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LETTER

Structure of hexafluorotetrapyridine dimolybdenum(III)

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The structures of binuclear transition metal compounds of the edge-sharing bioctahedron type have been the subject of many studies [1, 2]. Numerous examples of compounds containing Cl, Br, OH or OR as bridging ligands are known, but to our knowledge no compounds with bridging fluoro ligands have been characterized so far. We have been able to prepare $Mo_2F_6py_4$. We determined its structure in order to study the arrangement of the ligands on the axial and equatorial sites and the metal-to-metal bonding. The Mo–Mo distance may give insight into the electronic structures of this compound, especially in comparison with the related $Ta_2Cl_6py_4$ [3] and $W_2Cl_6py_4$ [4].

Experimental

Preparation of $Mo_2F_6py_4$

One gram of $MoCl_3$ and 30 ml of pyridine (Ventron-Alfa Chemicals) were refluxed under argon. The hot orange solution was rapidly filtered from a small residue of bulk material and layered carefully with pyridine/ethanol (1:1). Finally a 20% ethanol solution of tetramethylammonium fluoride [5] was added. After 24 h red crystals of $Mo_2F_6py_4$ appeared between the two liquid phases. Approximate yield: 400 mg.

Structure determination

A single crystal was mounted inside a Lindemann glass capillary. Data were collected on a Syntex $P2_1$ diffractometer at 140 K. The lattice constants were determined from 15 reflections in the range $21 < 2\theta < 30°$. One check reflection was monitored, varying in intensity less than 2%. Automated Patterson interpretation revealed the locations of the Mo atoms. The remaining atoms, including hydrogen atoms, were found using the standard methods of SHELX-XTL. The weighting scheme $w^{-1} = \sigma(F_o) + 0.0023F_o^2$ was used. Crystal data and data collection parameters are listed in Table 1; the final atomic positional and thermal parameters are listed in Table 2.

TABLE 1. Crystal data and data collection parameters

Formula	$Mo_2F_6N_4C_{20}H_{20}$
Formula weight	622.3
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.300(2)
b (Å)	22.303(5)
c (Å)	11.399(2)
β (°)	108.50(1)
V (Å^3)	2225
D_{calc} (g/cm^3)	1.86
Crystal size (mm)	$0.21 \times 0.25 \times 0.1$
μ(Mo Kα) (cm^{-1})	11.73
Absorption correction	empirical
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
Scan method	ω–2θ
Collection range, 2θ (°)	4–54
Total unique data	5163
Data with $I > 1.96\sigma(I)$	4030
No. parameters	369
R	0.0375
R_w	0.0354
Goodness-of-fit	1.482

Results and discussion

Preparative method

Starting from commercial $MoCl_3$ and by using the described routine, $Mo_2F_6py_4$ was obtained in low yield. $Mo_2F_6py_4$ could not be synthesized using highly crystalline, less reactive $MoCl_3$, prepared by vapour phase transport reactions [6], or starting from yellow $MoCl_3py_3$. We suggest, therefore, that part of the pairs of molybdenum atoms, which are present in solid $MoCl_3$, remained intact during the preparative routine. (Both polymorphs of $MoCl_3$, with hcp and ccp arrays of Cl atoms, contain Mo atoms in pairs of adjacent octahedral holes at a distance of 2.76 Å across a common edge.) No dimer formation has been observed so far in solutions containing hexacoordinated molybdenum(III) species [7].

Structure

Figure 1 shows an ORTEP plot of the molecular structure; principal dimensions are listed in Table 3. $Mo_2F_6py_4$ has no crystallographic symmetry, but

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TABLE 2. Atomic positional parameters and equivalent isotropic displacement parameters

Atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$U_{eq} \times 10^3$
Mo(1)	110(1)	6905(1)	6950(1)	21(1)
Mo(2)	1204(1)	4047(1)	2718(1)	23(1)
F(1)	1364(3)	7051(1)	8517(2)	33(1)
F(2)	−1731(3)	6783(1)	7339(2)	39(1)
F(3)	−797(2)	7028(1)	5263(2)	27(1)
F(4)	607(3)	6073(1)	6859(2)	42(1)
F(5)	−356(3)	5819(1)	8945(2)	29(1)
F(6)	−2454(3)	5778(1)	5696(2)	34(1)
N(1)	−289(3)	7909(1)	7014(3)	19(1)
N(2)	2233(3)	7144(2)	6449(3)	23(1)
N(3)	−3413(3)	5744(1)	7708(3)	24(1)
N(4)	−669(4)	4951(1)	7228(3)	25(1)
C(1)	−1477(4)	8154(2)	6147(3)	24(1)
C(2)	−1871(4)	8749(2)	6159(4)	32(1)
C(3)	−1003(5)	9109(2)	7098(4)	38(2)
C(4)	241(5)	8868(2)	7995(4)	35(2)
C(5)	550(4)	8270(2)	7923(3)	25(1)
C(6)	3610(4)	7088(2)	7280(4)	28(1)
C(7)	4927(4)	7172(2)	6986(4)	34(1)
C(8)	4855(5)	7330(2)	5822(5)	42(2)
C(9)	3460(6)	7417(3)	4973(5)	64(2)
C(10)	2176(5)	7321(3)	5317(4)	55(2)
C(11)	−3450(5)	5767(2)	8871(4)	37(2)
C(12)	−4758(6)	5697(3)	9172(5)	50(2)
C(13)	−6097(5)	5590(2)	8265(5)	49(2)
C(14)	−6080(5)	5563(2)	7075(5)	44(2)
C(15)	−4732(4)	5638(2)	6822(4)	32(1)
C(16)	−254(5)	4595(2)	8219(4)	29(1)
C(17)	205(5)	4007(2)	8178(4)	34(2)
C(18)	310(7)	3787(2)	7094(5)	48(2)
C(19)	−118(10)	4141(2)	6073(5)	81(3)
C(20)	−602(8)	4718(2)	6178(4)	59(2)

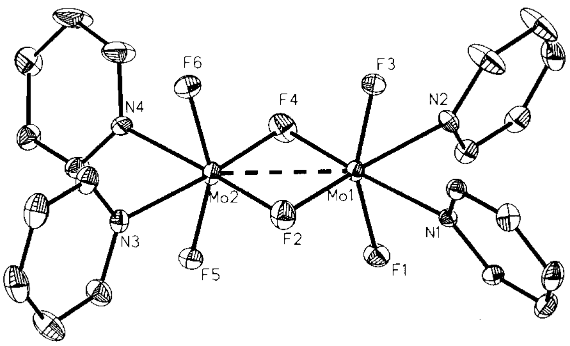

Fig. 1. An ORTEP drawing of the $Mo_2F_6py_4$ molecule. Thermal ellipsoids drawn at the 50% probability level; H atoms omitted for clarity.

TABLE 3. Selected bond distances (Å) and angles (°) (e.s.d.s of bond angles given are less than 0.15°)

Distances			
Mo(1)–Mo(2)	2.533(1)		
Mo(1)–F(1)	1.823(2)	Mo(2)–F(5)	1.831(2)
Mo(1)–F(2)	1.907(3)	Mo(2)–F(2)	1.920(3)
Mo(1)–F(3)	1.858(2)	Mo(2)–F(6)	1.852(2)
Mo(1)–F(4)	1.923(3)	Mo(2)–F(4)	1.900(3)
Mo(1)–N(1)	2.274(4)	Mo(2)–N(3)	2.289(4)
Mo(1)–N(2)	2.272(4)	Mo(2)–N(4)	2.294(3)
Angles			
F(1)–Mo(1)–F(2)	97.7	F(5)–Mo(2)–F(2)	98.7
F(1)–Mo(1)–F(3)	157.7	F(5)–Mo(2)–F(6)	154.9
F(1)–Mo(1)–F(4)	97.8	F(5)–Mo(2)–F(4)	99.5
F(1)–Mo(1)–N(1)	81.5	F(5)–Mo(2)–N(3)	82.2
F(1)–Mo(1)–N(2)	82.8	F(5)–Mo(2)–N(4)	81.0
F(2)–Mo(1)–F(3)	96.9	F(2)–Mo(2)–F(6)	98.6
F(2)–Mo(1)–F(4)	96.9	F(2)–Mo(2)–F(4)	97.2
F(2)–Mo(1)–F(3)	88.2	F(2)–Mo(2)–N(3)	86.4
F(2)–Mo(1)–N(2)	174.5	F(2)–Mo(2)–N(4)	177.6
F(3)–Mo(1)–F(4)	97.1	F(6)–Mo(2)–F(4)	96.2
F(3)–Mo(1)–N(1)	82.2	F(6)–Mo(2)–N(3)	81.0
F(3)–Mo(1)–N(2)	81.2	F(6)–Mo(2)–N(4)	80.9
F(4)–Mo(1)–N(1)	174.9	F(4)–Mo(2)–N(3)	175.8
F(4)–Mo(1)–N(2)	88.4	F(4)–Mo(2)–N(4)	85.2
N(1)–Mo(1)–N(2)	86.5	N(3)–Mo(2)–N(4)	91.2
Mo(2)–Mo(1)–F(1)	100.8	Mo(1)–Mo(2)–F(5)	102.9
Mo(2)–Mo(1)–F(2)	48.8	Mo(1)–Mo(2)–F(2)	48.4
Mo(2)–Mo(1)–F(3)	101.4	Mo(1)–Mo(2)–F(6)	102.1
Mo(2)–Mo(1)–F(4)	48.1	Mo(1)–Mo(2)–F(4)	48.9
Mo(2)–Mo(1)–N(1)	136.9	Mo(1)–Mo(2)–N(3)	134.7
Mo(2)–Mo(1)–N(2)	136.6	Mo(1)–Mo(2)–N(4)	134.1
Mo(1)–F(2)–Mo(2)	82.9	Mo(1)–F(4)–Mo(2)	83.0

bond lengths and angles are nearly identical at the octahedrally coordinated Mo(1) and Mo(2). The symmetry of the molecular core is very close to D_{2h} symmetry. The neutral pyridine ligands donate to equatorial positions only. The equatorial plane contains the metal atoms, the bridging ligands and the N-donor atoms of the pyridine molecules. The overall structure of $Mo_2F_6py_4$ is different from the structures of the related compounds $W_2Cl_6py_4$ [3] and $Ta_2Cl_6py_4$ [1]. Here pairs of pyridine ligands are coordinated equatorially at one metal atom and axially at the other.

The Mo–N(py) distances vary in the small range 2.272(4)–2.294(3) Å. They are slightly larger than in the related compound $[([9]aneN_3)_2Mo_2Cl_2(\mu\text{-}OH)_2](PF_6)_2$ [8]. The dihedral angles between the pyridine rings 1 to 4 and the molecular plane are 69.6, 75.2, 83.7 and 64.6°. Their π-systems may interact with M–M bonding and antibonding orbitals (see below). The mean values of the axial and bridging Mo–F bonds are 1.841 and 1.913 Å, respectively. Both types of Mo–F distances are rather short. For comparison, the Mo–F distance in MoF_3 (all Fs are bridging) is 2.042(2) Å, according to recent single crystal work [9]. The bond angles in the central Mo_2F_2 ring (F–Mo–F, 97.0°; Mo–F–Mo 83.0°) and the short Mo–Mo distance (2.533(1) Å) show that substantial Mo–Mo bonding occurs. The mutual repulsion between the axial ligands is relieved by their bonds bending away from perpendicularity. The respective bond angles are F–Mo–F, 156.3° and Mo–Mo–F, 102°. The F···F distances across the Mo–Mo bond are 3.286 and 3.291 Å, slightly larger than the sum of the covalent radii.

Considering the electron configuration in diamagnetic dimeric Mo(III) compounds, two possibilities exist for the ordering of metal–metal bonding and antibonding orbitals: the $\sigma^2\pi^2\delta^2$ or $\sigma^2\pi^2\delta^{*2}$ configuration. Slightly shorter Mo–Mo distances than in $Mo_2F_6py_4$ (2.533(1)Å) have been observed in the Mo(III) dimers $[([9]aneN_3)_2Mo_2Cl_2(\mu\text{-}OH)_2]^{2+}$ (2.501(3) Å) [8] and $[(acac)_2(CN\text{–}CMe_3)_2\text{-}(OCH_2\text{–}CMe_3)_2Mo_2(\mu\text{-}OCH_2CMe_3)_2]$ (2.508(2)Å) [10], both with Mo_2O_2 central cores. Although the Mo–O bridge bonds herein (2.13 and 2.05 Å) are considerably larger than the Mo–F bridge bonds in $Mo_2F_6py_4$, the Mo–Mo distances are shorter. Therefore, we suggest in the present case a $\sigma^2\pi^2\delta^{*2}$ configuration, i.e. a $\sigma^2\pi^2$ double bond with a small δ^{*2} antibonding contribution. But a final statement seems difficult because no homologous series of compounds $M_2F_6py_4$ with d^n–d^n configurations ($n = 1,2,3,4,5$) is known so far.

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