

Acta Chim. Slov. **1999**, 46(2), pp. 155-160

**STRUCTURAL IDENTIFICATION OF
TRANS-[Mo^{III}Br₂py₄]Br₃ (py=PYRIDINE, C₅H₅N)***

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(Received 30.3.1999)

Abstract

Trans-[Mo^{III}Br₂py₄]Br₃ crystallizes in the orthorhombic, Pcnm space group, with a=7.670(2), b=22.063(3) and c=15.237(1)Å. Unit cell contains 4 formula units. Mo-Br and Mo-N(pyridine) bonds are 2.552(1) and 2.210(7), 2.222(8)Å. Trans located pyridine rings are staggered. Tribromide ion is symmetrical, but not linear. The compound is isostructural with trans-[Mo^{III}Cl₂py₄]Br₃

Introduction

Trans-[Mo^{III}Br₂py₄]Br₃ is the product of the oxidative decomposition of trans, trans-[MoBr₂py₄][MoBr₄py₂] [1]. Several other halo-pyridine compounds of Molybdenum(III) are known. The first among them mer-MoX₃py₃ (X=Cl,Br) were prepared long time ago [2]. Later several compounds containing trans and cis-[MoX₄py₂]⁻ and [MoX₅py]²⁻ (X=Cl,Br), were characterised [3,4]. Trans-[Mo^{III}Br₂py₄]Br₃ was expected to be isostructural with trans-[Mo^{III}Cl₂py₄]Br₃ [5], and the crystal structure analysis was undertaken to prove this hypothesis.

*Dedicated to the memory of Prof.Dr.Jože Šiftar

Results and Discussion

Trans-[Mo^{III}Br₂py₄]Br₃ and trans-[Mo^{III}Cl₂py₄]Br₃ are the only examples of the monomeric coordination compounds in which four pyridine ligands are coordinated to molybdenum(III). Trans located pyridine rings are in staggered conformation. Almost identical cation geometry was found before in the structures of trans-[Ir^{III}Cl₂py₄]Cl·6H₂O [6], trans-[Rh^{III}Cl₂py₄][H(ONO₂)₂] [7] and trans-[Ru^{III}Cl₂py₄]-IH(ONO₂)₂ [8]. On the contrary pyridine rings in trans-[CrF₂py₄](PF₆) are in eclipsed conformation[9]. Eclipsed conformation was found as well in the cationic part of trans,trans-[MoX₂py₄][MoX₄py₂] [1].

Cation and anion are located on the two-fold axis. Mo-Br and Mo-N(pyridine) bonds have expected values around 2.55 and 2.20 Å (see Table 3.). Molybdenum atom has octahedral coordination with octahedral angles close to 90° and 180°. Acute angles between the equatorial plane defined by molybdenum and two nitrogen atoms and the pyridine rings are 45.6(4) and 47.5(4)°. Pyridine rings are planar within 0.01 Å. All bonds and angles are normal. Angles between the planes of the trans located pyridine rings are 86.0(4) and 93.8(4)°.

The tribromide ion is symmetrical and close to linear. As observed before, large cations favour symmetrical structure [10]

Table 1. Crystal data for trans-[Mo^{III}Br₂py₄]Br₃

Formula	C ₂₀ H ₂₀ Br ₅ MoN ₄	Volume(Å ³)	2578.1(1)
Formula weight	811.86	D _c (mg/m ³)	2.09
Space group	Pbcn	μ(MoKα)mm ⁻¹	8.19
Z	4	Indep.refl.	2261
a(Å)	7.670(2)	Observ.refl.	1234
b	22.064(3)	R, I>3σ(I)	0.045
c	15.237(1)	wR	0.054

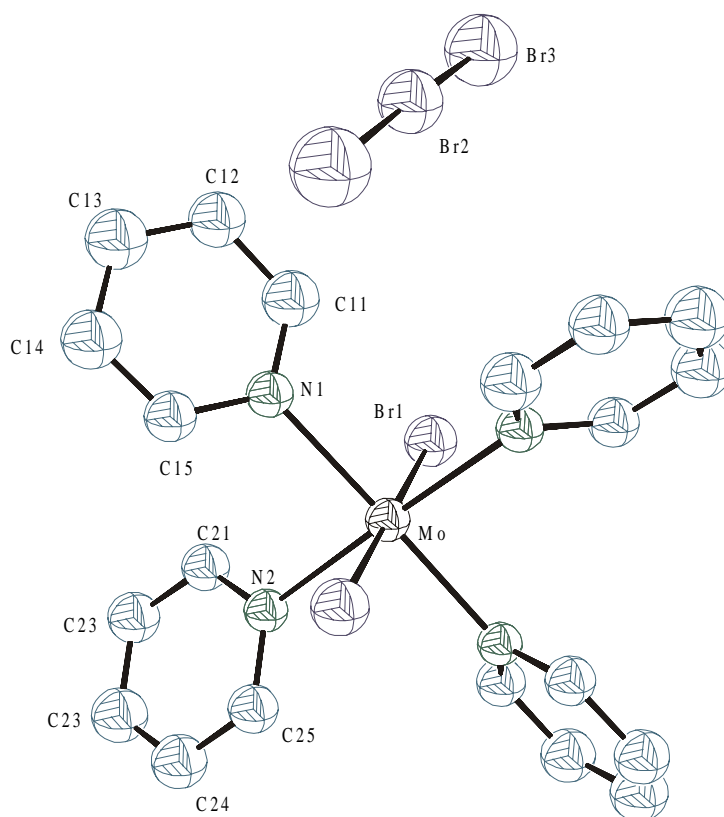


Fig. 1. ORTEP view of the molecule with the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level

Experimental

Trans-[Mo^{III}Br₂py₄]Br₃ was crystallized from the acetonitrile solution which was concentrated above sulfuric acid at room temperature. Yellow single crystals of square shape were used for X-ray structural analysis.

Enraf-Nonius CAD4 diffractometer and ω - 2θ scan mode was used for collecting the data. Reflections were corrected for Lorentz, polarization effects and absorption.

Important crystal data are collected in Table 1. Tables 2 and 3 contain atomic positions and dimensions. Figure 1 shows cation and anion with the numbering scheme. The phase problem was solved by direct methods. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in calculated

positions and included in the final refinement with the fixed positional and displacement parameters. Crystallographic calculations were carried out using CRYSTALS[11] and NRCVAX [12] program packages.

Table 2. Fractional atomic coordinates and equivalent displacement parameters(\AA^2).
Ueq is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	Ueq
Mo	0.00	0.38507(5)	0.25	0.0330(2)
Br1	0.24819(2)	0.38553(5)	0.36161(7)	0.0514(3)
Br2	0.00	0.64161(7)	0.25	0.0625(3)
Br3	0.2131(2)	0.63952(7)	0.3768(1)	0.0874(3)
N1	0.133(1)	0.3135(3)	0.1740(5)	0.034(1)
N2	0.141(1)	0.4549(3)	0.1727(5)	0.036(1)
C11	0.305(1)	0.3167(5)	0.1588(7)	0.042(2)
C12	0.392(1)	0.2739(5)	0.1111(8)	0.051(2)
C13	0.301(2)	0.2257(6)	0.0772(8)	0.059(2)
C14	0.129(2)	0.2221(5)	0.0939(8)	0.055(2)
C15	0.046(1)	0.2664(5)	0.1418(7)	0.044(2)
C21	0.151(1)	0.4499(4)	0.0852(1)	0.044(2)
C22	0.242(2)	0.4909(6)	0.0357(7)	0.059(2)
C23	0.326(2)	0.5378(5)	0.0762(8)	0.062(2)
C24	0.318(2)	0.5422(5)	0.1649(8)	0.053(2)
C25	0.222(2)	0.5001(5)	0.2107(7)	0.055(2)

Tables of observed and calculated structure factors, anisotropic displacement parameters and hydrogen atoms positions are available from the authors on request.

Table 3. Selected geometric parameters (Å, °)

Mo - N1	2.210(7)	Mo - Br1	2.552(1)
Mo - N2	2.222(8)	Br2 - Br3	2.531(2)
N1 - Mo - N2	89.6(3)	N1 - Mo - N1 ⁱ	88.7(3)
N1 - Mo - Br1	90.4(2)	N2 - Mo - N2 ⁱ	92.1(3)
N2 - Mo - Br1	89.3(2)	N1 - Mo - N2 ⁱ	178.1(3)
N1 ⁱ - Mo - Br1	89.9(2)	Br1 - Mo - Br1 ⁱ	179.55(6)
N2 ⁱ - Mo - Br1	90.4(2)	Br3 - Br2 - Br3 ⁱ	177.91(9)

Symmetry code: (i) -x, y, ½ -z

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Povzetek

Trans-[Mo^{III}Br₂py₄]Br₃ kristalizira v ortorombski prostorski skupini Pcnm z a=7.67(2), b=22.063(3) in c=15.237(1)Å. V osnovni celici so 4 formulske enote. Razdalje Mo-Br in Mo-N(piridin) so 2.552(1) in 2.210(7), 2.222(8)Å. Piridinski obroči, ki so v trans položajih drug napram drugem, tvorijo med seboj pravi kot. Tribromidni anion je simetričen, vendar ni linearen. Spojina ima enako strukturo kot trans-[Mo^{III}Cl₂py₄]Br₃.

