

Table 3. Average values of various structural parameters (volumes Å³, distances Å) in tris(acetylacetonato)iron(III)

Compound	Space group	Volume per molecule	Volume of cavity	Fe—O	O···O 'bite'	O···O other	C—O	C—C _m	C—C _b	Reference
(I)	<i>Pbca</i>	435		1.99	2.74	2.86	1.26	1.53	1.38	Iball & Morgan (1967)
(II)	<i>P2₁ca</i>	533	98	1.99	2.76	2.85	1.28	1.52	1.38	This work
(IV)	<i>R3</i>	557	122	2.00	2.75	2.86	1.27	1.51	1.39	Pang, Lucken & Bernardinelli, (1990)

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Structure of a 1:1 Addition Compound of Mercuric Bromide with 3-Methyl-4-nitropyridine 1-Oxide

BY HU SHENG-ZHI* AND SHI DA-SHUANG

Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

AND LI SONG-XIAN* AND YANG YAN-CHAO

Centre for Research in Solid Materials, Fuzhou University, Fuzhou 350002, People's Republic of China

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Abstract. Polymeric dibromo(3-methyl-4-nitropyridine 1-oxide)mercury, [HgBr₂(C₆H₆N₂O₃)], *M_r* = 514.53, monoclinic, *P2₁/c*, *a* = 13.338 (2), *b* = 11.599 (1), *c* = 7.096 (2) Å, β = 93.74 (3)°, *V* = 1095.5 Å³, *Z* = 4, *D_x* = 3.120 g cm⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 212.6 cm⁻¹, *F*(000) = 920, *T* = 294 K, *R* = 0.061 for 1387 observed reflections. The structure is polymeric through six bridging atoms, the Hg coordinating to two O atoms from the pyridine 1-oxide ligand and four Br atoms. The Hg atom has a very distorted octahedral environment. The HgBr₂ subunit deviates slightly from linearity [Br—Hg—Br = 172.67 (7)°] with a mean bond length of 2.424 Å. The closest non-bonded Hg···Hg contacts are at 4.119, 4.354 and 4.119 Å, in three directions.

Introduction. In previous research, some relationships were discovered among the frequency-doubling effect (the effect of a light wave at twice the frequency of an incident wave passing through a nonlinear

media), molecular electronic structure, and molecular orientation in some organic crystals (Li, Liu, Wu, Shi & Hu, 1987). In order to find crystals with a higher frequency-doubling effect, 15 complexes of some metal halides with the organic ligand 3-methyl-4-nitropyridine 1-oxide (pom) have been synthesized and investigated. Among them the crystal structures of complexes Cd(pom)₂Br₂ and Hg(pom)Br₂ have been determined. The former belongs to the orthorhombic space group *Fdd2* with *a* = 15.733 (3), *b* = 56.739 (11), *c* = 3.957 (1) Å, having the expected frequency-doubling effect, for which a structural report is in preparation. However, the latter belongs to the centrosymmetric space group *P2₁/c* and has no frequency-doubling effect, though Hg belongs to the same group as Cd (group IIB). In this paper the synthesis and crystal structure of Hg(pom)Br₂ are reported.

Experimental. Equimolar HgBr₂ and pom (3-methyl-4-nitropyridine 1-oxide) were dissolved in water/methyl alcohol under stirring at 323–343 K, then

* Authors to whom correspondence should be addressed.

cooled slowly, and placed quietly for about 2 d; transparent crystals were obtained. A crystal of dimensions 0.15 × 0.15 × 0.4 mm was selected and used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K α radiation and ω -2 θ scans. A total of 2123 reflections were measured within the range $-8 \leq h \leq 8$, $-13 \leq k \leq 0$, $-15 \leq l \leq 0$. Of these, 1387 were above the significance level of $3\sigma(I)$ and used for structure analysis. The maximum value of $(\sin\theta)/\lambda$ was 0.59 Å⁻¹. Two standard reflections ($\bar{4}\bar{5}\bar{2}$, $\bar{3}\bar{2}\bar{8}$) were measured hourly and showed no significant variation throughout the measurement. The lattice parameters were refined by a least-squares-fitting procedure using 25 reflections with $15 < \theta < 17^\circ$. Corrections for Lorentz and polarization effects were applied, and empirical absorption corrections were made with coefficients in the range 0.74–1.33 (DIFABS; Walker & Stuart, 1983). The secondary-extinction effect was corrected finally with a g value of 3.76×10^{-7} . The Hg atom was located from the Patterson function. From a ΔF synthesis the positions of remaining non-H atoms were derived. Positions of all H atoms were generated geometrically with assigned isotropic thermal parameters, and included in the last stage of refinement. Full-matrix least-squares refinement of 128 parameters based on F , anisotropic for the non-H atoms, converged to $R = 0.061$, $wR = 0.076$, $(\Delta/\sigma)_{\max} = 0.01$, with a weighting scheme $w = [1 + \sigma(F_{\text{obs}}) + 0.0004F_{\text{obs}}^2]^{-1}$, and the goodness of fit $S = 1.816$. A final difference Fourier map revealed a maximum residual electron density of 2.09 e Å⁻³ (near the Hg atom). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Anomalous-dispersion effects for Hg and Br were accounted for. All calculations were performed on a PDP11/44 computer using the SDP software package (B. A. Frenz & Associates, Inc., 1982).

Discussion. The final atomic coordinates for the non-H atoms are listed in Table 1,* and bond lengths and angles in Table 2. A perspective view of one Hg coordination subunit, including the atom-numbering scheme, is shown in Fig. 1. Fig. 2 gives a view of the part of the two-dimensional polymeric network structure formed by six bridging atoms.

The ligand geometry in the complex is quite different from that of the free ligand. Despite the larger standard deviations, it can still be seen that the

Table 1. Final atomic coordinates for non-H atoms, with their equivalent isotropic thermal parameters (Å²)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i a_j$$

	x	y	z	B _{eq}
Hg	0.08563 (7)	-0.15982 (8)	0.0182 (1)	2.77 (2)
Br1	0.0077 (2)	-0.3434 (2)	0.0805 (4)	3.75 (5)
Br2	0.1546 (2)	0.0325 (2)	-0.0074 (4)	3.96 (6)
O7	0.218 (1)	-0.278 (1)	-0.159 (2)	3.2 (3)
O11	0.551 (1)	-0.536 (2)	0.319 (2)	4.7 (5)
O12	0.435 (1)	-0.658 (2)	0.344 (3)	6.2 (5)
N1	0.276 (1)	-0.348 (2)	-0.050 (3)	2.9 (4)
N10	0.464 (1)	-0.569 (2)	0.285 (3)	3.3 (4)
C2	0.249 (2)	-0.459 (2)	-0.038 (3)	3.1 (5)
C3	0.308 (2)	-0.541 (2)	0.078 (3)	2.8 (5)
C4	0.395 (2)	-0.495 (2)	0.160 (3)	2.4 (5)
C5	0.422 (2)	-0.379 (2)	0.150 (3)	2.6 (5)
C6	0.361 (2)	-0.304 (2)	0.046 (4)	3.3 (5)
C8	0.275 (2)	-0.663 (2)	0.075 (4)	3.6 (5)

Table 2. Bond distances (Å) and angles (°)

Hg—Br1	2.4231 (19)	N1—C2	1.344 (22)
Hg—Br1 ⁱ	3.2109 (20)	N1—C6	1.376 (22)
Hg—Br2	2.4250 (20)	N10—C4	1.499 (22)
Hg—Br2 ⁱⁱ	3.5248 (23)	C2—C3	1.452 (23)
Hg—O7	2.620 (12)	C3—C4	1.376 (23)
Hg—O7 ⁱⁱⁱ	2.894 (12)	C3—C8	1.473 (24)
O7—N1	1.340 (17)	C4—C5	1.393 (24)
O11—N10	1.234 (18)	C5—C6	1.368 (24)
O12—N10	1.186 (19)		
Br1—Hg—Br1 ⁱ	94.08 (6)	C2—N1—C6	123 (2)
Br1—Hg—Br2	172.67 (7)	O11—N10—O12	122 (2)
Br1—Hg—Br2 ⁱⁱ	88.39 (6)	O11—N10—C4	118 (2)
Br1—Hg—O7	86.6 (3)	O12—N10—C4	120 (2)
Br1—Hg—O7 ⁱⁱⁱ	83.3 (2)	N1—C2—C3	122 (1)
Br1 ⁱ —Hg—Br2	90.99 (6)	C2—C3—C4	113 (2)
Br1 ⁱ —Hg—Br2 ⁱⁱ	74.78 (5)	C2—C3—C8	118 (2)
Br1 ⁱ —Hg—O7	74.2 (3)	C4—C3—C8	128 (2)
Br1 ⁱ —Hg—O7 ⁱⁱⁱ	155.7 (2)	N10—C4—C3	120 (2)
Br2—Hg—Br2 ⁱⁱ	87.83 (6)	N10—C4—C5	116 (1)
Br2—Hg—O7	99.9 (3)	C3—C4—C5	124 (2)
Br2—Hg—O7 ⁱⁱⁱ	94.3 (2)	C4—C5—C6	120 (2)
Br2 ⁱⁱ —Hg—O7	148.1 (3)	N1—C6—C5	118 (2)
Br2 ⁱⁱ —Hg—O7 ⁱⁱⁱ	129.1 (2)	Hg—Br1—Hg ⁱⁱⁱ	92.89 (6)
O7—Hg—O7 ⁱⁱⁱ	81.5 (3)	Hg—Br2—Hg ⁱⁱ	92.17 (6)
O7—N1—C2	118 (1)	Hg—O7—Hg ⁱ	96.5 (4)
O7—N1—C6	119 (1)		

Symmetry code: (i) $x, -\frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $-x, -y, -z$; (iii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$.

N1—O7 bond length (1.340 Å) is obviously longer than that (1.292 Å) in the free ligand (Shiro, Yamakawa & Kubota, 1977), and the C—C bonds parallel to the longer molecular axis have the same bond lengths as other C—C bond lengths within the standard deviations. These indicate that when the ligand takes part in coordination the contribution of the quinoid structure to the resonance forms is the least significant, in contrast to the free ligand. The twist angle between the nitro group and the pyridine plane is 20.1°, which is larger than that of 16.7° in the free ligand. According to Shiro, Yamakawa & Kubota (1977), there are two factors which influence the twist angle. The first is the steric effect of the methyl group substituted at vicinal positions, which

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55129 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

can be seen from a comparison between the twist angle of free 2-methyl-4-nitropyridine 1-oxide [4.9° (Li, Liu, Wu, Shi & Hu, 1987)] and that of the title ligand. The second is the intramolecular charge transfer (CT) between the nitro group and the substituent at its *p* position; the twist decreases with increasing CT. From the above values of the twist angle, it may be suggested that the CT contribution to stabilize the 3-pom moiety in the coordination complex is less than in the free ligand.

The crystal does not contain any individual Hg complex molecules. The complex adopts a two-dimensional polymeric network structure lying near the *bc* plane formed by six bridging atoms consisting of two O atoms from the pom ligands and four Br atoms, as shown in Fig. 2. From the symmetry codes in Table 2, it can be seen that Hg, Hgⁱⁱⁱ and Hgⁱ form a plane parallel to the *bc* plane, which is only about 0.2 Å from another plane formed by another three Hg atoms which are reflections of Hg, Hgⁱⁱⁱ and Hgⁱ through the symmetry centre between the Hg and

Hgⁱⁱ. The layers may be described as zigzag planes along the *b* axis. Consequently, the whole crystal structure could be described as consisting of these layers which are stacked in the direction of the *a* axis.

The HgBr₂ subunit deviates slightly from linearity [Br1—Hg—Br2 = 172.67 (7)°] with bond lengths Hg—Br of 2.423 (2) and 2.425 (2) Å, which are even slightly shorter than that found in HgBr₂ itself [2.48 Å (Verweel & Bijvoet, 1931)]. The coordination about Hg in the present complex is completed by two O atoms from the ligands and a further two Br atoms in the equatorial plane, which could be described as secondary bonds. Hg—O bond lengths are 2.620 (12) and 2.894 (12) Å which are comparable to that found in a similar oxygen-bridging compound (6-amino-1,3-dimethyl-5-formyl-uracil)HgCl₂ (Garcia-Megias, Colacio-Rodriguez, Garcia-Rodriguez, Simard & Beauchamp, 1989) and obviously longer than the normal Hg—O bond [2.07–2.23 Å (Howell & Hughes, 1976)]. The two Br atoms are at 3.211 (2) and 3.525 (2) Å from the metal, similar to those in (2,4-dimethylpyridine)-HgBr₂ (Bell, Goldstein, Jones & Nowell, 1980). The resulting coordination polyhedron could be described as octahedral, but the distortion is very large; a common feature for this type of system. This is best seen by considering the (axial Br)—Hg—(equatorial atoms) angles which vary from 83.3 (2) to 99.9 (3)°. To date, there are no strict rules for Hg compounds as to the number and arrangement of secondary bonds in the equatorial plane.

Though previous research on Hg compounds has shown that the Hg complexes are ready to form chain and other polymeric structures, the present complex in which all coordinated atoms participate in bridging to form a two-dimensional network structure is certainly a rarity.

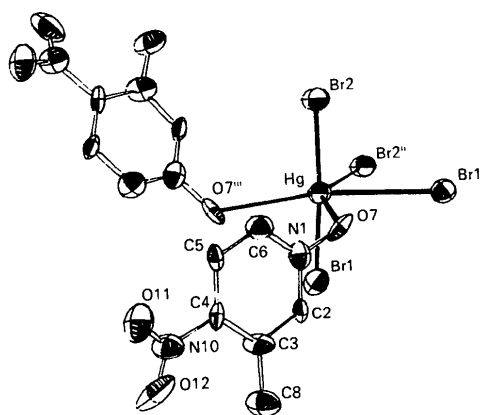


Fig. 1. A perspective view of an Hg coordination subunit, with the atomic labelling scheme. The thermal ellipsoids are drawn at the 50% probability level.

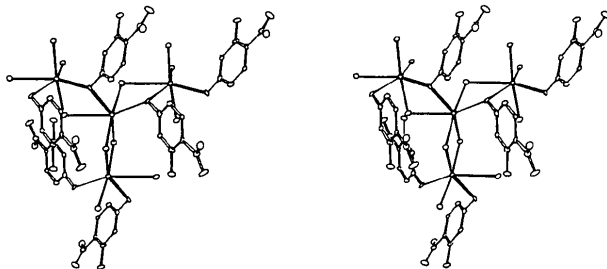


Fig. 2. Stereoview projected along the *a* axis showing part of the two-dimensional polymeric network structure. The thermal ellipsoids are drawn at the 20% probability level.

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