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Synthesis and identification of pentachloropyridinemolybdate(III) and pentabromopyridinemolybdate(III): crystal structures of $[NH_2(CH_3)_2]_2[MopyCl_5]$ and $[N(CH_3)_4]_2[MopyCl_5]$ (py = pyridine) ☆

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Abstract

The first reaction product between $(pyH)_3[MoX_6]$ (X = Cl,Br) and diluted pyridine at 20 °C or lower is $(pyH)_2[MopyX_5]$. $M^I_2[MopyX_5]$ with different cations ($M^I = NH_2(CH_3)_2^+$, $N(CH_3)_4^+$ and others) can be prepared from concentrated aqueous ammonia solutions of $(pyH)_2[MopyX_5]$. $M^I_2[MopyX_5]$ reacts further with pyridine; depending on the reaction conditions the products are *cis*- or *trans*-$M^I[Mopy_2X_4]$ or *mer*-$Mopy_3X_3$ (X = Cl,Br). The compounds were characterised by chemical analysis, infrared spectroscopy, conductivity measurements, magnetic measurements at room temperature, and X-ray powder diffraction, and two of them – $[NH_2(CH_3)_2]_2[MopyCl_5]$ (**A**) and $[N(CH_3)_4]_2[MopyCl_5]$ (**B**) – were characterised by single-crystal X-ray analysis. **A** and **B** crystallize in the monoclinic *C2/c* space group, with $Z = 4$. Molybdenum is octahedrally coordinated by 5 chlorine atoms and pyridine. The average Mo–Cl and Mo–N(pyridine) distances are 2.44(1) and 2.20(1) Å.

Keywords: Molybdenum complexes; Pyridine complexes; Crystal structures

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1. Introduction

It has been known for some time that substitution of halides by pyridine in $(pyH)_3[MoX_6]$ proceeds stepwise. At the boiling temperature of pyridine, first *trans*-$(pyH)[Mopy_2X_4]$ and then *mer*-$Mopy_3X_3$ is formed [1].

At room temperature, the reaction of pyridine diluted in acetonitrile with $(pyH)_3[MoCl_6]$ or $(NH_4)_2[MoBr_5 \cdot H_2O]$ gives a mixture of *cis*- and *trans*-$(pyH)[Mopy_2X_4]$ [2,3].

Cis,trans-$M^I[Mpy_2X_4]$ and *mer,fac*-Mpy_3X_3 compounds are known to exist for other trivalent metals such as rhodium and iridium. Examples are *cis,trans*-$K[Rhpy_2Cl_4] \cdot H_2O$, *cis,trans*-$K[Irpy_2Cl_4] \cdot H_2O$ [4] and *mer,fac*-Mpy_3X_3 (M = Rh,Ir) [5]. In rhodium and iridium chemistry there are also several known compounds with $[MpyX_5]^{2-}$ anions, such as $(pyH)_2[RhpyBr_5]$ [6] and $Cs_2[IrpyCl_5]$ [7].

The aim of this work was to find a way to synthesize molybdenum(III) compounds with the formula $[MopyX_5]^{2-}$ (X = Cl,Br).

2. Experimental

2.1. Materials

The $(pyH)_3[MoX_6)$ (X = Cl,Br) compounds were prepared as described previously [1]. The compounds were analysed for carbon, hydrogen and nitrogen contents on a Perkin-Elmer 2400 CHN analyser. All products are reasonably stable in dry atmosphere, but slowly oxidise in the presence of oxygen.

2.1.1. $(pyH)_2[MopyCl_5]$

5.5 mmol (3 g) of $(pyH)_3[MoCl_6]$ were added to 54 ml acetonitrile and 6 ml pyridine. The reaction mixture was stirred at room temperature for 20 h. The orange product was filtered and dried in vacuum. The average yield was 1.7 g (60%). *Anal.* Calc. for $(pyH)_2[MopyCl_5]$:

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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C, 35.15; H, 3.34; N, 8.20. Found: C, 34.90; H, 2.95; N, 8.10%.

2.1.2. $[NH_2(CH_3)_2]_2[MopyCl_5]$

0.5 mmol (0.26 g) of $(pyH)_2[MopyCl_5]$ was dissolved in 20 ml conc. aq. ammonia at room temperature. 3.5 ml of dimethylamine were added and the reaction mixture was left at −17 °C for 2 days. The orange crystalline product was filtered and dried in vacuum. The average yield was around 10% (0.05 g). *Anal.* Calc. for $[NH_2(CH_3)_2][MopyCl_5]$: C, 24.32; H, 4.76; N, 9.45. Found: C, 24.10; H, 4.52; N, 9.30%.

2.1.3. $[N(CH_3)_4]_2[MopyCl_5]$

0.5 mmol (0.26 g) of $(pyH)_2[MopyCl_5]$ was dissolved in 30 ml conc. aq. ammonia at room temperature. After the addition of 2 mmol (0.22 g) $[N(CH_3)_4]Cl$, an orange crystalline product precipitated; it was filtered and dried in vacuum. The average yield was 70% (0.36 g). *Anal.* Calc. for $[N(CH_3)_4]_2[MopyCl_5]$: C, 31.19; H, 5.84; N, 8.39. Found: C, 30.89; H, 5.70; N, 8.32%.

2.1.4. $(pyH)_2[MopyBr_5]$

5.5 mmol (3.94 g) of $(pyH)_3[MoBr_6]$ were reacted at 0 °C with 6 ml pyridine diluted in 54 ml acetonitrile. The reaction mixture was stirred for 1 h. The red-orange product that precipitated was filtered and dried in vacuum. The average yield was 1 g (25%). *Anal.* Calc. for $(pyH)_2[MopyBr_5]$: C, 24.52; H, 2.33; N, 5.72. Found: C, 24.66; H, 1.92; N, 5.61%.

2.1.5. $[NH_2(CH_3)_2]_2[MopyBr_5]$

0.4 mmol (0.29 g) of $(pyH)_2[MopyBr_5]$ was dissolved in 24 ml conc. aq. ammonia. 10 ml of dimethylamine were added and the solution was kept at −17 °C for 6 days. The crystalline product was filtered and dried in vacuum. The average yield was around 0.4 g (15%). *Anal.* Calc. for $[NH_2(CH_3)_2]_2[MopyBr_5]$: C, 16.21; H, 3.18; N, 6.30. Found: C, 16.15; H, 3.05; N, 6.40%.

2.1.6. $[N(CH_3)_4]_2[MopyBr_5]$

0.4 mmol (0.29 g) of $(pyH)_2[MopyBr_5]$ and 0.8 mmol (0.09 g) of $[N(CH_3)_4]Cl$ were dissolved in 50 ml conc. aq. ammonia. After one day at −17 °C a crystalline product was obtained. The average yield was around 0.14 g (50%). *Anal.* Calc. for $[N(CH_3)_4]_2[MopyBr_5]$: C, 21.60; H, 4.04; N, 5.81. Found: C, 21.30; H, 3.95; N, 5.70%.

2.2. Methods

Infrared (IR) spectra were measured on a Perkin-Elmer 1720-X FT-IR instrument from 4000 to 220 cm^{-1} (Nujol mulls between CsI plates).

The conductance of 0.001 M DMSO solutions was monitored at 20 °C with an ISKRA MA 5964 digital laboratory conductometer.

Table 1
Crystal data for $[NH_2(CH_3)_2]_2[MopyCl_5]$ (**A**) and $[N(CH_3)_4]_2[MopyCl_5]$ (**B**)

	A	**B**
Formula	$C_9H_{21}Cl_5MoN_3$	$C_{13}H_{29}Cl_5MoN_3$
Crystal size (mm)	0.4×0.25×0.15	0.4×0.4×0.52
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a (Å)	13.601(2)	14.060(1)
b (Å)	11.418(10)	11.257(1)
c (Å)	11.557(2)	13.639(1)
ß (°)	96.20(1)	96.07(1)
V (Å³)	1784.3(4)	2146.7(3)
Z	4	4
D_x (g cm^{-3})	1.655	1.549
D_m	1.66(2)	1.55(2)
Radiation	Mo Kα	Cu Kα
Wavelength (Å)	0.7093	1.54184
T (K)	293(2)	298(2)
Absorption coeff. (mm)	1.47	10.99
Independent reflections	2603	2143
Observed reflections	2467	1800
Criterion	$I > 2\sigma(I)$	$I > 3\sigma(I)$
R_1	0.018	0.033
R_w	0.043	0.035
Refinement	F^2	F

Table 2
Final coordinates and isotropic thermal parameters ($Å^2 \times 10^3$) for $[NH_2(CH_3)_2]_2[MopyCl_5]$ (**A**) and $[N(CH_3)_4]_2[MopyCl_5]$ (**B**) [a]

Compound	Atom	x	y	z	U_{eq}
A	Mo	0	0.1950(1)	0.25	30(1)
	Cl1	0	−0.0182(1)	0.25	48(1)
	Cl2	−0.0188(1)	0.1989(1)	0.0380(1)	46(1)
	Cl3	0.1795(1)	0.1953(1)	0.2476(1)	46(1)
	N1	0	0.3882(1)	0.25	36(1)
	C1	0.0445(1)	0.4490(1)	0.1710(1)	47(1)
	C2	0.0463(1)	0.5697(1)	0.1692(2)	62(1)
	C3	0	0.6311(2)	0.25	66(1)
	N2	−0.1673(1)	−0.0156(2)	−0.0224(1)	50(1)
	C21	−0.2349(2)	0.0703(2)	−0.0822(2)	78(1)
	C22	−0.2112(2)	−0.0926(2)	0.0593(2	64(1)
B	Mo	0	0.21682(4)	0.25	27(1)
	Cl1	0	0.4340(1)	0.25	42(1)
	Cl2	0.16918(7)	0.2128(1)	0.22105(8)	42(1)
	Cl3	0.04338(8)	0.2078(1)	0.42751(7)	40(1)
	N1	0	0.0217(4)	0.25	27(1)
	C1	−0.0382(3)	−0.0421(4)	0.3195(3)	39(1)
	C2	−0.0398(4)	−0.1636(4)	0.3210(3)	52(1)
	C3	0	−0.2266(6)	0.25	50(1)
	N2	0.2898(2)	−0.0124(3)	0.4931(3)	36(1)
	C21	0.3630(4)	−0.0990(5)	0.5348(5)	68(1)
	C22	0.2018(4)	−0.0781(5)	0.4521(4)	62(1)
	C23	0.2649(3)	0.0687(4)	0.5731(4)	53(1)
	C24	0.3288(5)	0.0568(6)	0.4134(4)	75(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Magnetic measurements at room temperature (22 °C) were made on a Sherwood Scientific magnetic balance. The balance was calibrated with Hg[Co(NCS)$_4$] [8]. Measurements were corrected for diamagnetism [9].

Experimental details for collection of the X-ray data are given in Table 1. Unit cell dimensions were calculated by least-squares refinement of the accurately measured angle settings of 25 reflections. Lorentz, polarization and empirical absorption corrections were made [10]. The data were collected on an Enraf-Nonius CAD-4 diffractometer.

Table 3
Selected bonds lengths (Å) and angles (°) for $[NH_2(CH_3)_2]_2[MopyCl_5]$ (**A**) and $[N(CH_3)_4]_2[MopyCl_5]$ (**B**)

	A	**B**
Mo–Cl1	2.434(1)	2.445(1)
Mo–Cl2	2.437(1)	2.452(1)
Mo–Cl3	2.445(1)	2.436(1)
Mo–N1	2.206(1)	2.196(4)
Cl1–Mo–Cl2	91.06(1)	91.05(2)
Cl1–Mo–Cl3	90.08(1)	92.39(3)
Cl1–Mo–N1	180	180
Cl2–Mo–Cl3	89.14(2)	90.80(3)
N1–Mo–Cl2	88.94(1)	88.95(2)
N1–Mo–Cl3	89.92(1)	87.61(2)

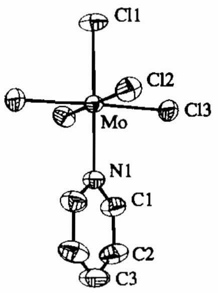

Fig. 1. ORTEP drawing of $[MopyCl_5]^{2-}$ with the numbering scheme.

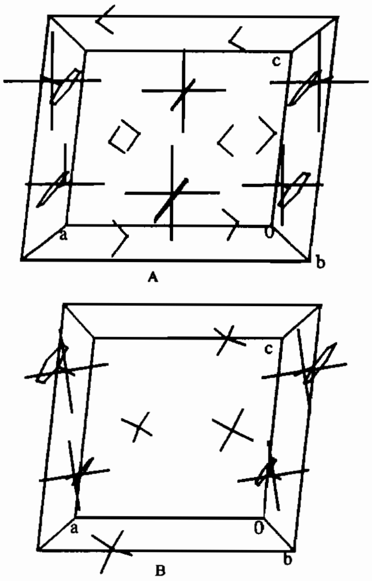

Fig. 2. Crystal packing of $[NH_2(CH_3)_2]_2[MopyCl_5]$ (**A**) and $[N(CH_3)_4]_2[MopyCl_5]$ (**B**) in the unit cell.

The structures were solved by Patterson and Fourier methods. Nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms, determined from difference-Fourier maps, were refined with isotropic temperature factors.

All calculations were performed with the SDP [11], MOLEN [12], SHELXL 93 [13] and NRCVAX [14] programs. Tables 2 and 3 contain positional parameters and selected dimensions with angles. Fig. 1 shows the anion along with the numbering scheme, which is the same for both compounds. Packing in the unit cell is depicted in Fig. 2.

3. Results and discussion

Stepwise substitution of halides in $[MoX_6]^{3-}$ goes through the following steps:

$$[MoX_6]^{3-} \xrightarrow{py} [MopyX_5]^{2-} \xrightarrow{py}$$

$$cis,trans\text{-}[Mopy_2X_4]^{2-} \xrightarrow{py} mer\text{-}Mopy_3X_3$$

$$(X=Cl, Br)$$

Substitution always ends with *mer*-Mopy$_3$X$_3$.

By contrast, in rhodium(III) and iridium(III) chemistry, further substitution products such as $[Mpy_4X_2]^+$ are also known [5]. The existence of $[Mpy_4X_2]^+$ proves that steric factors are not the only reason for the absence of $[Mopy_4X_2]^+$, especially because compounds such as $[Crpy_4F_2]NO_3$ with the smaller Cr^{3+} cation exist [15].

Compounds with the $[MopyX_5]^{2-}$ anion are paramagnetic, with magnetic moments at room temperature, μ_{eff}, from 3.70 to 3.80 B.M., which is in the expected range for spin-only values for d^3 systems [16].

0.001 M solutions in DMSO have equivalent conductivities from 60 to 80 Ω^{-1} cm^2 mol^{-1}, and they increase with time. DMSO probably reacts with solutes. Literature values for the 1:1 and 1:3 electrolytes in DMSO are 20–30 and around 110 Ω^{-1} cm^2 mol^{-1}, respectively [17]. Our values are in between, as expected.

Depending on the experimental conditions (mostly temperature and time), $M^I_2[MopyX_5]$ compounds react with the solutions of pyridine in acetonitrile to give first a mixture of *cis*- and *trans*-$M^I[Mpy_2X_4]$ and then react further to give *mer*-Mopy$_3$X$_3$. Bromides are more reactive towards further substitution than chlorides. Both chlorides and bromides can easily be oxidised to oxomolybdenum(V) compounds that contain pyridine.

$(pyH)_2[MopyX_5]$ compounds are soluble in concentrated aqueous ammonia, which offers the possibility

Table 4
IR spectral data from 400 to 220 cm^{-1} [a]

Compound	Mo–Cl	Mo–(py)	Mo–Br
$(pyH)_2[MopyCl_5]$	296vs	256m	
$[NH_2(CH_3)_2]_2[MopyCl_5]$	298vs	252sh	
$[N(CH_3)_4]_2[MopyCl_5]$	302vs, 284s	250sh	
$(pyH)_2[MopyBr_5]$		246s	234vs
$[NH_2(CH_3)_2]_2[MopyBr_5]$		250s	234vs
$[N(CH_3)_4]_2[MopyBr_5]$		247s	229vs

[a] s = strong, m = medium, vs = very strong, sh = shoulder.

of preparing compounds with different cations. Cations such as caesium, rubidium, tetraphenylarsonium or tetraphenylphosphonium and others can be used.

The interplanar spacings for the pairs $[NH_2(CH_3)_2]_2[MopyX_5]$ and $[N(CH_3)_4]_2[MopyX_5]$ confirm that the chlorides and bromides are isostructural. The same is not true for the pyridinium pair $(pyH)_2[MopyX_5]$.

The infrared spectra of $M^{I}_2[MopyX_5]$ compounds from 4000 to 400 cm^{-1} contain characteristic absorptions of coordinated pyridine, pyridinium, dimethylammonium and tetramethylammonium cations. It is known that the IR spectra of pyridine complexes do not contain any ligand band with frequencies below 400 cm^{-1} [18]. From 400 to 220 cm^{-1} we expect to see Mo–Cl, Mo–Br and Mo–N(pyridine) valence vibrations. Chlorides absorb strongly around 300 cm^{-1} and have a band of medium intensity or a weak shoulder at 250 cm^{-1}. Bromides absorb strongly at 250 and 230 cm^{-1}.

Preliminary assignments are proposed in Table 4. They are based on the argument that Mo–N(pyridine) vibrations should occur at approximately the same frequencies in the chloro and bromo analogues, and that the Mo–Br vibration frequencies, measured in cm^{-1}, are shifted 20–25% downfield [5]. For the $[MopyX_5]^-$ group with idealised C_{4v} symmetry, three Mo–X valence vibrations ($2A_1+E$) are expected [19]. Some of the expected valence vibrations could also be outside the range of the instrument, and no exact assignment is possible at this stage.

4. Crystal structures

$[NH_2(CH_3)_2]_2[MopyCl_5]$ (**A**) and $[N(CH_3)_4]_2[MopyCl_5]$ (**B**) crystallize in the same space group. The crystal structures contain eight cations on the general position and four anions with the C_2 axis, which includes the Cl1, Mo, N1 and C3 atoms. The average Mo–Cl distance for **A** and **B** is 2.44(1) Å, which is almost the same as that found in *trans*-$(PPh_4)[Mo(THF)_2Cl_4]$ [20] and $(NH_4)_2[MoCl_5 \cdot H_2O]$ [9]. The average Mo–N(pyridine) bond length is 2.20(1) Å, almost the same value as that found for *trans*-$(pyp)[Mopy_2Cl_4]$ [21] and *cis*-$Rb[Mopy_2Cl_4] \cdot H_2O$ [2]. There is no structural *trans* effect.

The pyridine plane is oriented so as to cut the Cl2–Cl3 direction, in order to minimise steric effects. No important contacts between the anion and cation are present in either of the crystal structures.

5. Supplementary material

Listings of anisotropic thermal parameters (2 pages), hydrogen atom positions (2 pages), and observed and calculated structure factors (25 pages) are available from J.V.B. on request.

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