $Th^{4+}$ and one of two for $Np^{4+}$ are best described as icosahedral. The binary $Ba(NO_3)_2$ and $Pb(NO_3)_2$ salts are significantly distorted away from icosahedral toward cuboctahedral, while the $[Ba(NO_3)_6]^4$ and $[Pb(NO_3)_6]^{4-}$ anions found in the structures reported in this paper approach the cuboctahedral structure more closely. It seems that release of the $MO_{12}$ polyhedra from the infinite interlocking array found in $Ba(NO_3)_2$ and $Pb(NO_3)_2$ allows them to relax toward a more cuboctahedral structure in the $[M(NO_3)_6]^{4-}$ anions.

Finally there are two structures, $[Th(NO_3)_6]^2$ and $[Np(NO_3)_6]^{2-}$, which are not well described as either icosahedra or

**Table 6** Angles N–M–N in $[M(NO_3)_6]^{n-}$ anions

| | | N–M–N/° | | | | |
|---|---|---|---|---|---|---|
| Compound | M–O[a] Å | *trans*[b] | *cis* | | | Ref. |
| Cuboctahedron | | 180 [3] | — | 109.5 [6] | 70.5 [6] | |
| Icosahedron | | 180 [3] | 90 [12] | | | |
| Distorted cuboctahedra | | | | | | |
| $Ba(NO_3)_2$ | 2.879–2.941 | 180 [3] | | 97.6 [6] | 82.4 [6] | 18 |
| $Pb(NO_3)_2$ | 2.748–2.869 | 180 [3] | | 97.9 [6] | 82.1 [6] | 17 |
| $[Ba(NO_3)_6]^{4-}$ | 2.876–2.944 | 180 [3] | | 105.4 [6] | 74.6 [6] | This work |
| $[Pb(NO_3)_6]^{4-}$ | 2.744–2.906 | 180 [3] | | 104.9 [6] | 75.1 [6] | This work |
| Icosahedra | | | | | | |
| $[Th(NO_3)_6]^{2-}$ | 2.551–2.587 | 180 [3] | 89.2–90.8 [12] | | | 19 |
| | 2.531–2.672 | 180 [3] | 88.7–91.3 [12] | | | 20 |
| | 2.511–2.585 | 180 [3] | | 91.9–93 [6] | 87.0–88.1 [6] | 20 |
| | 2.520–2.604 | 173.2–177.5 [3] | 89.3–91.7 [6] | 94.0–95.0 [2] | 85.6–87.9 [4] | 21 |
| $[Np(NO_3)_6]^{2-}$ | 2.476–2.527 | 180 [3] | 88.2–91.8 [12] | | | 22 |
| $[Ce(NO_3)_6]^{2-}$ | 2.482–2.524 | 180 [3] | 88.7–91.3 [4] | 93.7–93.8 [4] | 86.2–86.3 [4] | 23 |
| $[Ce(NO_3)_6]^{3-}$ | 2.612–2.675 | 177.8 [3] | 91.0 [3] | 93.9 [3] | 87.1–88.1 [6] | 24 |
| $[Ce(NO_3)_6]^{3-}$ | 2.629–2.679 | 180 [3] | 88.7–91.3 [4] | 92.0–92.7 [4] | 87.3–88.0 [4] | 25 |
| $[Nd(NO_3)_6]^{3-}$ | 2.578–2.650 | 176.9–179.3 [3] | 89.2–91.1 [6] | 91.3–92.1 [3] | 87.8–88.3 [3] | 26 |
| $[Lu(NO_3)_6]^{3-}$ | 2.642–2.696 | 174.5 [3] | 89.4–90.3 [6] | 93.9 [3] | 86.2 [3] | 27 |
| Twisted icosahedra | | | | | | |
| $[Th(NO_3)_6]^{2-}$ | 2.540–2.602 | 150.6–152.1 [3] | 89.0–93.9 [6] | 110.9–113.7 [3] | 72.1–74.1 [3] | 28 |
| $[Np(NO_3)_6]^{2-}$ | 2.455–2.540 | 148.4–152.0 [3] | 86.6–92.2 [6] | 114.8–115.8 [3] | 73.3–76.0 [3] | 29 |

[a] For each compound the range of metal–oxygen distances is listed. [b] For each angle type the range of observed angles is listed. The number in square brackets is the number of angles which fall within the listed range.

cuboctahedra. In these the *trans* angles are decreased from 180 to about 150°. Six of the *cis* angles are retained at 90° while three are increased and three are decreased. This distortion can be understood with reference to Fig. 3, which shows a $[M(NO_3)_6]^{x-}$ anion in a view perpendicular to the three-fold axis. Rotation of the top three nitrates around the three-fold axis with respect to the bottom three nitrates produces the distortion displayed by these two unique $[Th(NO_3)_6]^{2-}$ and $[Np(NO_3)_6]^{2-}$ anions. The cuboctahedral structure on the other hand results from pulling the top three nitrates away from the bottom three along the three-fold axis, while not twisting them. The icosahedral structure, of course, is the one where no distortion, either rotation or elongation, has occurred, and all 12 *cis* N–M–N angles remain at 90°.

It is not clear why the hexanitrato anions of $Ba^{2+}$ and $Pb^{2+}$ are cuboctahedral rather than icosahedral. They are the largest of the metal ions to be found in a hexanitrate coordination sphere, as can be seen from the bond distances in Table 6, so large size may be a factor. Also the $[L][M(NO_3)_6][NO_3]_2\cdot6H_2O$ salts may favour the cuboctahedral structure since they sandwich a $[M(NO_3)_6]^{4-}$ anion between two layers of 24-pyrimidinium crown 6 cations. These layers, which are perpendicular to the three-fold axis, place the highly charged cations in a position to attract the negatively charged nitrate ions and thus elongate the $[M(NO_3)_6]^{4-}$ anions along the three-fold axis.

## Acknowledgements

We appreciate helpful discussions with Professor Anthony Fratiello of California State University, Los Angeles.

## References

1 R. R. Williams, *J. Am. Chem. Soc.*, 1935, **57**, 229.
2 N. Shimahara, H. Asakawa, Y. Kawamatsu and H. Hirano, *Chem. Pharm. Bull.*, 1974, **22**, 2086.
3 J. A. Zoltewicz, G. Uray and G. M. Kauffman, *J. Am. Chem. Soc.*, 1980, **103**, 4900.
4 R. Evangelista, Ph.D. Thesis, Department of Chemistry, University of Hawaii, 1983.
5 E. Kim, M.S. Thesis, Department of Chemistry, University of Hawaii, 1987.
6 R. E. Cramer and M. J. Carrie, *Inorg. Chem.*, 1990, **29**, 3902.
7 H. J. Kagi, *J. Indian Chem. Soc.*, 1954, **31**, 763.
8 M. R. Nayar and C. S. Pandey, *Proc. Indian Acad. Sci.*, 1948, **27**, 284.
9 J. R. Saraf and J. Prasad, *J. Indian Chem. Soc.*, 1969, **46**, 754.
10 *DMS UV Atlas of Organic Compounds* II, Plenum, New York, 1966.
11 R. Bastian, R. Weberling and F. Palilla, *Anal. Chem.*, 1957, **29**, 1795.
12 M. H. Brooker and D. E. Irish, *Can. J. Chem.*, 1970, **48**, 1183.
13 M. H. Brooker, D. E. Irish and G. E. Boyd, *J. Chem. Phys.*, 1970, **53**, 1083.
14 F. El-Kabbany and S. Taha, *Thermochim. Acta*, 1988, **136**, 7.
15 SHELXTL PLUS, Program package for structure solution and refinement, Version 4.2, Siemens Analytical Instruments, Madison, WI, 1990.
16 R. E. Cramer, R. B. Maynard and J. A. Ibers, *J. Am. Chem. Soc.*, 1981, **103**, 76.
17 H. Nowotny and G. Heger, *Acta Crystallogr., Sect. C*, 1986, **42**, 133.
18 H. Nowotny and G. Heger, *Acta Crystallogr., Sect. C*, 1983, **39**, 952.
19 M. Wang, B. Wang, P. Zheng, W. Wang and J. Lin, *Acta Crystallogr., Sect. C*, 1988, **44**, 1913.
20 R. P. English, J. G. H. du Preez, L. R. Nassimbeni and C. P. J. Van Vuuren, *S. Afr. J. Chem.*, 1979, **32**, 119.
21 N. N. Rammo, K. R. Hamid and B. A. Khaleel, *J. Less Common Met.*, 1990, **162**, 1.
22 M. S. Grigor'ev, B. F. Gulev and N. N. Krot, *Radiokhimiya*, 1986, **28**, 685.
23 T. A. Beineke and J. Delgaudio, *Inorg. Chem.*, 1968, **7**, 715.
24 A. Zalkin, J. D. Forrester and D. H. Templeton, *J. Chem. Phys.*, 1963, **39**, 2881.
25 A. A. Dvorkin, N. F. Krasnova, Y. A. Simonov, V. M. Abashkin, V. N. Yakshin and T. I. Malinovskii, *Kristallografiya*, 1984, **29**, 471.
26 C. Huang, B. Li, Q. Yang, S. Tian and G. Xu, *Beijing Dax. Xue, Zir. Kex.*, 1984, 45.

27 M. R. Andersen, G. T. Jenkin and J. W. White, *Acta Crystallogr., Sect. B*, 1977, **33**, 3933.
28 M. A. Kahn, N. Kumar and D. G Tuck, *Can. J. Chem.*, 1984, **62**, 850.
29 M. S. Grigor'ev, A. I. Yanovskii, N. N. Krot and Y. T. Struchkov, *Radiokhimiya*, 1987, **29**, 574.
30 C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, *Q. Rev. Chem. Soc.*, 1971, **25**, 289.

*Received 22nd June* 1993; *Paper* 3/03586G