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Syntheses of *trans*-$[NH_4][MCl_4py_2]\cdot H_2O$ ($M = Mo, W$) and the Crystal Structure of $[NH_4][MoCl_4py_2]\cdot H_2O$

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The coordination chemistry of tungsten(III) and, to a lesser extent, of molybdenum(III) with the common nitrogen ligands has been moderately well explored. Sensitivity towards oxidation is the main barrier to more work being carried out on tungsten(III). It has been proved in the past that tungsten and molybdenum(III) compounds with the same chemical composition have identical crystal structures. A few examples are: *mer*-MX_3py_3, *mer*-MCl_3(4-pic)$_3$ and *trans*-$[pyH][MX_4py_2]$ (M = Mo, W; X = Cl, Br; py = pyridine, 4-pic = 4-methylpyridine) [1–3].

$[pyH][MCl_4py_2]$ (M = Mo, W) react with conc. ammonia solutions. Several products with the general formula $[NH_4][MCl_4py_2]\cdot A$ (A may be NH_3, H_2O, py or a combination) have been isolated [4]. $[NH_4][MoCl_4py_2]\cdot H_2O$ and $[NH_4][WCl_4py_2]\cdot H_2O$ are the most stable among the solvates and we believe they are worthy of characterization by chemical and physical methods.

Experimental

Preparation of $[NH_4][MoCl_4py_2]\cdot H_2O$

$[pyH][MoCl_4py_2]$ (0.002 mol, 0.96 g) was dissolved in 20 ml conc. NH_3. The solution was left in an evacuated desiccator over conc. H_2SO_4 for 4 h. A yellow crystalline product was filtered in air, washed with ether and dried in a vacuum; average yield 40%. The compound is stable when kept in a dry atmosphere. *Anal.* Calc. for $C_{10}H_{16}Cl_4MoN_3O$: C, 27.80; H, 3.73; N, 9.73. Found: C, 28.02; H, 3.75; N, 9.90%.

Preparation of $[NH_4][WCl_4py_2]\cdot H_2O$

$[pyH][WCl_4py_2]$ (0.0015 mol, 0.85 g) [2] was stirred for 4 h in a mixture of 12 ml H_2O and 13 ml conc. NH_3 under an Ar atmosphere. The suspension was filtered and the filtrate left at −20 °C for 3 days. The crystals were filtered and dried in a vacuum; the average yield was 15%. The orange–red crystalline product oxidizes in the air to WCl_4py_2. *Anal.* Calc. for $C_{10}H_{16}Cl_4N_3OW$: C, 23.10; H, 3.10; N, 8.08. Found: C, 24.14; H, 2.97; N, 8.25%.

TABLE 1. Crystal data for $[NH_4][MoCl_4py_2]\cdot H_2O$

Formula	$C_{10}H_{16}Cl_4MoN_3O$
Formula weight	432.01
Space group	$P2_1/c$
a (Å)	8.276(1)
b	12.867(2)
c	15.551(2)
β (°)	95.09(2)
Volume (Å^3)	1649.41
D_c (g cm^{-3})	1.74
D_m	1.75(2)
Z	4
μ(Mo Kα) (cm^{-1})	15.9

Physical Measurements

Infrared spectra were measured on a PE 521 instrument from 4000–250 cm^{-1}. Thermal behaviour up to 200 °C was monitored on a Mettler TA 2000 system. Visible and ultraviolet spectra for $[NH_4][MoCl_4py_2]\cdot H_2O$ were measured with a Specord M 40 Carl Zeiss instrument. A Guinier de Wolf camera and Cu Kα radiation were used to obtain interplanar spacings for powdered samples.

Crystal Structure of $[NH_4][MoCl_4py_2]\cdot H_2O$

Crystal data are given in Table 1. Unit cell parameters were obtained from the least-squares analysis of 44 reflections ($6° < \theta < 12°$) on a Enraf–Nonius CAD 4 computer-controlled diffractometer. Intensities were recorded on the same, instrument. Graphite-monochromated Mo Kα radiation and ω–2θ scan were used. From the 3953 reflections measured up to $\theta = 30°$, 2779 had $I > 2\sigma(I)$ and these were taken as observed. The intensities were corrected for Lorenz and polarization effects but not for absorption.

The Mo and Cl atoms were found from the Patterson map. Fourier syntheses identified the rest of the atoms. Mixed refinement, anisotropic for Mo and Cl atoms, ended with $R_1 = 0.034$ and $R_2 = 0.042$. Hydrogen atoms were not taken into consideration. An X-ray system of crystallographic programs was applied [5].

The atomic coordinates, equivalent isotropic and isotropic temperature factors are shown in Table 2. Bond distances and angles for $MoCl_4py_2^-$ are given in Table 3. The numbering scheme can be found in Fig. 1.

Results and Discussion

trans-$WX_4L_2^-$ is basic in the coordination chemistry of W(III) compounds. Several compounds con-

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TABLE 2. Fractional atomic coordinates ($\times 10^4$), equivalent[a] and isotropic thermal parameters ($\times 10^2$)

Atom	x	y	z	U or U_{eq}
Mo(1)	0	0	0	2.61(2)
Mo(2)	5000	5000	0	2.43(1)
Cl(11)	826(1)	1616(1)	741(1)	3.99(5)
Cl(12)	2474(1)	−822(1)	628(1)	3.93(5)
Cl(21)	2148(1)	4579(1)	53(1)	3.61(4)
Cl(22)	4920(1)	−3920(1)	1278(6)	3.90(5)[b]
N(11)	1236(3)	478(2)	−1134(2)	3.04(5)
C(12)	2773(5)	814(3)	−1060(2)	3.74(8)
C(13)	3586(5)	1087(3)	−1767(3)	4.38(9)
C(14)	2784(5)	996(4)	−2589(3)	4.61(9)
C(15)	1205(5)	646(3)	−2666(3)	4.31(9)
C(16)	471(5)	400(3)	−1930(2)	3.69(7)
N(21)	5678(3)	3630(2)	801(2)	2.95(6)
C(22)	4925(5)	2712(3)	662(2)	3.77(8)
C(23)	5311(5)	1842(3)	1152(3)	4.54(9)
C(24)	6537(6)	1904(4)	1803(3)	4.76(9)
C(25)	7314(6)	2846(4)	1962(3)	5.12(10)
C(26)	6856(5)	3688(3)	1452(3)	4.14(8)
N(3)	982(5)	6838(3)	706(3)	5.21(9)
O	1196(5)	3373(3)	7991(3)	6.76(9)

[a] $U_{eq} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix). [b] Isotropic temperature factors are of the form $\exp[-2\pi^2 U (\sin\theta/\lambda)^2]$.

taining this anion with the general formula $M^I[WX_4L_2]$ (X = Cl, Br; L = pyridine, 4-methylpyridine; M^I = pyH^+, 4-$picH^+$ or $LH...L^+$) have been structurally characterized [2, 3, 6, 7]. The compounds $[LH][WX_4L_2]$ dissolve in aqueous ammonia. Adducts of the general formula $[NH_4][WX_4L_2]\cdot A$ crystallize from the solution [4]. A recent and interesting example is the compound $[NH_4][WCl_4(4\text{-pic})_2]\cdot 4H_2O$ [8].

Molybdenum compounds containing *trans*-$MoX_4L_2^-$ are rare. A few examples are $[PPh_4][MoCl_4(THF)_2]$ [9], $[PPh_4][MoCl_4bipy]$ [10] and $[pyp][MoCl_4py_2]$ (pyp = 1-(4-pyridyl)pyridinium) [11].

$[NH_4][MCl_4py_2]\cdot H_2O$ (M = Mo, W) are isostructural. Interplanar spacings of $[NH_4][WCl_4py_2]\cdot H_2O$ can be indexed from the unit cell dimensions of $[NH_4][MoCl_4py_2]\cdot H_2O$ (see Table 4). The unit cell of $[NH_4][MoCl_4py_2]\cdot H_2O$ contains four NH_4^+, $MoCl_4py_2^-$ (two independent pairs) and four water molecules. The water molecules are bonded to NH_4^+ by one hydrogen bond (2.842(6) Å). Infrared spectra support the presence of lattice water molecules in both compounds. Pairs of absorptions located at 3545 and 3465 cm^{-1} together with their sharpness indicate the absence of strong hydrogen bonds.

Average Mo–Cl and M–N(pyridine) bonds of 2.434 and 2.203 Å are comparable to the values found in $[pyp][MoCl_4py_2]$: 2.422 and 2.195 Å [11]. Average C–N and C–C bonds in the pyridine rings, which are planar, are 1.342 and 1.381 Å.

TABLE 3. Bond lengths (Å) and angles (°)[a]

$MoCl_4N_2^-$	
Mo(1)–Cl(11)	2.445(1)
Mo(1)–Cl(12)	2.431(1)
Mo(1)–N(11)	2.203(3)
Mo(2)–Cl(21)	2.431(1)
Mo(2)–Cl(22)	2.431(1)
Mo(2)–N(21)	2.203(3)
Cl(11)–Mo(1)–Cl(12)	89.45(3)
N(11)–Mo(1)–Cl(11)	89.44(8)
N(11)–Mo(1)–Cl(12)	89.51(8)
Cl(21)–Mo(2)–Cl(22)	89.84(3)
N(21)–Mo(2)–Cl(21)	89.89(8)
N(21)–Mo(2)–Cl(22)	88.91(8)
py(1)	
N(11)–C(12)	1.339(5)
C(12)–C(13)	1.384(6)
C(13)–C(14)	1.392(6)
C(14)–C(15)	1.378(6)
C(15)–C(16)	1.379(6)
C(16)–N(11)	1.343(5)
N(11)–C(12)–C(13)	122.9(3)
C(12)–C(13)–C(14)	119.0(4)
C(13)–C(14)–C(15)	118.4(4)
C(14)–C(15)–C(16)	119.6(4)
C(15)–C(16)–N(11)	122.3(4)
C(16)–N(11)–C(12)	117.8(3)
py(2)	
N(21)–C(22)	1.343(5)
C(22)–C(23)	1.377(6)
C(23)–C(24)	1.381(6)
C(24)–C(25)	1.382(7)
C(25)–C(26)	1.375(6)
C(26)–N(21)	1.344(5)
N(21)–C(22)–C(23)	122.6(3)
C(22)–C(23)–C(24)	118.9(4)
C(23)–C(24)–C(25)	118.7(4)
C(24)–C(25)–C(26)	119.1(4)
C(25)–C(26)–N(21)	122.8(4)
C(26)–N(21)–C(22)	118.1(3)

[a] Standard deviations are in parentheses.

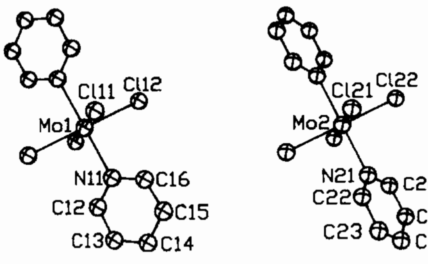

Fig. 1. Numbering schemes for the $MoCl_4py_2^-$ groups.

TABLE 4. Calculated interplanar spacings (Å) for $[NH_4][MoCl_4py_2]\cdot H_2O$ (A) and measured values for $[NH_4][MoCl_4py_2]\cdot H_2O$ (B) and $NH_4[WCl_4py_2]\cdot H_2O$ (C)

No.	*h*	*k*	*l*	A	B	Int.[a]	C	Int.[a]
1	0	0	2	7.74	7.7	8	7.7	8
2	1	1	−1	6.52	6.5	10	6.5	10
3	0	2	0	6.44	6.4	7	6.4	8
4	1	1	1	6.17	6.1	10	6.15	10
5	0	2	2	4.95	4.9	7	4.92	7
6	1	2	−1	4.90	4.25	6	4.25	7
7	1	1	−3	4.30				
8	1	2	2	4.14	4.10	3	4.10	3
9	0	3	1	4.13				
10	2	0	0	4.12				
11	0	2	3	4.03	4.00	1	4.00	3
12	1	1	3	4.00				
13	2	1	0	3.93	3.90	3		
14	2	1	−1	3.88	3.88	1	3.88	1
15	0	0	4	3.87				

[a] Intensities were estimated visually.

The infrared spectra of both compounds confirm the presence of NH_4^+ (N–H valence vibration at 3140 cm^{-1}), vibrations due to the coordinated pyridine and, at the low energy end, absorptions which are due to the Mo–Cl or W–Cl valence vibrations (two bands: 315 and 295 cm^{-1} for $[NH_4][MoCl_4py_2]\cdot H_2O$; 310 and 270 cm^{-1} for $[NH_4][WCl_4py_2]\cdot H_2O$).

$[NH_4][MCl_4py_2]\cdot H_2O$ react with pyridine to form monoclinic *mer*-MCl_4py_3 [1]. Both compounds are stable with respect to the loss of the water molecule. Up to 100 °C there is no change of mass at the heating rate of 2 °C/min. Even after heating for 1h at 130 °C, the infrared spectrum still shows the presence of water. At 150 °C the compounds decompose to $[NH_4][MCl_4py_2]$ and further heating initiates decomposition.

Visible and ultraviolet spectra of $[NH_4][MoCl_4py_2]\cdot H_2O$ measured in water or conc. ammonia solutions contain several absorptions. The first is located at 513 nm (ϵ = 10) and may belong to the d–d transition. The unresolved broad doublet at 364 and 347 nm (ϵ = 1565 and 1590) and the band at 274 nm (ϵ = 2190) are charge-transfer bands. In analogy to work known from the literature [12], the 513 nm band could be assigned to the $^4A_{2g} \rightarrow {^4T_{2g}}$ transition.

Supplementary Material

Tables of anisotropic thermal parameters and calculated and observed structure factors are available from the authors on request.

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