# Refinement of the Crystal and Molecular Structure of Potassium Tetranitritomercurate(II) Nitrate by Neutron Diffraction

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A neutron diffraction study of the title compound has been carried out. Crystals are orthorhombic, space group *Pnma*, $Z = 4$, $a = 12.290(6)$, $b = 10.644(1)$, $c = 9.377(1)$ Å. Full matrix least-square refinements have produced *R* 0.034. The neutron-diffraction results agree well with results from an earlier *X*-ray diffraction study. The structure consists of $K^+$, $[Hg(NO_2)_4]^{2-}$, and $(NO_3)^-$ as discrete ions, with the four nitrite groups co-ordinated to the mercury through both oxygens as bidentate chelates. The arrangement of the eight oxygens about the mercury can be described in terms of a highly distorted square antiprism or alternatively as a highly distorted undecahedron.

A NEUTRON diffraction refinement of potassium tetranitritomercurate(II) nitrate has been carried out because the presence of heavy atoms gives rise to a high percentage of scattering in the *X*-ray method, resulting in low accuracy of positional co-ordinates of the light atoms. Also, the presence of four bidentate nitrite groups, giving rise to a highly distorted square antiprism or undecahedron about the mercury ion, presents an arrangement of light oxygen atoms around a large metal ion for which only a few structures have been previously determined.

A previous *X*-ray study of the structure of potassium tetranitritomercurate(II) nitrate has been carried out.[1a]

## EXPERIMENTAL

*Crystal Data.*—$K_3[Hg(NO_2)_4]NO_3$, $M = 563.95$, Orthorhombic, $a = 12.290(6)$, $b = 10.644(1)$, $c = 9.377(1)$ Å, $U = 1\,226.7$ Å$^3$, $D_c = 3.14$, $Z = 4$, $D_m = 3.0 \pm 0.1$ g cm$^{-3}$ (ref. 1*a*). Calculated neutron absorption coefficient, $\mu = 0.75 \pm 0.1$ cm$^{-1}$. Space group *Pnma* (No. 62, $D_{2h}^{16}$).

Large single crystals of potassium tetranitritomercurate(II) nitrate were grown by slow evaporation of a solution of mercury(II) nitrate with an excess of potassium nitrite. A well formed sample 1.28 mm$^3$ in volume was mounted on a computer-controlled four-circle neutron diffractometer 2TanA at the Lucas Heights High-Intensity Flux Atomic Reactor. Data were recorded automatically by use of a crystal-monochromated neutron beam of wavelength $\lambda = 0.981$ Å. The orthorhombic cell constants were refined by least-square techniques from the diffractometer setting angles observed for 87 reflections well-distributed in reciprocal space. No significant change in the intensity of one standard reflection, measured at regular intervals, was observed.

Four sets of equivalent reflections were recorded by use of the standard $\omega$—$2\theta$ step-scan technique. Estimated standard deviations were assigned to individual reflections on the basis of a least squares polynomial regression of the form: $\sigma^2_M(I) = \sum_{n=1}^{N} A_n I^{n-1}$ to determine $A_n$, where $\sigma^2_M(I)$ is the variance of the mean obtained for each quartet of equivalent reflections. The analysis was performed on the absorption-corrected intensities before the application of the Lorentz correction. This approach was adopted in order to estimate non-counting errors in the data set. Equivalent reflections were then averaged to yield a unique set of 1 045 reflections, all of which were used in the refinement.

*Structure Refinement.*—The atomic co-ordinates from the *X*-ray analysis [1a] were refined isotropically by block-diagonal least-squares to a conventional *R* of 12%; introduction of anisotropic temperature factors for each atom then reduced this to 8%.

The structure was further refined by use of the Brookhaven full-matrix least-squares programme LINUS with experimental weights. Neutron scattering lengths used were: $b_K$ 0.370, $b_{Hg}$ 0.266, $b_N$ 0.940, $b_O$ 0.577 ($10^{-12}$ cm). The quantity minimized in the refinements was $\Sigma w(|F_o|^2 - |F_c|^2)^2$. Each reflection was assigned a weight *w* inversely proportional to the estimated variance of the observation $w^{-1} = \sigma^2(F^2)$.

In the last cycle of refinement where 104 parameters were varied including an isotropic extinction parameter,[1b] no parameter varied by $>0.001\sigma$. The final agreement factors are $R_{F^2}$ $(= \Sigma||F_o^2| - |F_c^2||/\Sigma|F_o^2|)$ 0.049, and $R'_{F^2}\{= [\Sigma w(|F_o^2| - F_c^2|)^2/\Sigma w|F_o^4|]^{\frac{1}{2}}\}$ 0.052, and the conventional *R* factor is 0.034.

Positional and thermal parameters are shown in Table 1, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21558 (10 pp., 1 microfiche).†

## DISCUSSION

The neutron refinement has confirmed the gross results of the *X*-ray analysis, *i.e.*, the formula of the compound is $K_3[Hg(NO_2)_4]NO_3$ with four nitrite groups acting as bidentate ligands. The arrangement of the nitrogen and oxygen atoms about mercury is shown in Figure 1, and a unit-cell projection down the *z* axis is shown in Figure 2.

The mirror plane contains the mercury atom and the atoms O(4), O(5), N(2), and N(3) of the $[Hg(NO_2)_4]^{2-}$ ion. Atoms N(1), O(1), O(2), and O(3) reflect across this plane, and this results in eight oxygen and four nitrogen atoms for the complex ion. Atoms N(4) and O(7) of the nitrate ion are in the plane, as is K(1). O(6) of the nitrate ion reflects across the plane as does K(2). This can be seen clearly in Figure 2.

The dimensions of the complex are listed in Table 2 together with the dimensions for the $NO_3^-$ ion, and corresponding results from the *X*-ray diffraction study of

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[1] (*a*) D. Hall and R. V. Holland, *Inorg. Chim. Acta*, 1969, **3**, 235; (*b*) W. H. Zachariasen, *Acta Cryst.*, 1967, **23**, 558.

ref. 1*a*. There is reasonable agreement between the bond distances. Standard deviation ranges given in ref. 1*a* are: Hg-O, Hg-N 0.027—0.03 9Å, and for O,N-O,N 0.018—0.058 Å. The neutron results show the bond lengths in the nitrate ion to be essentially equal and close to the accepted value of (1.245 ± 0.01) Å for a regular environment.[2] The range of standard deviations given in ref. 1 for O-N-O angles is 2.0—3.9° and for N-Hg-N 0.5—1.4°. The angles computed from the neutron study generally lie outside these ranges; however the nitrate angles are much closer to the ideal value (120°) expected for a discrete ion. Also, the three O-N-O nitrate angles listed from the neutron study compare more favourably with each other and with the value found for sodium nitrite [114.9(5)°].[3] The O-N-O angle in the nitrite ion would be expected to be less than the ideal when co-ordinated in a bidentate arrangement,[4,5] and this is indicated here. Evidence for this exists also for the bidentate nitrate ion for which a reduction in O-N-O angle has been noted on co-ordination.[6,7] The effect of co-ordination upon the structures of the nitrite ions appears slight. The mean of the N-O distances involving the oxygen atoms which form the shorter bonds to mercury [1.249(3) Å] is greater than the mean of the five N-O distances involving oxygen atoms which form long bonds to mercury [1.233(1) Å]. This

TABLE 1

Final atomic co-ordinates and thermal parameters * (× 10⁴), with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| K(1) | 0.012 75(23) | 0.250 00(0) | 0.599 45(24) | 34(2) | 49(2) | 73(2) | 0(0) | 9(2) | 0(0) |
| K(2) | 0.299 92(18) | 0.006 42(15) | 0.437 34(17) | 44(2) | 59(1) | 80(2) | −1(1) | −6(1) | 1(1) |
| Hg | 0.088 64(7) | 0.250 00(0) | 0.188 18(6) | 50(1) | 39(1) | 60(1) | 0(0) | −6(1) | 0(0) |
| N(1) | 0.037 50(7) | 0.004 73(6) | 0.303 30(7) | 55(1) | 44(1) | 102(1) | −3(0) | 1(1) | 13(1) |
| N(2) | 0.331 02(10) | 0.250 00(0) | 0.158 36(11) | 42(1) | 63(1) | 95(1) | 0(0) | 4(1) | 0(0) |
| N(3) | −0.030 19(12) | 0.250 00(0) | −0.081 15(9) | 52(1) | 69(1) | 61(1) | 0(0) | −13(1) | 0(0) |
| N(4) | 0.248 22(9) | 0.250 00(0) | 0.734 04(9) | 28(1) | 54(1) | 60(1) | 0(0) | 1(1) | 0(0) |
| O(1) | 0.022 18(14) | 0.028 82(11) | 0.176 39(13) | 78(2) | 68(1) | 101(1) | −10(1) | −28(1) | 2(1) |
| O(2) | 0.078 35(13) | 0.092 70(11) | 0.373 12(12) | 61(1) | 71(1) | 75(1) | −1(1) | 1(1) | −9(1) |
| O(3) | 0.277 16(13) | 0.152 26(10) | 0.166 51(13) | 67(2) | 56(1) | 117(2) | −7(1) | −10(1) | −10(1) |
| O(4) | −0.082 29(16) | 0.250 00(0) | 0.031 04(18) | 34(2) | 84(2) | 93(2) | 0(0) | 4(1) | 0(0) |
| O(5) | 0.070 87(22) | 0.250 00(0) | −0.066 10(17) | 45(2) | 93(2) | 81(2) | 0(0) | 15(2) | 0(0) |
| O(6) | 0.221 28(12) | 0.149 21(10) | 0.678 86(12) | 54(2) | 58(1) | 106(1) | −2(1) | 8(1) | −18(1) |
| O(7) | 0.297 61(18) | 0.250 00(0) | 0.849 03(18) | 34(2) | 134(2) | 79(2) | 0(0) | −12(2) | 0(0) |

* The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE 2

Molecular bond distances and angles of the $[Hg(NO_2)_4]^{2-}$ and the $NO_3^-$ ions

| | Neutron | *X*-ray * |
|---|---|---|
| (*a*) Bond lengths (Å) | | |
| N(1)–O(1) | 1.231(1) | 1.22 |
| N(1)–O(2) | 1.248(1) | 1.21 |
| N(2)–O(3) | 1.235(1) | 1.28 |
| N(3)–O(4) | 1.232(2) | 1.25 |
| N(3)–O(5) | 1.250(3) | 1.30 |
| Hg–O(1) | 2.494(1) | 2.49 |
| Hg–O(2) | 2.414(1) | 2.45 |
| Hg–O(3) | 2.548(2) | 2.52 |
| Hg–O(4) | 2.566(2) | 2.58 |
| Hg–O(5) | 2.394(2) | 2.34 |
| Hg–N(1) | 2.894(1) | 2.86 |
| Hg–N(2) | 2.992(2) | 3.04 |
| Hg–N(3) | 2.917(1) | 2.96 |
| N(4)–O(7) | 1.237(2) | 1.30 |
| N(4)–O(6) | 1.236(1) | 1.25 |
| (*b*) Angles (°) | | |
| O(1)–N(1)–O(2) | 114.34(09) | 118.5 |
| O(3)–N(2)–O(3′) | 114.72(17) | 107.5 |
| O(4)–N(3)–O(5) | 114.84(15) | 110.2 |
| N(1)–Hg–N(2) | 104.54(03) | 104.9 |
| N(1)–Hg–N(3) | 102.37(03) | 101.2 |
| N(1)–Hg–N(1) | 128.86(04) | 131.3 |
| N(2)–Hg–N(3) | 114.68(05) | 113.2 |
| O(6)–N(4)–O(7) | 119.74(04) | 121.6 |
| O(6)–N(4)–O(6′) | 120.41(15) | 116.7 |

* From ref. 1*a*.

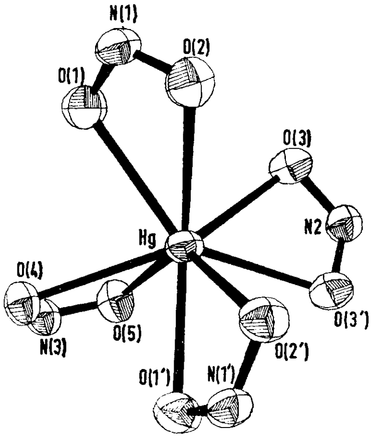

FIGURE 1 Numbering scheme for the $[Hg(NO_2)_4]^{2-}$ ion; thermal ellipsoids scaled at 50% probability

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[2] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

[3] M. I. Kay and B. C. Frazier, *Acta Cryst.*, 1961, **14**, 56.

[4] M. G. B. Drew and D. Rogers, *Chem. Comm.*, 1965, 476.

[5] I. M. Procter and F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 1248.

[6] G. Bergman, jun., and F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1208, and refs. therein.

[7] (*a*) F. A. Cotton and J. G. Bergman, *J. Amer. Chem. Soc.*, 1964, **86**, 2941; (*b*) G. A. Jeffrey and D. W. Cruickshank, *Quart. Rev.*, 1953, **4**, 335.

appears to be significant ($\Delta/\sigma$ 7.8).[7a] Nitrate groups show this same effect to a lesser degree for uni- and bidentate co-ordination through the oxygen atom(s).[6] An inverse relation also exists between the nitrito-bond length to the mercury ion and the O–N–O bond angle.

Hall and Holland have referred to the eight oxygen atoms of the nitrito-groups as forming a highly distorted square antiprism about mercury. The angles N(1)–Hg–N(2) [N(1′)–Hg–N(2)], N(1)–Hg–N(3) [N(1′)–Hg–N(3)], N(2)–Hg–N(3), and N(1)–Hg–N(1′) are 104.54, 102.37, 114.68, and 128.86°. Hence, if one regards each nitrito-group as forming only one bond to mercury, with the bond pointing towards the nitrogen atom, then the four such bonds form a slightly distorted tetrahedron. The sum of these six angles is (657.36 ± 0.21)° as compared to 656.82°, the sum of six angles of size 109.47°. The tendency for constrained pairs of atoms to interact such that the mean positions of the pairs are roughly at the vertices of one of the usual co-ordination polyhedra has been noted previously.[6,7]

The idealized arrangements of the eight ligand oxygens are shown in Figure 3. In arrangement (a), the square antiprismatic type ($D_{4d}$, $\bar{8}2m$) in which the mirror plane is perpendicular to the paper and contains the line (6)—(8), the chelates span the positions (6)—(8) [O(5)–N(3)–O(4)], (3)—(7) and the symmetry-related (2)—(5) [O(1)–N(1)–O(2)], and (1)—(4) [O(3)–N(2)–O(3′)]. Figure 3(b) shows how the oxygen arrangement can be derived from an undecahedron ($C_{2v}$, $mm2$), containing one rectangular and ten triangular faces. This Figure is labelled similarly to the antiprism, with the mirror plane perpendicular to the paper through (6)—(8) so that the geometric similarities between the two distorted arrangements can be seen. The undecahedron was accorded major theoretical status by Kimball[8] but no experimental evidence has been forthcoming. The discussion by Hoard and Silverton[9] of the possible stereoisomers of a tetrakis-bidentate molecule in the square antiprismatic configuration assumed that bridging as across (6)—(8) in Figure 3(a) could not occur. Similarly, studies evaluating the relative merits of the possible stereoisomers of eight-co-ordinated metal complexes for identical and symmetric bidentate ligands by mapping the ligand–ligand repulsive energy for a range of normalized ligand bites assume spanning of the polyhedral edges.[10]

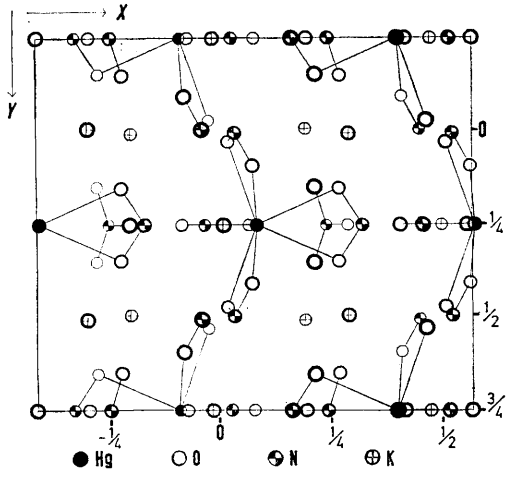

FIGURE 2 Unit-cell projection of the crystal structure on the $xy$ plane. The thickness of the boundary ellipse is a function of the height of the atom from the projection plane

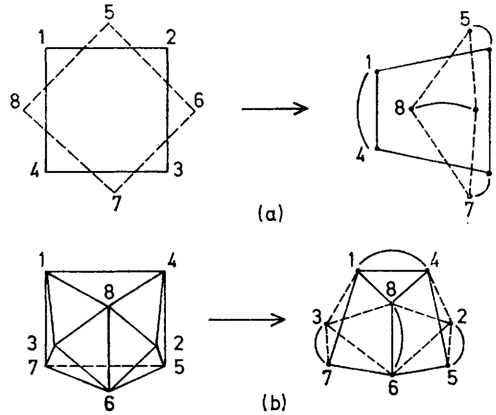

FIGURE 3 Relationship of the oxygen arrangement to (a) a square antiprism, and (b) to an undecahedron. The similarity of the two final arrangements on the right of the Figure can be seen by rotation of the square antiprismatic arrangement clockwise through 90°

For a perfect bicapped trigonal prism, the triangular faces [faces 148 and 567 in Figure 3(b)] are parallel, whereas an angle of 25.7° is expected between the corresponding faces in the most-favoured square antiprism.[11] The angle found between these two triangular faces is 17.70°.

TABLE 3

Close approaches (>3.2 Å) to the potassium ions

| | | | |
|---|---|---|---|
| K(1) · · · O($7^{\mathrm{VII}}$) | 2.688 | K(2) · · · O(6) | 2.894 |
| K(1) · · · O(2) | 2.821 | K(2) · · · O(2) | 2.936 |
| K(1) · · · O($2^{\mathrm{VI}}$) | 2.821 | K(2) · · · O($1^{\mathrm{VII}}$) | 2.942 |
| K(1) · · · O(6) | 2.876 | K(2) · · · O($6^{\mathrm{III}}$) | 2.947 |
| K(1) · · · O($6^{\mathrm{VI}}$) | 2.876 | K(2) · · · O($4^{\mathrm{VII}}$) | 2.984 |
| K(1) · · · N($1^{\mathrm{IV}}$) | 2.926 | K(2) · · · O(3) | 2.990 |
| K(1) · · · N($1^{\mathrm{II}}$) | 2.926 | K(2) · · · O($7^{\mathrm{III}}$) | 3.094 |
| K(1) · · · N(3) | 3.041 | K(2) · · · O($1^{\mathrm{III}}$) | 3.154 |
| K(1) · · · N(4) | 3.157 | K(2) · · · O($5^{\mathrm{III}}$) | 3.158 |
| K(2) · · · O($3^{\mathrm{III}}$) | 3.893 | | |

Roman numeral superscripts refer to the following equivalent positions, relative to the reference molecule at $x, y, z$:

I $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$
II $-x, \frac{1}{2}+y, -z$
III $\frac{1}{2}-x, -y, \frac{1}{2}+z$
IV $-x, -y, -z$
V $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$
VI $x, \frac{1}{2}-y, z$
VII $\frac{1}{2}+x, y, \frac{1}{2}-z$

Only one plane could be drawn through four of the oxygen atom positions, namely the plane 1457, and this is required by symmetry.

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[8] G. E. Kimball, *J. Chem. Phys.*, 1940, **8**, 188.

[9] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[10] D. G. Blight and D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1556.

[11] T. J. Pinnavaia, G. Podolsky, and P. W. Codding, *J.C.S. Chem. Comm.*, 1973, 242.

It would appear that the distorted square antiprismatic description of the observed stereochemistry is a better approximation to the observed stereochemistry than a bicapped trigonal prism.[12]

The closer approaches of the potassium ions are listed in Table 3. K(1) has nine oxygen or nitrogen neighbours at <3.2 Å while K(2) has ten. K(1) lies in the mirror plane and its approaches to atoms not in the plane duplicate. There is no evidence for a particular polyhedral arrangement about these ions, each occupying a more or less spherical cavity.

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[12] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1969, **91**, 1636.