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trans-Tribromotris(1,3-thiazole-*N*)-molybdenum(III)

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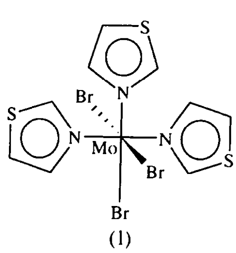
Abstract

The title compound, $[MoBr_3(C_3H_3NS)_3]$, has been synthesized by the solid-state reaction of $Cu(thiazole)_2Br_2$ and $Mo(CO)_6$ under argon. A pseudo-octahedral Mo centre is formed by the N-bonded thiazole ligands and the Br ligands. The thiazole rings display orientational disorder due to 180° rotations about their Mo—N bonds.

Comment

Relatively few trivalent compounds of molybdenum are presently known. They almost exclusively fall into the MoL_3X_3 class of compounds, some examples being MoL_3Cl_3, where L = pyridine (Brenčič, 1974), thf (Hofacker *et al.*, 1989) or PR_3 (Yoon, Parkin & Rheingold, 1992), and $[MoX_6]^{3-}$, where X = F (Toth, Brunton & Smith, 1969), Cl (Amilius, von Larr & Rietveld, 1969) or NCS (Knox & Ereks, 1968). This aspect of molybdenum chemistry contrasts sharply with that of chromium, for which a large number of CrL_3X_3 compounds have been isolated.

To our knowledge, the title compound, (1), is the first Mo^{III} compound to be synthesized containing thiazole. The pseudo-octahedral structure of (1) is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. Observed ligand—Mo—ligand bond angles show only slight deviations from 90° and 180°.



(1)

The average Mo—N distance in (1) of 2.187 (6) Å is similar to that of the monoclinic [2.20 (1) Å (Brenčič & Leban, 1978)] and triclinic [2.21 (3) Å (Brenčič & Leban, 1982)] polymorphs of *trans*-$Mo(4\text{-}Mepy)_3Br_3$ (where Mepy = methylpyridine). Although no significant *trans* influence is observed for either of these compounds, it is noteworthy that for (1), the shorter Mo—N bond is *trans* to a Br atom, while the opposite is true in the case of *trans*-$Mo(4\text{-}Mepy)_3Br_3$ (Brenčič & Leban, 1978), where the two shorter Mo—N bonds occupy positions that are mutually *trans* with respect to one another.

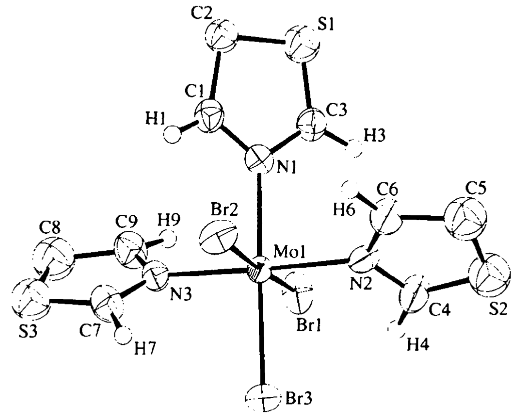


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title compound. All atoms are represented by displacement ellipsoids drawn at the 50% probability level.

A much greater range of Mo—N distances was observed in the case of *trans*-$Mo(py)_3Cl_3$ (where py = pyridine) [2.163 (2)–2.223 (2) Å] by Brenčič (1974). He attributed this feature to crystal-packing effects rather than a *trans* influence, as the two pyridine molecules that differed considerably in Mo—N distance were located *trans* to each other. In the same study, he suggested that *trans*-$Mo(py)_3Br_3$ formed an isostructural compound.

The average Mo—Br bond distance in (1) of 2.568 (1) Å is also consistent with those observed for both polymorphs of *trans*-$Mo(4\text{-}Mepy)_3Br_3$ [2.565 (2) (Brenčič & Leban, 1978) and 2.57 (2) Å (Brenčič & Leban, 1982)].

Despite the fact that the thiazole ligands of (1) show very little deviation (<0.02 Å) from planarity, extensive disorder is found at the S and adjacent C sites due to 180° rotations about the Mo—N bonds. Constrained refinement of the occupation factors of the sites containing the majority of S gave values of 0.55 (1), 0.58 (1) and 0.63 (1) for the three thiazole rings. The distances between the non-disordered atoms of the thiazole ligands are typical of those found in other metal–thiazole complexes (Estes, Gavel, Hatfield & Hodgson, 1978; James, Kawaguchi & Tatsumi, 1997). The remaining distances and angles are consistent with the level of disorder at these sites.

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Experimental

Cu(thiazole)$_2$Br$_2$ was prepared as described elsewhere (Estes *et al.*, 1978). Cu(thiazole)$_2$Br$_2$ (1 mmol) and Mo(CO)$_6$ (1 mmol) were reacted together under argon gas in a Schlenk tube in an oil bath at 373 K for 20 h. The dark-grey solid residue was washed with hot benzene to remove any traces of Mo(CO)$_6$ and recrystallized from dimethylformamide in air. After 2 weeks, orange crystals of the title compound, (1), were obtained along with deep-green needle-like crystals of Cu(thiazole)$_2$Br$_2$. Once removed from solution, the crystals of (1) proved to be air sensitive and so were sealed in a glass capillary for X-ray diffraction measurements.

Crystal data

[MoBr$_3$(C$_3$H$_3$NS)$_3$]
M_r = 591.02
Monoclinic
$P2_1/n$
a = 9.507 (7) Å
b = 11.989 (7) Å
c = 14.874 (9) Å
β = 92.31 (6)°
V = 1694 (2) Å^3
Z = 4
D_x = 2.317 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 23 reflections
θ = 11.0–12.2°
μ = 8.229 mm^{-1}
T = 296.2 K
Prism
0.40 × 0.30 × 0.25 mm
Orange

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.052, T_{max} = 0.128
3282 measured reflections
3155 independent reflections

2299 reflections with $I > 3\sigma(I)$
R_{int} = 0.055
θ_{max} = 25°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 14$
$l = -17 \rightarrow 0$
3 standard reflections every 150 reflections intensity decay: 0.34%

Refinement

Refinement on F
R = 0.049
wR = 0.061
S = 2.346
2299 reflections
151 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00029|F_o|^2]$

$(\Delta/\sigma)_{max}$ = 0.0120
$\Delta\rho_{max}$ = 0.99 e Å^{-3}
$\Delta\rho_{min}$ = −1.22 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo1	0.01995 (6)	0.09264 (5)	0.75364 (4)	0.0276 (2)
Br1	0.07491 (9)	−0.09039 (7)	0.83803 (6)	0.0477 (2)
Br2	−0.01875 (9)	0.28283 (6)	0.67653 (6)	0.0451 (2)
Br3	−0.12154 (9)	−0.00575 (7)	0.62676 (6)	0.0468 (2)
S1†	0.1963 (4)	0.2483 (3)	1.0178 (3)	0.056 (2)
S1′‡	0.2967	0.3176	0.9417	0.055 (1)
S2§	−0.3858 (5)	0.0602 (4)	0.9130 (3)	0.075 (2)
S2′¶	−0.3700	0.1998	0.9060	0.071 (2)
S3††	0.3894 (4)	0.0953 (3)	0.5621 (2)	0.068 (2)
S3′‡‡	0.4693	0.0406	0.6604	0.075 (3)
N1	0.1331 (6)	0.1811 (5)	0.8623 (4)	0.032 (2)
N2	−0.1737 (6)	0.1121 (5)	0.8273 (4)	0.036 (2)
N3	0.2180 (6)	0.0770 (5)	0.6846 (4)	0.035 (2)
C1	0.2323 (9)	0.2594 (6)	0.8513 (5)	0.041 (2)
C2†	0.2967 (4)	0.3176 (3)	0.9417 (2)	0.045 (6)
C2′‡	0.1963	0.2483	1.0178	0.039 (5)
C3	0.1064 (8)	0.1710 (7)	0.9510 (5)	0.040 (2)
C4	−0.2497 (9)	0.0266 (7)	0.8550 (6)	0.050 (3)
C5§	−0.3700 (5)	0.1998 (4)	0.9060 (3)	0.076 (8)
C5′¶	−0.3858	0.0602	0.9130	0.052 (8)
C6	−0.231 (1)	0.2097 (7)	0.8524 (7)	0.055 (3)
C7	0.233 (1)	0.1061 (7)	0.5997 (6)	0.049 (2)
C8††	0.4693 (6)	0.0406 (5)	0.6604 (4)	0.074 (7)
C8′‡‡	0.3894	0.0953	0.5621	0.043 (7)
C9	0.3418 (9)	0.0407 (8)	0.7223 (6)	0.049 (2)

† Site occupancy = 0.451 (7). ‡ Site occupancy = 0.549. § Site occupancy = 0.576 (7). ¶ Site occupancy = 0.424. †† Site occupancy = 0.627 (6). ‡‡ Site occupancy = 0.373.

Table 2. *Selected geometric parameters (Å, °)*

Mo1—Br1	2.571 (1)	Mo1—N2	2.192 (6)
Mo1—N1	2.180 (6)	Mo1—Br3	2.561 (1)
Mo1—Br2	2.572 (1)	Mo1—N3	2.188 (6)
Br1—Mo1—Br2	175.4 (1)	Br2—Mo1—N3	88.7 (2)
Br1—Mo1—Br3	93.3 (1)	Br3—Mo1—N1	177.6 (2)
Br1—Mo1—N1	88.2 (2)	Br3—Mo1—N2	89.5 (2)
Br1—Mo1—N2	90.3 (2)	Br3—Mo1—N3	92.9 (2)
Br1—Mo1—N3	89.7 (2)	N1—Mo1—N2	88.7 (2)
Br2—Mo1—Br3	91.1 (1)	N1—Mo1—N3	88.9 (2)
Br2—Mo1—N1	87.5 (2)	N2—Mo1—N3	177.6 (2)
Br2—Mo1—N2	91.2 (2)		

The structure was solved by direct methods and developed by alternating cycles of difference Fourier syntheses and full-matrix least-squares refinements. The positions of the non-H atoms were determined unequivocally; however, the thiazole ligands were found to display static disorder between adjacent C and S sites due to a 180° rotation about their Mo—N bonds. In these cases, the disorder was modelled by refinement of jointly occupied S/C sites. The minority component of these jointly occupied sites is indicated by a primed label. The occupation factors of S atoms were refined only at the S/C′ sites, while the C′ and S′ occupation factors were constrained so as to give fully occupied sites. The non-H atoms were refined anisotropically, with the exception of the atoms at the disordered sites which were refined isotropically. H atoms were placed at calculated positions adjacent to ordered C sites.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN* and *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1185). Services for accessing these data are described at the back of the journal.

References

Amilius, Z., von Larr, B. & Rietveld, H. M. (1969). *Acta Cryst.* **B25**, 400–402.
Brenčič, J. V. (1974). *Z. Anorg. Allg. Chem.* **403**, 218–224.

Brenčič, J. V. & Leban, I. (1978). *Z. Anorg. Allg. Chem.* **445**, 251–256.
Brenčič, J. V. & Leban, I. (1982). *Acta Cryst.* B**38**, 1292–1295.
Estes, W. E., Gavel, D. P., Hatfield, W. E. & Hodgson, D. J. (1978). *Inorg. Chem.* **17**, 1415–1421.
Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control.* Rigaku Corporation, Tokyo, Japan.
Hofacker, P., Friebel, C., Dehnicke, K., Bauml, P., Hiller, W. & Strahle, J. (1989). *Z. Naturforsch. Teil B*, **44**, 1161–1166.
James, M., Kawaguchi, H. & Tatsumi, K. (1997). *Polyhedron*, **16**, 1873–1876.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Knox, J. R. & Ereks, K. (1968). *Inorg. Chem.* **7**, 84–90.
Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software.* Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1995). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Toth, L. M., Brunton, G. D. & Smith, G. P. (1969). *Inorg. Chem.* **8**, 2694–2697.
Yoon, K., Parkin, G. & Rheingold, A. L. (1992). *J. Am. Chem. Soc.* **114**, 2210–2218.

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$[(Mg_{0.5},Mn_{0.5})_4\{\mu_3,\eta^2\text{-}OCH_2\overline{CH(CH_2)_3O}\}_4\text{-}(EtOH)_4Cl_4].0.5EtOH$

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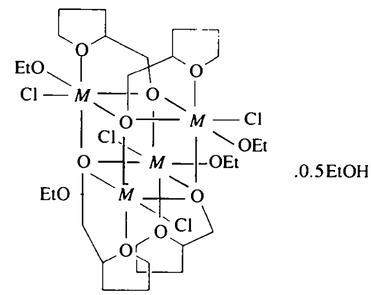
Abstract

The reaction of $MnCl_2$ with $[Mg\{OCH_2\overline{CH(CH_2)_3O}\}_2]$ in EtOH results in a mixed Mg^{II}/Mn^{II} tetranuclear complex, tetrakis(μ_3-tetrahydrofuran-2-ylmethanolato-*O*,*O*′:*O*′:*O*′)tetrakis{chloro(ethoxo)[manganese(II),-magnesium(II)]} hemiethanol solvate, $[(Mg_{0.5},Mn_{0.5})_4Cl_4(C_2H_6O)_4(C_5H_9O_2)_4].0.5C_2H_6O$, in which all metal sites have distorted octahedral coordination spheres and metal ions together with alkoxo O atoms form a cubane-like framework.

Comment

This work is a part of our systematic study on complexes with O-atom donor functions in bidentate alkoxo ligands such as 2-tetrahydrofurfuryl alcohol (thffo). The structures and properties of magnesium(II) (Sobota, Utko, Janas & Szafert, 1996) and vanadium(III)–magnesium(II) (Janas, Sobota, Kasprzak & Głowiak, 1997) compounds have been reported previously. In this paper, we describe the structure of a magnesium(II)/manganese(II)–alkoxide complex, (I).



M = Mg,Mn

(I)

The crystal structure of (I) comprises discrete complex molecules and an ethanol molecule of crystallization. The complex consists of four crystallographically independent distorted octahedral metal sites with shared common edges. Magnesium(II) and manganese(II) ions are distributed in equal proportions among all the sites. The coordination sphere of each metal ion is formed by Cl^- anions, ethanol molecules and a chelating tetrahydrofuran-2-ylmethanolato ligand. On the other hand, the metal ions and alkoxo O atoms form a distorted cubane-like framework (Fig. 1 and Table 2) due to steric requirements resulting from the formation of five-membered chelate rings. The *M*—μ-O bonds (where $M = Mn^{II}/Mg^{II}$) of 2.106 (2)–2.191 (2) Å are comparable with *M*—μ_3-O distances found in magnesium(II) compounds: 1.934 (3)–2.226 (3) Å in $[Mg_4\{\mu_3,\eta^2\text{-}OCH_2\overline{CH(CH_2)_3O}\}_2\{\mu,\eta^2\text{-}OCH_2CH(CH_2)_3O\}_4Cl_2]$ (Sobota, Utko, Janas & Szafert, 1996) and 2.060 (1)–2.083 (2) Å in $[Mg_4(\mu_3\text{-}EtOH)_4(C_5H_5)_4]$ (Lehmkuhl, Mehler, Benn, Rufinski & Kruger, 1986). The changes of *M*—μ-O bond lengths are reflected in the intramolecular *M*···*M* distances. Two cubane-face diagonal vectors *M*(1)···M(2) and *M*(3)···*M*(4) are longer by *ca* 0.145 (3) Å than the other four (Table 2). The *M*—O(ether) bond lengths in the title compound change from 2.145 (2) to 2.193 (2) Å. In the structure of the octahedral magnesium(II) $[MgCl(thf)_5]^+$ cation (Sobota, Płuzinski, Utko & Lis, 1989) and the manganese(II) $[Mn\{OCH_2\overline{CH(CH_2)_3O}\}_2Cl_2]$ (Sobota, Utko & Jerzykiewicz, 1997) complex, the ether O atoms are 2.156 (4) and 2.223 (2) Å away from the metal ion, respectively. The ethanol ligands give a relatively long *M*—O distance of 2.231 (2) Å, probably because of the intramolecular hydrogen bonds in which they are involved. Every coordinated hydroxyl group forms a strong hydrogen bond with the chlorine anion bonded to a neighbouring metal ion (Table 3). The average *M*—Cl