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Ammonium *cis*-Tetrachlorobispyridine-molybdate(III)–Pyridine–Water (1/1/0.5)

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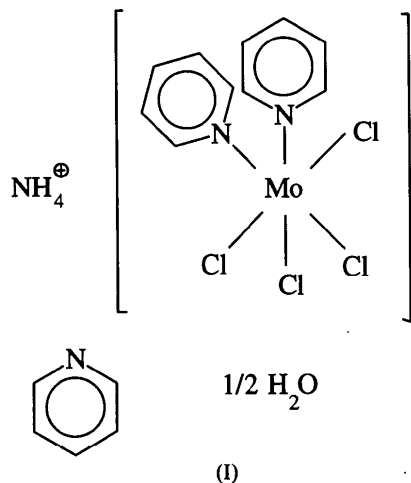
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Abstract

The structure of $(\text{NH}_4)[\text{Mo}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4] \cdot \text{C}_5\text{H}_5\text{N} \cdot 0.5\text{H}_2\text{O}$ consists of ammonium cations, *cis*-tetrachlorobispyridinemolybdate(III) anions, pyridine and water molecules. The distances and angles in the distorted octahedral $[\text{MoCl}_4\text{py}_2]^-$ anion and in the pyridine molecule are generally as expected. The structural moieties are held together by hydrogen bonds of the types $\text{N}-\text{H} \cdots \text{Cl}$ and $\text{N}-\text{H} \cdots \text{O}$.

Comment

Crystal structures of several *mer*- MX_3py_3 ($M = \text{Cr}, \text{Mo}$; $X = \text{Cl}$; $\text{py} = \text{pyridine}$) complexes have been described in the literature (Howard & Hardcastle, 1985, and references therein) and just recently the crystal structure of *mer*- VCl_3py_3 was reported (Sorensen, Ziller & Doherty, 1994). During several attempts to prepare *fac*- MoCl_3py_3 from *cis*-(pyH) $[\text{MoCl}_4\text{py}_2]$ (Brenčič, Leban & Modec, 1994), the crystalline product with the composition $\text{MoCl}_3\text{py}_3 \cdot \text{NH}_4\text{Cl} \cdot 0.5\text{H}_2\text{O}$ was obtained. It was believed to be *fac*- MoCl_3py_3 . Because chemical and spectroscopic methods do not easily differentiate between *fac*- and *mer*- MoCl_3py_3 , the crystal structure analysis was undertaken to resolve this dilemma, revealing the title compound (I).



The distortion of the octahedral $[\text{MoCl}_4\text{py}_2]^-$ anion is a result of the interactions with the NH_4^+ cation. The $\text{Mo}-\text{Cl}3$ and $\text{Mo}-\text{Cl}2$ distances are longer than the $\text{Mo}-\text{Cl}1$ and $\text{Mo}-\text{Cl}4$ distances. Two $\text{Cl} \cdots \text{NH}_4^+$ contacts were found: $\text{Cl}3 \cdots \text{N}$ and $\text{Cl}4 \cdots \text{N}$; the $\text{Cl}1 \cdots \text{N}$ and $\text{Cl}2 \cdots \text{N}$ distances are longer than 3.35 Å. The pyridine solvate molecule forms only one contact with the NH_4^+ cation [$\text{N}31^i \cdots \text{N}$ 2.760 (11) Å; symmetry code: (i) $1-x, 1-y, 1-z$]. There is also a hydrogen bond between NH_4^+ and a water molecule situated on the centre of symmetry (Fig. 2).

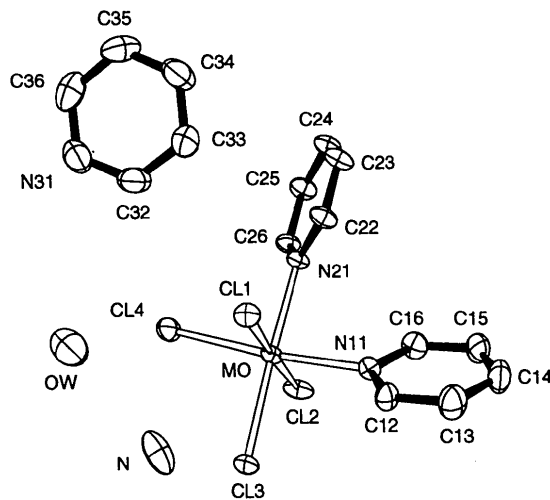


Fig. 1. ORTEP (Johnson, 1971) view of the asymmetric unit of the structure with atomic numbering. Anisotropic displacement ellipsoids are at the 30% probability level. H atoms are omitted for clarity.

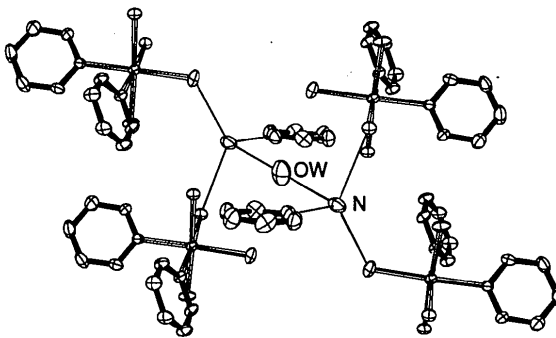
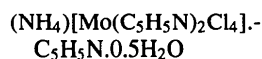


Fig. 2. ORTEP (Johnson, 1971) view of the environment of the NH_4^+ cation and the water molecule. Hydrogen bonds are indicated by thin lines.

Experimental

0.48 g (0.001 mol) of *cis*-(pyH) $[\text{MoCl}_4\text{py}_2]$ was dissolved in 25 ml of concentrated aqueous NH_3 . 5 ml of pyridine was added and the resulting yellow solution was left in the desiccator over concentrated H_2SO_4 at 281 K. After 2 d yellow platelets were obtained (0.2 g, yield 40%). Analysis calculated (found): C 35.88 (35.34), H 4.00 (3.79), N 11.16% (10.90%).

Crystal data



$$M_r = 502.1$$

Monoclinic

$$P2_1/c$$

$$a = 7.384 (1) \text{ \AA}$$

$$b = 32.637 (4) \text{ \AA}$$

$$c = 8.860 (1) \text{ \AA}$$

$$\beta = 97.23 (2)^\circ$$

$$V = 2118.2 (5) \text{ \AA}^3$$

$$Z = 4$$

$$D_x = 1.574 \text{ Mg m}^{-3}$$

Data collection

Enraf-Nonius CAD-4

diffractometer

 $\omega/2\theta$ scans of variable rate

Absorption correction:

by integration from crystal shape

$$T_{\min} = 0.789, T_{\max} = 0.868$$

11 881 measured reflections

5599 independent reflections

Mo $K\alpha$ radiation

$$\lambda = 0.7107 \text{ \AA}$$

Cell parameters from 25 reflections

$$\theta = 10\text{--}12^\circ$$

$$\mu = 1.121 \text{ mm}^{-1}$$

$$T = 293 (2) \text{ K}$$

Prismatic

$$0.37 \times 0.17 \times 0.14 \text{ mm}$$

Yellow

4307 observed reflections

$$[I > 2\sigma(I)]$$

$$R_{\text{int}} = 0.030$$

$$\theta_{\text{max}} = 28.91^\circ$$

$$h = 0 \rightarrow 10$$

$$k = -44 \rightarrow 44$$

$$l = -12 \rightarrow 11$$

3 standard reflections

frequency: 120 min

intensity variation: 2.27%

Refinement

Refinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.058$$

$$wR(F^2) = 0.126$$

$$S = 1.391$$

5586 reflections

225 parameters

Only H-atom U 's refined

$$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 10.9983P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = -0.274$$

$$\Delta\rho_{\text{max}} = 0.581 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.940 \text{ e \AA}^{-3}$$

Extinction correction: none

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 (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Mo	0.27038 (6)	0.36673 (2)	0.44699 (5)	0.02918 (12)
Cl1	0.5166 (2)	0.39838 (5)	0.3311 (2)	0.0404 (3)
Cl2	0.0297 (2)	0.33192 (6)	0.5586 (2)	0.0478 (4)
Cl3	0.4533 (2)	0.37182 (5)	0.6962 (2)	0.0394 (3)
Cl4	0.1265 (2)	0.43376 (6)	0.4649 (2)	0.0505 (4)
N11	0.3918 (6)	0.30663 (15)	0.4079 (5)	0.0337 (10)
N12	0.5712 (8)	0.3007 (2)	0.4377 (8)	0.0446 (15)
N13	0.6533 (12)	0.2646 (3)	0.4024 (10)	0.068 (2)
N14	0.5470 (13)	0.2334 (2)	0.3350 (11)	0.073 (3)
N15	0.3646 (12)	0.2393 (2)	0.3035 (9)	0.061 (2)
N16	0.2894 (9)	0.2757 (2)	0.3419 (8)	0.047 (2)
N21	0.1102 (6)	0.3595 (2)	0.2210 (5)	0.0335 (11)
N22	0.1908 (8)	0.3537 (2)	0.0962 (7)	0.043 (2)
N23	0.0964 (10)	0.3498 (2)	-0.0458 (7)	0.051 (2)
N24	-0.0887 (9)	0.3519 (2)	-0.0639 (7)	0.048 (2)
N25	-0.1757 (8)	0.3575 (2)	0.0635 (7)	0.046 (2)
N26	-0.0733 (8)	0.3617 (2)	0.2035 (6)	0.0404 (14)
N31	0.2291 (11)	0.5187 (2)	0.0891 (9)	0.072 (2)
N32	0.3008 (13)	0.4818 (3)	0.1074 (9)	0.074 (3)
N33	0.3233 (13)	0.4569 (3)	-0.0100 (10)	0.071 (2)
N34	0.2704 (13)	0.4698 (3)	-0.1535 (10)	0.080 (3)
N35	0.1966 (13)	0.5072 (3)	-0.1766 (10)	0.079 (3)

C36	0.1742 (13)	0.5313 (3)	-0.0532 (13)	0.080 (3)
N	0.7707 (10)	0.4385 (2)	0.6424 (9)	0.079 (2)
OW	1/2	1/2	1/2	0.120 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mo—N11	2.202 (5)	Mo—Cl4	2.446 (2)
Mo—N21	2.206 (4)	N...Cl3	3.276 (8)
Mo—Cl2	2.423 (2)	N...OW	2.997 (7)
Mo—Cl1	2.429 (2)	N...Cl4 ⁱ	3.231 (8)
Mo—Cl3	2.4446 (15)	N...N31 ⁱⁱ	2.760 (11)
N11—Mo—N21	86.8 (2)	N21—Mo—Cl4	88.09 (13)
N11—Mo—Cl2	88.89 (13)	Cl2—Mo—Cl4	92.63 (7)
N21—Mo—Cl2	89.04 (13)	Cl1—Mo—Cl4	90.08 (6)
N11—Mo—Cl1	88.35 (13)	Cl3—Mo—Cl4	94.33 (6)
N21—Mo—Cl1	90.35 (13)	Cl3...N...OW	93.1 (2)
Cl2—Mo—Cl1	177.20 (7)	Cl3...N...Cl4 ⁱ	132.8 (3)
N11—Mo—Cl3	90.75 (13)	Cl3...N...N31 ⁱⁱ	97.7 (3)
N21—Mo—Cl3	177.58 (14)	OW...N...Cl4 ⁱ	111.5 (2)
Cl2—Mo—Cl3	90.77 (5)	OW...N...N31 ⁱⁱ	87.2 (3)
Cl1—Mo—Cl3	89.72 (5)	Cl4 ⁱ ...N...N31 ⁱⁱ	122.1 (3)
N11—Mo—Cl4	174.68 (13)	N...OW...N ⁱⁱ	180.0 (2)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, 1 - z$.

A well formed single crystal was sealed in a glass capillary as the crystals proved to be sensitive to air and humidity. Space group $P2_1/c$ was determined from the intensity statistics. For six systematically absent reflections 'weak but significant intensity' was observed, which was not verified by photographs. The alternative space group $P2_1$ was also possible. The refinement was also performed in this space group with 11 130 reflections and assuming racemic twinning with Flack's (1983) factor $\chi = 0.57 (8)$. The $wR(\text{all})$ and $R(F_{\text{obs}})$ factors were 0.125 and 0.038, respectively. The centrosymmetric space group $P2_1/c$ was retained based on the arguments of Marsh & Herstein (1988) and on the fact that the e.s.d.'s of bond distances and angles did not differ between the two refinements. All H atoms were located in the difference map apart from those of the ammonium cation and the water molecule. The residual electron density was observed around these moieties, but it was not possible to interpret in terms of discrete H atoms. Common isotropic displacement parameters, U , used for H atoms at calculated positions on the pyridines in the anion and on the pyridine solvate molecules were 0.064 (7) and 0.095 (14) \AA^2 , respectively.

The structure was solved using *SHELXS86* (Sheldrick, 1985) and refined with *SHELXL93* (Sheldrick, 1993). Calculations were performed on the VAX 8550 cluster at the University Computer Centre, Ljubljana, under VMS 5.5-2, and partially on a PC 486. Additionally, *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989), the *GX* package (Mallinson & Muir, 1985) and *PLUTON* (Spek, 1991) were used for data processing and the final interpretation of structural geometry. Molecular graphics were produced using *ORTEP* (Johnson, 1971) and *PLUTON*, and the material for publication was prepared using *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AB1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Potassium Salt of 9-(2,4,6-Trinitroanilino)carbazole

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Abstract

The picryl ring in the potassium salt of 9-(2,4,6-trinitroanilino)carbazole [potassium *N*-(9-carbazolyl)-2,4,6-trinitroanilide, K⁺.C₁₈H₁₀N₅O₆⁻] is in a boat conformation. The C—N bond between C1 of the picryl ring and the adjacent N atom of the hydrazine moiety is shortened, indicating delocalization of the -1 charge into the picryl ring system. The K⁺ ion, which has replaced the proton on the N atom bonded to C1, is ionically bonded to this N atom and to an O atom in an *ortho* nitro group of the parent molecule. K⁺ also coordinates with four O atoms from three other molecules and with the π cloud of a phenyl ring of the carbazole group of a fourth molecule.

Comment

It has long been known that addition of bases to solutions of 2,2-diphenyl-1-picrylhydrazine (DH) and 9-(2,4,6-trinitroanilino)carbazole (AH) results in the removal of the hydrazinic protons. The p*K*_a's of DH and AH in methanol/hf are 8.94 (6) and 7.96 (5), respectively (Nelson, 1994). Whereas X-ray crystallographic analyses show that the picryl rings in both hydrazines

are essentially planar (Wang, Barton, Robertson & Weil, 1991; Wang, Barton, Robertson, Weil & Brown, 1987), X-ray analysis of the potassium salt of DH, K⁺D⁻, shows that the picryl ring is severely distorted (into a twist-boat conformation) due to the presence of ionic bonding between K⁺ and N4 and O1 of the anion (Gopal, Robertson & Weil, 1983). The present structural study was undertaken to determine if similar ionic bonding and distortion of the picryl ring is observed in the potassium salt of AH. The important resonance structures of the A⁻ anion contributing to the electronic structure of this species in its ground state are similar to the resonance structures of the D⁻ anion (Gopal, Robertson & Weil, 1983) and are illustrated in Fig. 1.

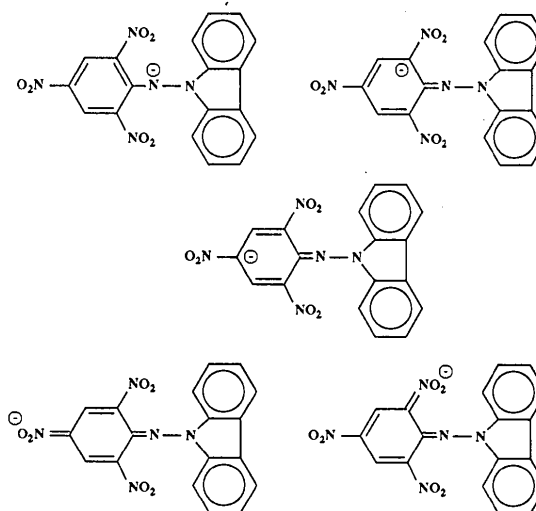


Fig. 1. Resonance structures for the A⁻ ion.

The X-ray structure determination of the title compound (Fig. 2) shows that the picryl ring has the boat form; the least-squares planes through C1, C2 and C6 and through C3, C4 and C5 are inclined at 18.8 (2) and 9.3 (2)°, respectively, to the least-squares plane through C2, C3, C5 and C6. The hydrazine linkage to the picryl ring is nearly coplanar with the plane through C1, C2 and C6, and the carbazole moiety is rotated by 49.0 (1)° with respect to the plane through C2, C3, C5 and C6 to minimize steric interaction between it and the nitro group at C6.

The plane of the nitro group at C2 is rotated by 17.5 (1)° with respect to the least-squares plane through C2, C3, C5 and C6, while the nitro group at C6 is rotated by 34.4 (1)° with respect to the same plane. The nitro group at C4 is rotated by 9.7 (2)° with respect to the plane through C3, C4 and C5. The different rotation angles for the nitro groups probably occur in order to optimize the geometry of coordination to K⁺ in the crystal structure. This ionic bonding constrains the C2 nitro group to be almost coplanar with C1,