$[FeBrL_5]BPh_4$ (L = $P(OMe)_3$, $P(OEt)_3$).[15] The appropriate phosphite (60 mmol) was added to a solutoin of $FeBr_2$ (10 mmol, 2.17 g) in methanol or ethanol (80 mL). The reaction mixture was stirred for 2 h and added, after filtration, to a solution of $NaBPh_4$. After the solution was cooled to −30 °C, yellow crystals separated out in 1 day, which were filtered, washed with diethyl ether, and stored under vacuum at −20 °C; yield ≥60%.

Anal. Calcd for $\{FeBr[P(OMe)_3]_5\}BPh_4$: C, 43.56; H, 6.09. Found: C, 43.68; H, 6.23.

Calcd for $\{FeBr[P(OEt)_3]_5\}BPh_4$: C, 50.44; H, 7.45. Found: C, 50.12; H, 7.21.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 683 infrared spectrophotometer. Solid-state spectra were obtained from KBr pellets; solution spectra were obtained of potassium bromide cells. Proton magnetic resonance spectra were collected on a Varian EM 390 NMR spectrometer with tetramethylsilane as an internal standard. Fourier mode, proton noise decoupled phosphorus-31 NMR spectra were collected on a Varian FT 80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Electron spectra were recorded on a Cary 219 spectrophotometer. Magnetic susceptibilities in solution were determined by the Evans method.[16] Conductivities of 10^{-3} M solution of complexes in nitromethane at 25 °C were measured with an "Halosis" bridge.

Acknowledgment. The financial support of the MPI and CNR, Rome, is gratefully acknowledged. We thank Daniela Baldan for her technical assistance.

Registry No. I·BPh_4 (L = $P(OEt)_3$), 91741-94-5; I·BPh_4 (L = $P(OMe)_3$), 91741-96-7; II·BPh_4 (L = $P(OEt)_3$, R = 4-$CH_3C_6H_4$), 91741-98-9; II·BPh_4 (L = $P(OEt)_3$, R = 4-$CH_3OC_6H_4$), 91742-00-6; II·BPh_4 (L = $P(OEt)_3$, R = 2,6-$(CH_3)_2C_6H_3$), 91742-02-8; II·BPh_4 (L = $P(OEt)_3$, R = 4-$NO_2C_6H_4$), 91742-04-0; II·BPh_4 (L = $P(OEt)_3$, R = C_6H_5), 91742-06-2; II·BPh_4 (L = $P(OMe)_3$, R = 4-$CH_3C_6H_4$), 91742-08-4; $\{FeBr[P(OMe)_3]_5\}BPh_4$, 70318-01-3; $\{FeBr[P(OEt)_3]_5\}BPh_4$, 70323-65-8.

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Crystallographic Characterization of the Novel $(Ag_5Br_8)_n{}^{3n-}$ Polyanion

John D. Kildea and Allan H. White*

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In seeking to synthesize silver(I) analogues of the unusual 1:1 copper iodide:methyl isocyanide "displaced-stair polymer",[1] we have reacted silver(I) cyanide with excess alkyl halide/acetonitrile in sealed tubes at 100 °C for several days. One preparation involving *tert*-butyl bromide yielded a quantity of colorless highly crystalline (prismatic) material shown, by preliminary crystallographic examination, to have an unusually large unit cell. Subsequent structure determination, reported below, shows the presence of the novel $(Ag_5Br_8)_n{}^{3n-}$ polyanion.

Crystallography

Crystal Data: $C_{18}H_{42}Ag_5Br_8N_3O_3$, M_r = 1527, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), a = 28.84 (1) Å, b = 6.350 (2) Å, c = 36.48 (1) Å, β = 108.25 (3)°, V = 6345 (3) Å^3. D_{calcd} (Z = 8) = 1.96 g cm^{-3}, $F(000)$ = 3620, monochromatic Mo Kα radiation, λ = 0.7106 6$_9$ Å, μ_{Mo} = 64 cm^{-1}. A^*_{min}, A^*_{max} = 1.46, 3.81. Specimen: 0.22 × 0.34 × 0.06 mm, T = 295 K.

Table I. Non-Hydrogen Atom Coordinates

atom	x	y	z
		Anion	
Ag(1)	0.4338 (1)	0.4499 (4)	0.65813 (8)
Ag(2)	0.4295 (1)	−0.0489 (4)	0.65337 (8)
Ag(3)	$^1/_2$	−0.0345 (7)	$^3/_4$
Br(1)	0.3520 (1)	0.6925 (6)	0.62731 (9)
Br(2)	0.4487 (1)	0.2038 (6)	0.60152 (9)
Br(3)	0.4191 (1)	0.1922 (6)	0.71254 (9)
Br(4)	0.5082 (1)	0.7153 (6)	0.69133 (9)
		Cation 1	
C(11)	0.6328 (9)	0.309 (6)	0.2602 (8)
C(12)	0.6726 (9)	0.447 (5)	0.2674 (8)
O(1)	0.6837 (6)	0.563 (3)	0.2421 (5)
N(1)	0.7020 (7)	0.471 (4)	0.3050 (6)
C(13)	0.7462 (9)	0.598 (5)	0.3218 (8)
C(14)	0.7819 (10)	0.564 (6)	0.2999 (9)
C(15)	0.7676 (11)	0.540 (7)	0.3624 (8)
C(16)	0.7324 (12)	0.838 (6)	0.3157 (11)
		Cation 2	
C(21)	0.0776 (10)	0.273 (5)	0.1853 (7)
C(22)	0.0941 (9)	0.112 (5)	0.1627 (8)
O(2)	0.1327 (6)	0.014 (3)	0.1764 (5)
N(2)	0.0669 (7)	0.086 (4)	0.1261 (5)
C(23)	0.0758 (11)	−0.061 (5)	0.0972 (7)
C(24)	0.0748 (13)	−0.282 (6)	0.1103 (8)
C(25)	0.0356 (13)	−0.005 (7)	0.0592 (9)
C(26)	0.1246 (11)	−0.023 (6)	0.0928 (9)
		Cation 3	
C(31)	0.8002 (11)	0.320 (5)	0.0707 (9)
C(32)	0.8085 (9)	0.415 (4)	0.0354 (7)
O(3)	0.7818 (7)	0.369 (4)	0.0014 (5)
N(3)	0.8414 (8)	0.561 (4)	0.0382 (7)
C(33)	0.8559 (12)	0.669 (5)	0.0079 (9)
C(34)	0.8975 (15)	0.817 (7)	0.0293 (10)
C(35)	0.8154 (12)	0.799 (6)	−0.0156 (11)
C(36)	0.8765 (15)	0.515 (6)	−0.0127 (11)

Structure Determination. A unique data set, measured to $2\theta_{max}$ = 50° on a Syntex P$\bar{1}$ four-circle diffractometer in conventional 2θ–θ scan mode, yielded 5371 independent reflections. Of these, 1706 with $I > 3\sigma(I)$ were considered observed and used in the full-matrix least-squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U)_H$ were included constrained at idealized values. Residuals at convergence (R, R') on $|F|$ were 0.053 and 0.062, reflection weights being $(\sigma^2(F_o) + 0.0005(F_o{}^2))^{-1}$. Neutral complex scattering factors[2] were employed; computation used the X-RAY 76 program system[3] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. No extinction correction was considered necessary.

Abnormal Features. Following the successful refinement of the heavy-atom component of the structure in terms of the $(Ag_5Br_8)_n{}^{3n-}$ species, residual difference map densities were modeled in terms of three *N-tert*-butylacetamide groups, necessarily protonated on stoichiometric grounds, presumably on the oxygen. The final refinement included all hydrogen atoms, except one of the oxygen that was regarded as ambiguous. Anisotropic refinement of the non-hydrogen atoms yielded a nonpositive definite thermal tensor (C(24)), probably a result of high cation thermal motion and limited data, rather than a deficient cation model; it should be noted, however, that cation

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0020-1669/84/1323-3825$01.50/0

Table II. Anion Geometry[a]

	Distances (Å)		
Ag(1)-Br(1)	2.745 (4)	Ag(2)-Br(3)	2.739 (7)
Ag(1)-Br(2)	2.730 (7)	Ag(2)-Br(1^{ii})	2.697 (4)
Ag(1)-Br(3)	2.707 (7)	Ag(2)-Br(4^{ii})	2.708 (4)
Ag(1)-Br(4)	2.699 (4)	Ag(2)···Ag(3)	3.476 (9)
Ag(1)···Ag(2)	3.172 (4)	Ag(3)-Br(3)	2.718 (4)
Ag(1)···Ag(2^{i})	3.188 (4)	Ag(3)-Br(4^{ii})	2.735 (7)
Ag(2)-Br(2)	2.667 (6)		
	Angles (deg)		
Br(1)-Ag(1)-Br(2)	109.3 (2)	Br(3)-Ag(3)-Br(4^{ii})	100.7 (2)
Br(1)-Ag(1)-Br(3)	109.2 (2)	Br(3)-Ag(3)-Br(3^{iii})	116.0 (2)
Br(1)-Ag(1)-Br(4)	107.1 (1)	Br(3)-Ag(3)-Br(4^{iv})	115.5 (1)
Br(2)-Ag(1)-Br(3)	107.9 (2)	Br(4^{ii})-Ag(3)-Br(4^{iv})	109.0 (2)
Br(2)-Ag(1)-Br(4)	113.9 (2)	Ag(1)-Br(1)-Ag(2^{i})	71.7 (1)
Br(3)-Ag(1)-Br(4)	109.5 (2)	Ag(1)-Br(2)-Ag(2)	72.0 (2)
Br(2)-Ag(2)-Br(3)	108.7 (2)	Ag(1)-Br(3)-Ag(2)	71.3 (2)
Br(2)-Ag(2)-Br(1^{ii})	116.7 (2)	Ag(1)-Br(3)-Ag(3)	112.5 (2)
Br(2)-Ag(2)-Br(4^{ii})	111.7 (2)	Ag(2)-Br(3)-Ag(3)	79.1 (2)
Br(3)-Ag(2)-Br(1^{ii})	109.5 (2)	Ag(1)-Br(4)-Ag(2^{i})	72.2 (1)
Br(3)-Ag(2)-Br(4^{ii})	100.8 (2)	Ag(1)-Br(4)-Ag(3^{i})	117.6 (2)
Br(1^{ii})-Ag(2)-Br(4^{ii})	108.2 (2)	Ag(2^{i})-Br(4)-Ag(3^{i})	79.4 (2)

[a] Transformations: (i) (x, $1 + y$, z); (ii) (x, $y - 1$, z); (iii) ($1 - x$, y, $1^1/_2 - z$); (iv) ($1 - x$, $y - 1$, $1^1/_2 - z$).

Table III. Cation Non-Hydrogen Geometries

	cation		
	1	2	3
	Distances (Å)		
C(1)-C(2)	1.40 (4)	1.48 (4)	1.51 (4)
C(2)-O	1.29 (4)	1.24 (3)	1.27 (3)
C(2)-N	1.38 (3)	1.33 (3)	1.31 (4)
N-C(3)	1.47 (3)	1.49 (4)	1.47 (4)
C(3)-C(4)	1.51 (5)	1.49 (5)	1.53 (5)
C(3)-C(5)	1.46 (4)	1.54 (4)	1.47 (4)
C(3)-C(6)	1.58 (5)	1.49 (5)	1.47 (6)
	Angles (deg)		
C(1)-C(2)-O	126 (2)	122 (2)	122 (2)
N-C(2)-O	116 (2)	121 (3)	116 (3)
C(1)-C(2)-N	118 (3)	117 (2)	122 (2)
C(2)-N-C(3)	131 (2)	127 (2)	130 (2)
N-C(3)-C(4)	110 (2)	110 (2)	105 (2)
N-C(3)-C(5)	109 (3)	104 (3)	110 (3)
N-C(3)-C(6)	109 (2)	111 (2)	109 (3)
C(4)-C(3)-C(5)	111 (2)	115 (3)	108 (3)
C(4)-C(3)-C(6)	104 (3)	107 (3)	107 (3)
C(5)-C(3)-C(6)	113 (3)	110 (3)	117 (3)

formulations in terms of alternative species such as *N-tert*-butylacetamidinium are also plausible possibilities.

Results are given in Tables I–III and Figures 1 and 2 as is atom numbering.

Discussion

The heavy-atom component of the structure has been successfully modeled in terms of the novel $(Ag_5Br_8)_n{}^{n}$- polyanion. $(AgX_2)_n{}^{n-}$ polyanions may be regarded as a string of edge-shared tetrahedra, with a spine of silver atoms; a double string in which halide atoms generating a second set of shared edges become the spine yield $(Ag_2X_3)_n{}^{n-}$, while the addition of a third set, with a central silver spine again, yields $(Ag_3X_4)_n{}^{n-}$. Removal of every second silver atom from the spine yields the present $(Ag_5X_8)_n{}^{3n-}$ (X = Br) species, the central spine coinciding with a crystallographic twofold axis with metal-to-metal repeat as unit *b*. In consequence of the loss of every second spinal silver atom, there are no four-coordinate halide atoms; those in the body of the polymer are three-coordinate and those at the periphery two-coordinate. All silver atoms are four-coordinate pseudotetrahedral, with various deviations from ideal geometry. The central silver, Ag(3), has two considerably different angles (116.0 (2), 109.0 (2)°) astride the spine, with two twofold rotor-related pairs of 115.5 (1) and 100.7 (2)°.

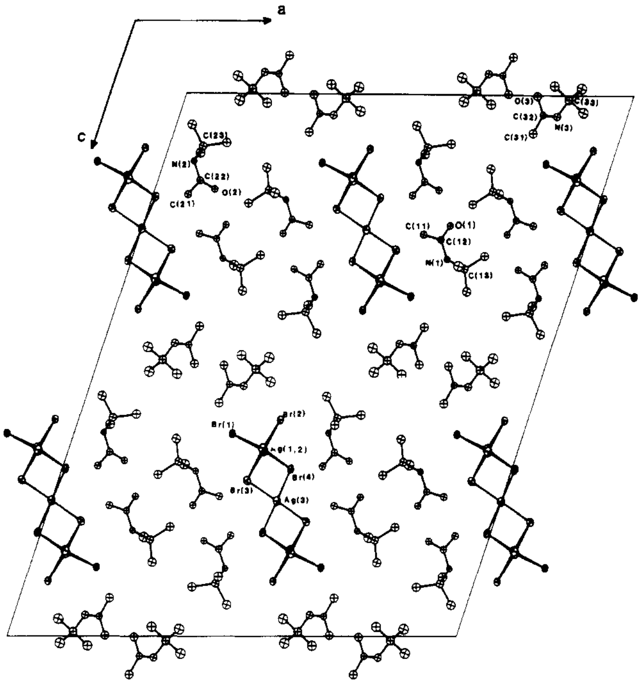

Figure 1. Projection of the unit cell down *b*, the spine of the polymer. Non-hydrogen atom numbering is shown.

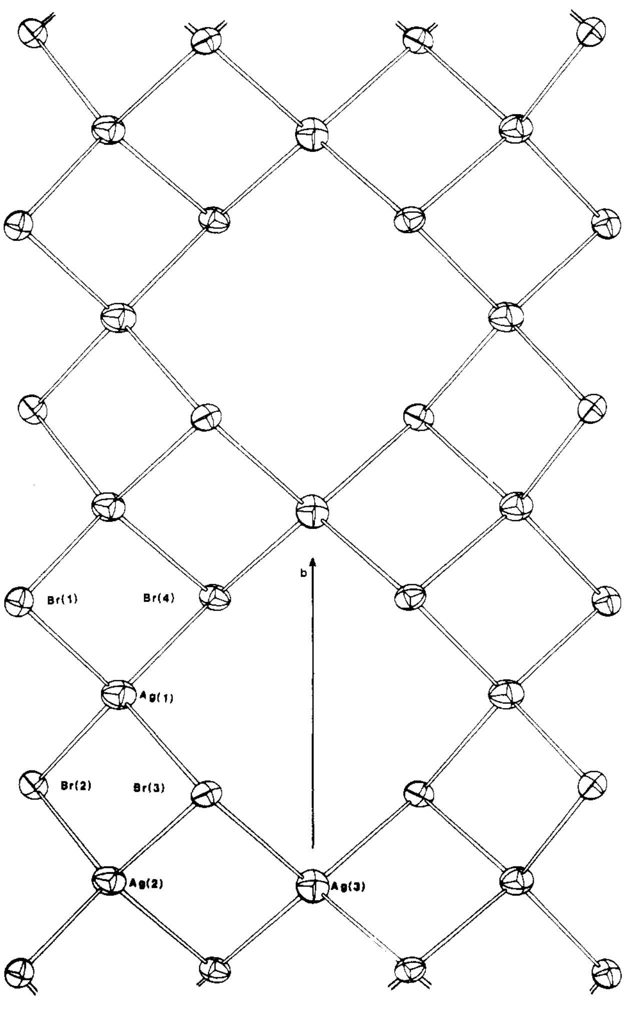

Figure 2. Projection of the $(Ag_5Br_8)_n{}^{3n-}$ polyanion normal to *b*. 20% thermal ellipsoids are shown.

The least distorted angular geometry is that of Ag(1), reflecting the fact that its coordination tetrahedron shares only one edge. About Ag(2) the angle between peripheral bromines Br(2)–Ag–Br(1) ($x, y - 1, z$) is enlarged to 116.7 (2)°, while that subtending the shared edge to Ag(3), Br(3)–Ag(2)–Br(4) ($x, y - 1, z$) is dimished (100.8 (2)°). Among the bond lengths, only slight differences are found about Ag(3) (2.718 (4), 2.735 (7) Å), with greater differences about Ag(1) (range 2.699 (4)–2.745 (4) A) and considerable differences about Ag(2) (2.667 (6)–2.739 (7) Å). Interestingly, silver⋯silver distances are more compact than in $(Ag_2I_3)_n^{n-}$ where Ag⋯Ag across the polymer is 3.045 (9) and longitudinally 3.697 (9) Å; the corresponding distances in the present polymer are 3.476 (9) and 3.172 (4) Å with the shortest Ag⋯Ag distance occurring in the *iodide*. The cation geometries (Table III) are consistent with the proposed $MeCOHNHCMe_3$ cation, presumably arising out of a prolonged high-temperature reaction of methyl and *tert*-butyl cyanide and traces of moisture remaining in the freshly precipitated silver cyanide. The C–C-O–NC skeletons are planar (σ (least-squares plane), 0.014, 0.011, 0.021 Å) in consequence of amide conjugation, also evident in the geometries. O(H) nearest-neighbor contacts are consistent with reasonable and anticipated hydrogen-bonding expectations (O(1)⋯O(2) ($x + \frac{1}{2}, y + \frac{1}{2}, z$), 2.41 (2) Å; O(3)⋯O(3) ($1\frac{1}{2} - x, \frac{1}{2} - y, z$), 2.35 (3) Å).

Acknowledgment. We gratefully acknowledge assistance of a program by Dr. Lutz M. Engelhardt in solving the structure.

Registry No. $(C_6H_{14}NO)_3[Ag_5Br_8]$, 92219-58-4.

Supplementary Material Available: Listings of thermal and hydrogen parameters and structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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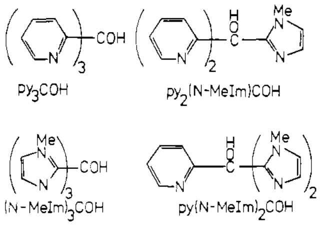
Coordination Chemistry of Methylmercury(II) with Flexible Tripod Ligands Containing Pyridyl and *N*-Methylimidazolyl Groups, Including the Crystal Structure of [Bis(*N*-methylimidazol-2-yl)(pyridin-2-yl)methanol-*N*,*N′*,*N″*]methylmercury(II) Nitrate, $[MeHg(py(N\text{-}MeIm)_2COH)]NO_3$

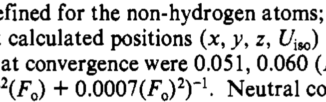
Allan J. Canty,*[1] Jennifer M. Patrick,[2] and Allan H. White[2]

Received January 23, 1984

In its complexes with tripod ligands containing pyridine and *N*-methylimidazole groups studied crystallographically, $[MeHgL]NO_3$ (L = $(py)_3COH$, $(py)_2(N\text{-}MeIm)COH$),[3] the ligands are present as tridentates. The complexes have one strong Hg–N coordination interaction and two weaker Hg⋯N interactions. However, in the $(N\text{-}MeIm)_3COH$ complex, $MeHg^{II}$ is bound to one *N*-MeIm group and weakly to the hydroxy group, with two *N*-MeIm groups uncoordinated.[4]



We report here the crystal structure determination for $[MeHg(py(N\text{-}MeIm)_2COH)]NO_3$, completing the series of complexes involving $(py)_n(N\text{-}MeIm)_{3-n}COH$ (n = 0–3). The synthesis and spectroscopic study of $[MeHgL]NO_3$ (L = $pyCH_2OH$, $N\text{-}MeImCH_2OH$, $pyzCH_2OH$) are also reported, as the first two of these are model ligands closely related to the tripod ligands.



Experimental Section

Reagents. Methylmercuric nitrate,[5] $py(N\text{-}MeIm)_2COH$,[6] $pyzCH_2OH$,[7] and $N\text{-}MeImCH_2OH$[8] were prepared and purified as described, and $pyCH_2OH$ (Fluka) was distilled under reduced pressure.

Preparation of Complexes. The complex $[MeHg(py(N\text{-}MeIm)_2COH)]NO_3$ was prepared as described,[4] and for the new complexes equimolar quantities of $MeHg^{II}$ nitrate and ligand in acetone gave microcrystalline $[MeHg(pyCH_2OH)]NO_3$ immediately (yield 81%) and microcrystalline $[MeHg(pyzCH_2OH)]NO_3$ (41%) and $[MeHg(N\text{-}MeImCH_2OH)]NO_3$ (92%) formed on slow evaporation over several days. Characterization data for the new complexes are summarized in Table I. Microanalyses were by the Australian Microanalytical Service.

Physical Measurements. ^1H NMR spectra at 100 MHz were measured on a JEOL JNM-4H-100 spectrometer. Chemical shifts were measured relative to 1,4-dioxane as internal standard; shifts upfield of 1,4-dioxane are taken as negative. Apparent protonation constants log K_H (pK_a of LH^+) were measured in 50% dioxane–water following an experimental procedure given earlier.[9-11]

Crystallography

Crystal Data: $C_{15}H_{16}HgN_6O_4$, M_r = 544.9, monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14, variant), a = 15.786 (4) Å, b = 15.065 (3) Å, c = 7.715 (2) Å, β = 91.24 (2)°, V = 1834.2 (8) Å^3, D_{measd} = 1.95 (1) g cm^{-3}, D_{calcd} (Z = 4) = 1.97 g cm^{-3}, $F(000)$ = 1040, monochromatic Mo Kα radiation, λ = 0.7106$_9$ Å, μ_{Mo} = 81 cm^{-1}. Specimen: pseudospherical polyhedron, maximum and minimum diameters 0.30 and 0.25 mm, approximately as Syntex sphere 0.28 mm in diameter for absorption correction, A^*_{min}, A^*_{max} = 3.31, 4.82; T = 295 K.

Structure Determination. A unique data set was measured within the limit $2\theta_{max}$ = 45° on a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta-\theta$ scan mode; 2510 independent reflections were measured, 1798 with $I > 3\sigma(I)$ being considered observed and used in the six-block least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms were included at calculated positions (x, y, z, U_{iso}) and constrained. Residuals on $|F|$ at convergence were 0.051, 0.060 (R, R'), reflection weights being $(\sigma^2(F_o) + 0.0007(F_o)^2)^{-1}$. Neutral complex scattering factors were used;[12] computation used the X-RAY 76 program system[13] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Atom numbering is shown in the molecular projection; fractional coordinates for non-hydrogen atoms are given in Table II, and interatomic distances and angles, in Table III.

Unusual Features. High thermal motion on the nitrate ion may

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(1) University of Tasmania.
(2) University of Western Australia.
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