

lar graphics: *SHELXTL/PC*. Geometrical calculations: *PARST* (Nardelli, 1983). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1254). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Dichlorotetrakis(pyridine-*N*)-molybdenum(III) Tribromide

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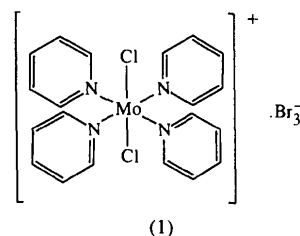
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Abstract

In the title compound, *trans*-[Mo^{III}Cl₂(C₅H₅N)₄]Br₃, the Cl and pyridine N atoms define a slightly distorted octahedron around the Mo atom. Both cations and anions lie on twofold axes. Pyridine rings which are located *trans* with respect to one another are staggered. The tribromide ion, Br₃⁻, is essentially linear.

Comment

It is known that pyridine can occupy up to three coordination positions around an Mo^{III} ion. Several examples of compounds such as [NH₂(CH₃)₂][MoCl₅(py)] (Brenčič, Leban, Modec & Carugo, 1995), *cis*-Rb[MoCl₄(py)₂].H₂O (Brenčič, Leban & Modec, 1994) and *mer*-MoCl₃(py)₃ (Brenčič, 1974) have been prepared and structurally characterized. *trans*-[Mo^{III}Cl₂(py)₄]Br₃, which was isolated from *trans,trans*-[MoCl₂(py)₄][MoCl₄(py)₂] (Brenčič, Golič, Leban, Rotar & Sieler, 1996) in the form of the tribromide, (1), is the first complex in which four pyridine ligands are coordinated to the same Mo^{III} atom. Pyridine rings which are *trans* with respect to one another but are not symmetry related are in a staggered conformation.



The acute interplanar angle between the N11, C12–C16 (ring I) and N21, C22–C26 (ring II) planes is 60.6(3)°. The interplanar angles between two pyridine rings in a staggered conformation [ring I and ring II at (–x, y, ½–z)] is 84.9(2)°. The angle between ring I and ring I at (–x, y, ½–z) is 60.8(2)°, and between ring II and ring II at (–x, y, ½–z) is 70.1(2)°. The Mo–Cl bond length of 2.407(2) Å is shorter than those found in corresponding anions, for example, in [MoCl₄(py)₂]⁻ (Brenčič & Čeh, 1989), for steric reasons. The two Cl atoms in [MoCl₂(py)₄]⁺ can approach the central Mo atom more closely than in [MoCl₄(py)₂]⁻, where four Cl atoms occupy more space around the central Mo atom. The shortening of the Mo–Cl bond is also in agreement with the positive charge of the bulky cation.

Although the tribromide ion is symmetrical, it is not exactly linear. As was noted previously, large cations favour symmetrical tribromide ions (Atwood, Junk, May & Robinson, 1994). Almost identical cation geometry was found previously in the structures of *trans*-[Ir^{III}Cl₂(py)₄]Cl.6H₂O (Gillard, Mitchell, Williams & Vagg, 1984), *trans*-[Rh^{III}Cl₂(py)₄][H(ONO₂)₂] (Dobinson, Mason & Russel, 1967) and *trans*-[Ru^{III}Cl₂(py)₄][H(ONO₂)₂] (Al-Zamil, Evans, Gillard, James, Jenkins, Lancashire & Williams, 1982). All the cations have a staggered conformation of the *trans* pyridine rings. It is noteworthy that *trans*-[M^{III}Cl₂(py)₄][H(ONO₂)₂], where M = Rh or Ru, crystallize in the same space group (*Pbcn*) as *trans*-[Mo^{III}Cl₂(py)₄]Br₃, with cations located on a twofold axis with the same relative positions of the atoms.

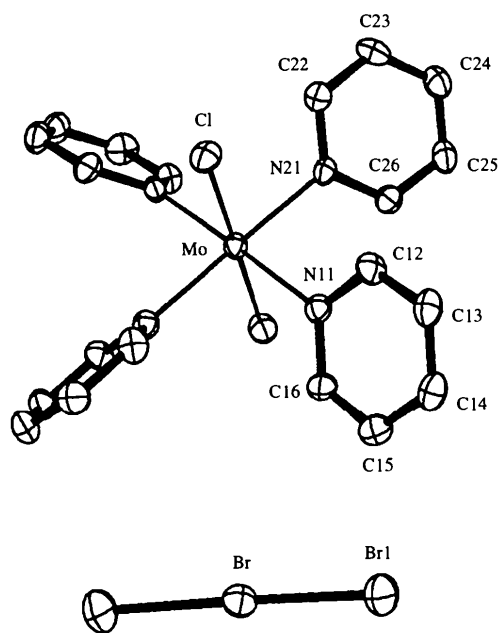


Fig. 1. ORTEP (Johnson, 1971) view of the title molecule with the atomic numbering scheme. H atoms have been omitted for clarity. Displacement ellipsoids are plotted at the 30% probability level.

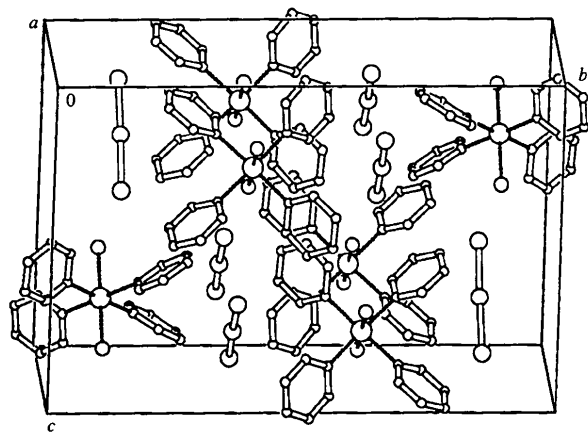


Fig. 2. Unit-cell contents (PLUTON; Spek, 1991).

Experimental

trans-[Mo^{III}Cl₂(py)₄]₂Br₃ was prepared from *trans,trans*-[MoCl₂(py)₄][MoCl₄(py)₂] by oxidation with bromine. The *trans*-[MoCl₄(py)₂] by-product was filtered off. Single crystals of the title compound suitable for X-ray diffraction analysis were grown from saturated nitromethane.

Crystal data

[MoCl₂(C₅H₅N)₄]₂Br₃
M_r = 722.96

Mo *K*α radiation
 λ = 0.71073 Å

Orthorhombic

Pbcn

a = 7.577 (1) Å
b = 22.058 (3) Å
c = 15.098 (2) Å
V = 2523.4 (6) Å³
Z = 4
D_x = 1.903 Mg m⁻³
D_m = 1.90 (5) Mg m⁻³
D_m measured by flotation in
 CCl₄/bromoform

Cell parameters from 25

reflections
 θ = 7–10°
 μ = 5.497 mm⁻¹
T = 293 (1) K
 Plate
 0.38 × 0.18 × 0.10 mm
 Dark yellow

Data collection

Enraf–Nonius CAD-4
 diffractometer
 Variable rate $\theta/2\theta$ scans
 Absorption correction:
 by integration from crystal
 shape
T_{min} = 0.365, *T_{max}* =
 0.608
 10 595 measured reflections
 2761 independent reflections
 1514 observed reflections
 $[I > 2\sigma(I)]$

R_{int} = 0.1009
 θ_{\max} = 27.0°
h = -9 → 9
k = -28 → 28
l = -19 → 19
 3 standard reflections
 monitored every 700
 reflections
 frequency: 180 min
 intensity decay: 1.67%

Refinement

Refinement on *F*²
R(*F*) = 0.0525
wR(*F*²) = 0.1327
S = 1.024
 2761 reflections
 138 parameters
 H-atom parameters not
 refined
 $w = 1/[\sigma^2(F_o^2) + (0.0593P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.076$

$\Delta\rho_{\max} = 0.945 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.875 \text{ e \AA}^{-3}$
 Extinction correction:
 empirical (Larson, 1970)
 Extinction coefficient:
 0.0007 (2)
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Mo	0	0.38793 (3)	1/4	0.0322 (2)
Br1	0.71870 (12)	0.14006 (4)	0.12315 (6)	0.0757 (3)
Br	1/2	0.14182 (4)	1/4	0.0534 (3)
Cl	-0.2362 (2)	0.38769 (8)	0.14343 (11)	0.0459 (4)
N11	0.1355 (7)	0.3175 (2)	0.1742 (3)	0.0371 (13)
C12	0.3126 (8)	0.3208 (3)	0.1589 (4)	0.042 (2)
C13	0.4005 (9)	0.2775 (3)	0.1124 (4)	0.049 (2)
C14	0.3129 (10)	0.2289 (3)	0.0779 (5)	0.053 (2)
C15	0.1322 (10)	0.2248 (3)	0.0943 (5)	0.050 (2)
C16	0.0508 (9)	0.2699 (3)	0.1412 (4)	0.045 (2)
N21	0.1409 (6)	0.4569 (2)	0.1718 (3)	0.0353 (12)
C22	0.2289 (9)	0.5029 (3)	0.2103 (5)	0.046 (2)
C23	0.3220 (9)	0.5447 (3)	0.1619 (5)	0.055 (2)
C24	0.3293 (10)	0.5403 (3)	0.0712 (5)	0.053 (2)
C25	0.2404 (10)	0.4936 (4)	0.0314 (5)	0.051 (2)
C26	0.1481 (9)	0.4532 (3)	0.0826 (4)	0.044 (2)

Table 2. Selected geometric parameters (Å, °)

Mo—N11	2.186 (5)	Mo—Cl	2.407 (2)
Mo—N21	2.202 (5)	Br1—Br	2.5328 (9)
N11—Mo—N11 ⁱ	89.4 (3)	N11 ⁱ —Mo—Cl	89.96 (14)
N11—Mo—N21 ⁱ	178.4 (2)	N21—Mo—Cl	90.20 (14)

N11—Mo—N21	89.0 (2)	N21—Mo—Cl ⁱ	89.97 (14)
N21 ⁱ —Mo—N21	92.6 (3)	Cl—Mo—Cl ⁱ	179.75 (9)
N11—Mo—Cl	89.86 (14)	Br1 ⁱⁱ —Br—Br1	178.24 (6)

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

The space group *Pbcn* (No. 60) was chosen from the systematic absences. All H atoms were found in the difference electron-density map, but were included in the refinement at calculated positions with 1.4 times the isotropic displacement parameters of the attached heavy atoms. Calculations were performed on a PC 486. Additionally, *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and *PLUTON* (Spek, 1991) were used for data processing and final interpretation of structural geometry.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971) and *PLUTON*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(*N,N*-diethyldithiocarbamato-*S,S'*)-(thionitrosyl-*N*)molybdenum(III), [Mo(η^2 -S₂CNEt₂)₃(NS)]

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Abstract

The structure of the title compound consists of a neutral [Mo(C₅H₁₀NS₂)₃(NS)] unit, with the ligands arranged in a distorted pentagonal bipyramidal configuration. The thionitrosyl ligand occupies an axial site, with an N—S bond length of 1.568 (4) Å. At 2.6083 (14) Å, the axial Mo—S bond is considerably elongated with respect to those in the pentagonal plane [average 2.509 (16) Å].

Comment

Nitrosyl complexes of transition metals have been the subject of considerable interest for many years, while in comparison, compounds containing the heavier thionitrosyl ligand are relatively rare (Roesky & Pandey, 1983; Hübener, Abram & Strähle, 1994). One of the earliest reports of thionitrosyl complexes concerned the preparation of the molybdenum(III) complexes [Mo(η^2 -S₂CNR₂)₃(NS)] [*R* = Me, Et or (CH₂)₂], formed upon thermolysis of the dioxo complexes [MoO₂(η^2 -S₂CNR₂)₂] with trimethylsilyl azide (Bishop, Chatt & Dilworth, 1979). The dimethyldithiocarbamate complex (*R* = Me) was the first thionitrosyl complex to be characterized by X-ray crystallography (Hursthouse & Motevalli, 1979) and revealed some interesting features of the ligand, namely an essentially linear Mo—N—S vector and a short sulfur–nitrogen interaction. During the course of our studies on the thermal rearrangement of the dithiocarbamate ligand at high-valent molybdenum centres (Coffey, Forster & Hogarth, 1996), we serendipitously prepared the title complex, (I), and report here its crystal structure.

