

## Tribromotris(4-methylpyridine)molybdenum(III)–0.5(4-Methylpyridine)

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(Received 26 April 1979; accepted 8 November 1979)

**Abstract.**  $[\text{MoBr}_3(\text{C}_6\text{H}_7\text{N})_3] \cdot 0.5\text{C}_6\text{H}_7\text{N}$ ,  $\text{C}_{18}\text{H}_{21}\text{Br}_3\text{MoN}_3 \cdot 0.5\text{C}_6\text{H}_7\text{N}$ , monoclinic,  $P2_1/n$ ,  $a = 8.721$  (2),  $b = 17.827$  (8),  $c = 16.172$  (7) Å,  $\beta = 96.26$  (2)°,  $Z = 4$ ,  $D_o = 1.77$  (3) (by flotation in dibromoethane/carbon tetrachloride),  $D_c = 1.764$  Mg m<sup>-3</sup>;  $R = 0.056$  for 1806 reflections [ $I > 1.8\sigma(I)$ ]. The structure contains  $[\text{MoBr}_3\text{pic}_3]$  [pic = 4-methylpyridine (4-picoline)] octahedra with the ligands in the *trans* positions. Average Mo–Br and Mo–N(4-methylpyridine) bonding distances are 2.57 (2) and 2.20 (2) Å. The unit cell contains two additional molecules of 4-methylpyridine on the general position with half occupancy.

**Introduction.** Many coordination compounds of Mo<sup>III</sup> have  $[\text{MoL}_3\text{X}_3]$  stoichiometry ( $X = \text{halogen}$  and  $L = \text{ligand}$ ) (Stiefel, 1977). Crystal structures for two of these  $\{[\text{MoCl}_3\text{py}_3]$  (py = pyridine) (Brenčič, 1974) and  $[\text{MoBr}_3\text{pic}_3]$  (Brenčič & Leban, 1978) $\}$  are known. Both molecules have octahedral and *trans* structures. Most of these compounds have a high tendency to crystallize with additional solvent molecules, which can be the same as the ligand  $L$  or different. Generally, such adducts are thermally unstable, losing solvated molecules even at room temperature. However, when 4-methylpyridine forms the solvated part in compounds  $[\text{Mpic}_3\text{X}_3] \cdot 0.5\text{pic}$  ( $M = \text{Cr, Mo}$ ;  $X = \text{Cl, Br}$ ) (Brenčič & Leban, 1978), the thermal stability is surprising.

It is known from their spectroscopic and chemical behaviour that both  $[\text{MoBr}_3\text{pic}_3]$  and  $[\text{MoBr}_3\text{pic}_3] \cdot 0.5\text{pic}$  contain *trans*- $\text{MoBr}_3\text{pic}_3$  octahedra. The reason for undertaking a complete structural analysis of  $[\text{MoBr}_3\text{pic}_3] \cdot 0.5\text{pic}$  was to find out whether the relative stability of the solvate has any structural basis. Also, space group  $P2_1/n$  does not allow  $Z = 4$  with the stoichiometry  $[\text{MoBr}_3\text{pic}_3] \cdot 0.5\text{pic}$  and the structural analysis could also explain how the extra molecules are included in the unit cell.

$[\text{MoBr}_3\text{pic}_3] \cdot 0.5\text{pic}$  was prepared and recrystallized as described previously (Brenčič & Leban, 1978). A good crystal used for the structural analysis was defined by the following planes (numbers in parentheses are the distances in mm from the crystal faces to an arbitrary origin inside the crystal):  $\pm(011)$  (0.11),  $\pm(0\bar{1}1)$  (0.11),  $(1\bar{3}\bar{1})$  (0.18),  $(\bar{1}2\bar{1})$  (0.18),  $(21\bar{1})$  (0.22),  $(\bar{1}04)$  (0.14).

The unit-cell dimensions were determined from the least-squares analysis of 44 randomly chosen reflections. 20 values were measured on the diffractometer at 293 (1) K.

The intensity data were collected at 293 (1) K with an Enraf–Nonius CAD-4 diffractometer. Experimental conditions were: graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\omega$ - $2\theta$  scan,  $\theta_{\text{min}} = 1^\circ$ ,  $\theta_{\text{max}} = 27^\circ$ ,  $2\theta$  scan width (°) =  $0.9 + 0.2 \tan \theta$ , aperture (mm) =  $2.6 + 0.9 \tan \theta$ , maximum scan time = 40 s, background:  $\frac{1}{4}$  of the scan time at each of the scan limits. 5789 independent reflections were measured. Reflections with  $I < 1.8\sigma(I)$  were rejected and the remaining 1806 were used for the solution and refinement of the structure. Structure factors on a relative scale were obtained by applying Lorentz, polarization and absorption corrections to the measured intensities [ $\mu(\text{Mo } K\alpha) = 5.62$  mm<sup>-1</sup>].

The positions of the heavy atoms were found on the  $E$  map calculated from 250 normalized structure amplitudes, signed by the program *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). 4-Methylpyridine rings belonging to the  $[\text{MoBr}_3\text{pic}_3]$  molecule were found from a Fourier calculation using the  $|F_o|$ 's with signs taken from the  $|F_c|$ 's based on the heavy-atom positions. A difference Fourier map then revealed the remaining unit-cell contents. It was concluded from the peak heights that two extra 4-methylpyridines were located in a statistically disordered manner around the symmetry centre.

Solvated 4-methylpyridine rings were included in the refinement by taking account of the population parameters. The structure was refined by full-matrix least-squares techniques with anisotropic temperature factors for Mo and Br atoms and isotropic for the rest.

Table 1. Positional ( $\times 10^5$ ) and thermal ( $\times 10^2$ ) parameters for Mo and Br atoms with standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ (Å <sup>2</sup> )
Mo	54405 (16)	36731 (7)	29532 (8)	3.20 (8)
Br(1)	41709 (20)	48726 (9)	23369 (12)	4.83 (10)
Br(2)	64613 (21)	33494 (10)	15594 (10)	4.80 (10)
Br(3)	44175 (21)	38881 (9)	43650 (11)	4.84 (10)

The structure factors included the real and imaginary components of anomalous scattering. The function minimized in the least-squares calculation was:  $\sum w(|F_o| - |F_c|)^2$ . The empirical weighting scheme was such that: when  $|F_o| < 39.0$ :  $W_F = (|F_o|/39.0)^{0.5}$ ; when  $39.0 \leq F_o \leq 85.0$ :  $W_F = 1.0$ ; when  $|F_o| > 85.0$ :  $W_F = (85.0/|F_o|)^{2.0}$ ; when  $\sin \theta < 0.2$ :  $W_S = (\sin \theta/0.20)^{2.0}$ ; when  $0.2 \leq \sin \theta \leq 0.32$ :  $W_S = 1.0$ ; when  $\sin \theta > 0.32$ :  $W_S = (0.32/\sin \theta)^{1.0}$ ;  $W = W_F W_S$ .

The final  $R$  values are:  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.056$  and  $R_w = [\sum W(|F_o| - |F_c|)^2 / \sum WF_o^2]^{1/2} = 0.065$ . The average shift-to-error ratio for all parameters was 0.13. The final difference Fourier map showed only insignificant ripples around Mo and Br atoms.

All calculations were performed on the DCD Cyber computer of RRC Ljubljana with the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), adapted by Professor L. Golič.

Atomic scattering factors for neutral atoms tabulated by Cromer & Mann (1968) and the values for  $f'$  and  $f''$  for the anomalous-dispersion correction compiled by Cromer (1965) were applied.

The positional and thermal parameters for Mo and Br atoms are listed in Table 1, and for the other atoms

Table 2. Positional parameters ( $\times 10^4$ ) and thermal parameters ( $\times 10^2$ ) for C and N atoms with standard deviations

The isotropic temperature factor is in the form:  $\exp[-B(\sin \theta/\lambda)^2]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
N(1)	3348 (14)	3033 (6)	2545 (7)	3.6 (3)
C(10)	2625 (20)	3142 (9)	1788 (10)	4.7 (4)
C(11)	1313 (18)	2717 (8)	1475 (9)	3.9 (4)
C(12)	752 (18)	2175 (8)	1964 (10)	3.9 (4)
C(13)	1468 (20)	2086 (9)	2743 (10)	4.6 (4)
C(14)	2767 (18)	2515 (9)	3033 (10)	4.1 (4)
C(15)	-635 (22)	1704 (10)	1618 (11)	5.4 (5)
N(2)	6627 (14)	2647 (6)	3479 (7)	3.7 (3)
C(20)	6450 (20)	1982 (9)	3087 (10)	4.8 (4)
C(21)	7224 (21)	1347 (10)	3405 (11)	5.0 (4)
C(22)	8149 (20)	1367 (9)	4153 (10)	4.5 (4)
C(23)	8267 (21)	2051 (9)	4556 (11)	4.8 (4)
C(24)	7495 (19)	2668 (8)	4203 (10)	4.1 (4)
C(25)	8971 (23)	677 (11)	4531 (12)	6.1 (5)
N(3)	7536 (14)	4320 (7)	3367 (7)	3.6 (3)
C(30)	7449 (18)	4963 (8)	3785 (9)	3.9 (4)
C(31)	8753 (19)	5409 (9)	4018 (10)	4.4 (4)
C(32)	10134 (19)	5238 (9)	3767 (10)	4.4 (4)
C(33)	10249 (21)	4592 (10)	3318 (11)	5.0 (5)
C(34)	8952 (21)	4135 (9)	3153 (11)	4.7 (4)
C(35)	11554 (25)	5732 (12)	3956 (12)	6.7 (6)
N,C(41)	11332 (28)	5935 (13)	568 (16)	7.3 (7)
C(42)	9084 (57)	4056 (27)	96 (31)	7.5 (1.3)
C(43)	10010 (29)	4739 (13)	699 (15)	7.7 (7)
C(44)	10467 (49)	5303 (22)	12 (28)	6.6 (1.2)
C(45)	10734 (51)	5365 (23)	1121 (26)	6.7 (1.2)

Table 3. Dimensions of the [MoBr<sub>3</sub>pic<sub>3</sub>] octahedron with standard deviations in parentheses

(A) Bond lengths (Å)			
Mo—Br(1)	2.559 (2)	Mo—N(1)	2.193 (12)
Mo—Br(2)	2.578 (2)	Mo—N(2)	2.225 (12)
Mo—Br(3)	2.569 (2)	Mo—N(3)	2.202 (12)
(B) Bond angles (°)			
Br(1)—Mo—N(2)	177.9 (3)	N(1)—Mo—Br(1)	90.4 (3)
Br(2)—Mo—Br(3)	175.6 (1)	N(1)—Mo—Br(2)	88.6 (3)
N(1)—Mo—N(3)	179.7 (5)	N(1)—Mo—N(2)	91.4 (4)
		N(1)—Mo—Br(3)	89.3 (3)
Br(1)—Mo—Br(2)	91.3 (1)	N(3)—Mo—Br(1)	89.4 (3)
Br(2)—Mo—N(2)	87.7 (3)	N(3)—Mo—Br(2)	91.7 (3)
N(2)—Mo—Br(3)	88.6 (3)	N(3)—Mo—N(2)	88.8 (4)
Br(3)—Mo—Br(1)	92.5 (1)	N(3)—Mo—Br(3)	90.5 (3)
(C) Br...Br and Br...N contacts (Å)			
Br(1)—Br(2)	3.673 (3)	N(1)—N(2)	3.161 (17)
Br(2)—N(2)	3.336 (12)	N(1)—Br(3)	3.356 (12)
N(2)—Br(3)	3.356 (12)	N(3)—Br(1)	3.360 (12)
Br(3)—Br(1)	3.705 (3)	N(3)—Br(2)	3.438 (12)
N(1)—Br(1)	3.382 (11)	N(3)—Mo—N(2)	3.097 (16)
N(1)—Br(2)	3.342 (13)	N(3)—Br(3)	3.398 (13)

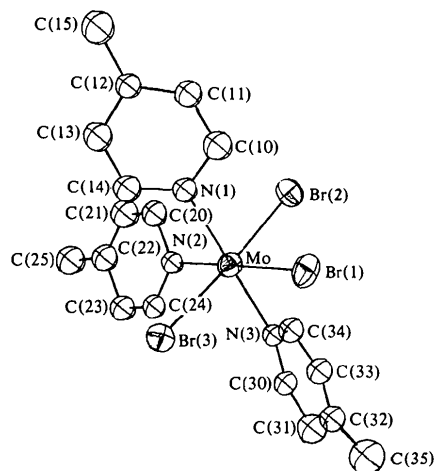


Fig. 1. Atom-numbering scheme for the disordered 4-methylpyridine.

in Table 2.\* A schematic representation of the disordered 4-methylpyridine is shown in Fig. 1. The molecular conformation and atomic numbering of the [MoBr<sub>3</sub>pic<sub>3</sub>] octahedron are in Fig. 2. The packing of the molecules in the unit cell is presented in Fig. 3. Interatomic distances and angles are in Table 3.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34895 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

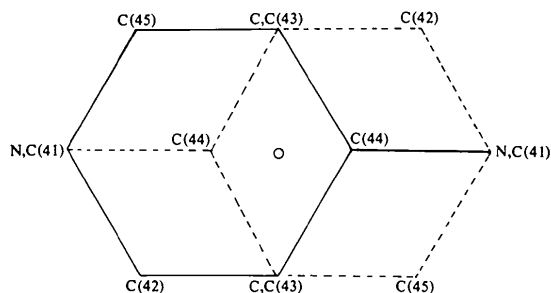


Fig. 2. Molecular conformation of the [MoBr<sub>3</sub>pic<sub>3</sub>] octahedron.

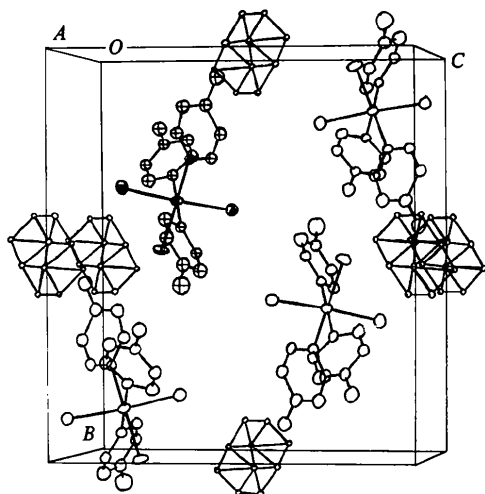


Fig. 3. Packing of the molecules in the unit cell.

**Discussion.** [MoBr<sub>3</sub>pic<sub>3</sub>].0.5pic is another example of a compound with octahedral coordination around Mo<sup>III</sup> containing ligands in *trans* positions.

Mo—Br and Mo—N bond distances, 2.559–2.578 and 2.193–2.225 Å, are nearly equal to those found in the unsolvated [MoBr<sub>3</sub>pic<sub>3</sub>] (Brenčič & Leban, 1978). The same is true for the angles of the MoBr<sub>3</sub>N<sub>3</sub> skeleton, which are all 90 (3) or 180 (5)°. The 4-methylpyridine which is *trans* to the Br atom has an Mo—N distance which is of the order of two  $\sigma$ 's longer. However, it is questionable whether this value reflects specific bonding conditions or whether it is the accidental result of the packing forces.

The 4-methylpyridines are planar within 0.02 Å. Average C—N, C—C, C—C(CH<sub>3</sub>) bonding distances and C—N—C, C—C—C angles are 1.34 (2), 1.38 (2), 1.52 (2) Å and 117 (1), 121 (1)°. Aromatic rings are in propeller-like positions with respect to the plane defined by one Br and three N atoms.

Special attention should be devoted to the extra 4-methylpyridines. Chemical analysis, thermal decom-

position and the experimental density all indicate the presence of additional 4-methylpyridine molecules. The initial problem is that space group  $P2_1/n$  does not contain positions which could allow two additional 4-methylpyridine molecules. The difference map clearly showed a group of peaks located around the symmetry centre.

The unit cell contains two extra 4-methylpyridine molecules on the general fourfold position with half occupancy. Half of the unit cells have one orientation for the 4-methylpyridines and half have another related by the centre of symmetry. The superposition of these two orientations is what the X-rays register. C(43) and N,C(41) belong to both orientations and have unit occupation; the remaining atoms have an occupation of one half. The model was confirmed by the least-squares refinement. The accuracy of the C—C and C—N distances in the solvated part is low. Average values for C(44)—C(41), C—C and N—C are 1.58 (5), 1.47 (5) and 1.30 (5) Å. This is expected when we take into account the accumulation of errors around the symmetry centre (Speakman, 1972).

The shortest contact between the solvated 4-methylpyridines and the [MoBr<sub>3</sub>pic<sub>3</sub>] groups is C(45)( $x,y,z$ )...C(21)( $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ) 3.28 (5) Å. The most interesting contacts, all rather long, are C(45)( $x,y,z$ )...Br(1)( $1+x, y, z$ ) 3.51 (4) and C(42)( $x,y,z$ )...Br(2)( $x,y,z$ ) 3.69 (5) Å, which could indicate at least weak hydrogen bonding between the [MoBr<sub>3</sub>pic<sub>3</sub>] octahedron and the additional 4-methylpyridines and could also explain the relative stability of the adduct.

All attempts to find another double unit cell were unsuccessful.

We are indebted to the Boris Kidrič Foundation and the University of Ljubljana for assistance.

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