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Preparation and Structure of the Compound $Mo_2(NCS)_4(Ph_2Ppy)_2 \cdot 2THF \cdot 2toluene$ (Ph_2Ppy = 2-(diphenylphosphino)pyridine)

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Abstract

The reaction of $Mo_2(O_2CCF_3)_4$ with $(CH_3)_3SiNCS$ in the presence of Ph_2Ppy produces $Mo_2(NCS)_4(Ph_2Ppy)_2$ (where Ph_2Ppy = 2-(diphenylphosphino)pyridine) in good yield. The compound was obtained in crystalline form as $Mo_2(NCS)_4(Ph_2Ppy)_2 \cdot 2THF \cdot 2toluene$, whose structure was determined by X-ray crystallography. The unit cell is monoclinic (space group $C2/c$) with the following dimensions: $a = 15.930(4)$, $b = 19.875(5)$, $c = 19.124(3)$ Å, $\beta = 99.40(2)°$, $V = 5973(4)$ Å^3 and $Z = 4$. The molecule has a crystallographic twofold symmetry axis perpendicular to the mean plane of the Mo_2 unit and the two P–C–N bridging units and consists of a quadruply bonded Mo_2^{4+} core with two bridging Ph_2Ppy ligands arranged in a transoid, head-to-tail fashion and four N-bonded thiocyanate ions. There are two very loosely coordinated THF molecules while the toluene molecules are interstitial. The Mo–Mo bond length is 2.191(1) Å.

Introduction

The ligand 2-(diphenylphosphino)pyridine, Ph_2Ppy, is well suited to serve as a bridging bidentate ligand in compounds containing M_2 cores, but to date, little has been reported concerning its use in such compounds. In 1982 Balch and coworkers reported some compounds containing both homo- and heteronuclear species with M–M single bonds [1]. In 1984 it was reported [2] that the ligand reacts with $Re_2Cl_8^{2-}$ and $Re_2Cl_6(PR_3)_2$ to give various derivatives of the triply-bonded Re_2^{6+} core including one in which a Ph_2Ppy ligand had been orthometallated. However, in all products there were two or more Ph_2Ppy molecules behaving in the expected manner as bridging, bidentate, neutral ligands. In 1986 the compound $Os_2Cl_4(O_2CCH_3)(Ph_2Ppy)_2$ was reported [3]. Recently we prepared the simple Mo_2^{4+} complex $Mo_2Cl_4(Ph_2Ppy)_2$ but this proved to be too insoluble to obtain in crystalline form; upon reaction with acetic acid, however, it afforded crystalline $Mo_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$, whose structure was determined [4].

Our recent excursions into the chemistry of thiocyanato complexes of dimetal units [5, 6] encouraged us to believe that the $Mo_2(NCS)_4(Ph_2Ppy)_2$ compound might be more crystallizable and we therefore undertook its synthesis. We have been able to obtain it in crystalline form and determine its structure, and that work is reported here.

Experimental

Preparation

$Mo_2(O_2CCF_3)_4$, 50 mg (7.8×10^{-5} mol) was dissolved in 10 ml THF, containing 62 mg (0.47 mmol) of $(CH_3)_3SiNCS$. This was carefully layered with a toluene solution (10 ml) of 2-(diphenylphosphino)pyridine, 0.12 g (0.47 mmol). The reagents were allowed to interdiffuse for 2 weeks. The reaction mixture was filtered, the crystalline precipitate washed with toluene and vacuum dried. The yield was 60 mg (60% based on Mo). Higher yields of microcrystalline product can be obtained when stoichiometric amounts of reagents are stirred in a THF–toluene mixture for 2 days at room temperature.

X-ray Crystallography

Single crystals taken directly out of the reaction mixture were glued inside thin-wall capillaries filled with mineral-oil/mother-liquor mixture (5:1). Indexing revealed a monoclinic *C*-centered cell. Axial dimensions, centering and Laue class were confirmed with oscillation photographs. Lorentz, polarization and absorption corrections based on selected ψ scans were applied to the data. Based on systematic absences the space group was determined to be $C2/c$ or Cc. The centrosymmetric space group $C2/c$ was tried first and was shown to be a correct choice based on a successful refinement.

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The structure was solved by a Patterson interpretation provided by SHELX-86, which revealed positions of almost all atoms. A few cycles of least-squares refinement and a difference Fourier map revealed the missing atoms of the dinuclear molecule and the axially coordinated THF molecules.

At this point there were still two regions of high electron density which were assigned to disordered toluene molecules. One toluene molecule lies on a twofold axis with the axis passing through two of the ring atoms and the methyl group disordered over two positions. The second toluene molecule resides near but not on an inversion center, thus creating two superimposed toluene images. This toluene molecule was assigned half occupancy. Overall there are two toluene molecules per Mo dimer. All the atoms except those in the solvent molecules were refined anisotropically. The refinement converged to give agreement factors $R_1 = 0.0456$ and $R_w = 0.0635$. The relevant crystallographic and refinement data are given in Table 1.

Results

The title compound was obtained in crystalline form, albeit with several molecules of solvent of crystallization, so that the actual formula of the solid compound is $Mo_2(NCS)_4(Ph_2Ppy)_2 \cdot 2THF \cdot 2toluene$. Figure 1 shows a drawing of the $Mo_2(NCS)_4(Ph_2Ppy)_2 \cdot 2THF$ unit and Table 2 gives selected bond lengths and angles within this unit. The unit shown has C_2 rotational symmetry imposed crystallographically. The Ph_2Ppy ligands have a transoid, head-to-tail relationship. There is a small but distinct twist about the Mo–Mo bond of 11.0°. The axial THF molecules make only weak bonds to the molybdenum atoms, with the Mo–O distances being 2.730(4) Å. The two independent Mo–N–C–S chains are each nearly, but not exactly, linear, with mean Mo–N–C and N–C–S angles of 172.8° and 178.4°, respectively.

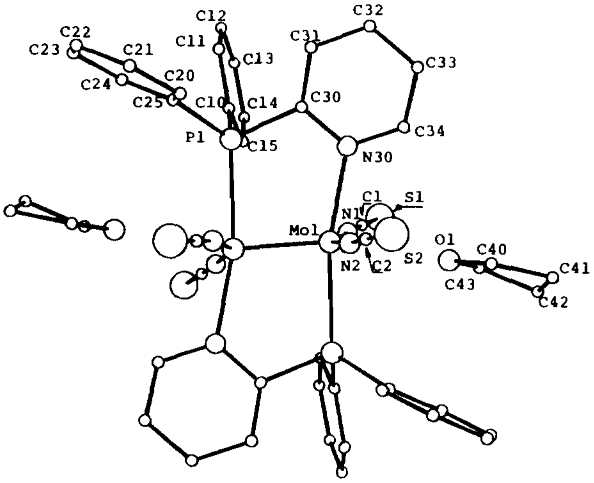

Fig. 1. A PLUTO drawing of the $Mo_2(NCS)_4(Ph_2Ppy)_2 \cdot 2THF$ portion of the structure. A twofold axis relates the labeled and unlabeled atoms.

TABLE 1. Crystal Data for $Mo_2(NCS)_4(Ph_2Ppy)_2 \cdot 2THF \cdot 2C_6H_5CH_3$

Formula	$Mo_2S_4P_2O_2N_6C_{60}H_{60}$
Formula weight	1279.27
Space group	$C2/c$
Systematic absences	hkl: $h + k \neq 2n$, $h0l$: $l \neq 2n$
a (Å)	15.930(4)
b (Å)	19.875(5)
c (Å)	19.124(3)
α (°)	90.0
β (°)	99.40(2)
γ (°)	90.0
V (Å^3)	5973(4)
Z	4
D_{calc} (g/cm^3)	1.422
Crystal size (mm)	0.6 × 0.15 × 0.15
μ(Mo Kα) (cm^{-1})	6.471
Data collection instrument	P3
Radiation (monochromated in incident beam)	Mo Kα ($\lambda_\alpha = 0.71073$ Å)
Orientation reflections, no., range (2θ)	25, $20 < 2\theta < 30$
Temperature (°C)	20
Scan method	$2\theta - \omega$
Data collection range, 2θ (°)	4, 45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3696, 2927
No. parameters refined	324
Transmission factors, max., min.	0.9997, 0.8012
R^a	0.04567
$R_w{}^b$	0.06353
Quality-of-fit indicator^c	1.438
Largest shift/e.s.d., final cycle	0.47
Largest peak (e/Å^3)	0.54

$^aR = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Discussion

The synthetic method utilized here has been widely employed with the Me_3SiX (X = Cl, Br) compounds as reagents, but only recently were the pseudohalide reagents (X = NCS, NCO) first employed, at least in application to dimetal systems [6], when $Mo_2(NCS)_4(PMe_3)_4$ and $Mo_2(NCO)_4(PMe_3)_4$ were prepared.

Relatively few molybdenum compounds containing the thiocyanate ion as a ligand have been

TABLE 2. Selected Bond Distances (Å) and Bond Angles (°) for $Mo_2(NCS)_4(Ph_2Ppy)_2 \cdot 2THF$

Atom 1	Atom 2	Distance
Mo1	Mo1	2.191(1)
Mo1	P1	2.545(2)
Mo1	O1	2.730(4)
Mo1	N1	2.084(5)
Mo1	N2	2.086(5)
Mo1	N30	2.228(5)
S1	C1	1.622(8)
S2	C2	1.627(7)
N1	C1	1.136(9)
N2	C2	1.142(8)

Atom 1	Atom 2	Atom 3	Angle
Mo1	Mo1	P1	86.10(4)
Mo1	Mo1	O1	166.7(1)
Mo1	Mo1	N1	103.6(1)
Mo1	Mo1	N2	100.4(1)
Mo1	Mo1	N30	104.9(1)
P1	Mo1	O1	80.6(1)
P1	Mo1	N1	96.2(2)
P1	Mo1	N2	88.9(2)
P1	Mo1	N30	167.2(1)
N1	Mo1	N2	155.8(2)
N1	Mo1	N30	87.8(2)
N2	Mo1	N30	82.7(2)
Mo1	N1	C1	172.7(5)
Mo1	N2	C2	172.8(5)
Mo1	N30	C30	120.9(4)
S1	C1	N1	177.9(7)
S2	C2	N2	178.9(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

reported previously, but in all cases, as in the present one, the thiocyanate ions are N-bonded. Besides the compound $Mo_2(NCS)_4(PMe_3)_4$ mentioned above, there are the following others: $(NH_4)_4[Mo_2(NCS)_8] \cdot nH_2O$ ($n = 4$, 6) [7], several $Mo_2(NCS)_4(PR_3)_4$ compounds obtained by ligand exchange on $Mo_2Cl_4(PR_3)_4$ compounds [8], several compounds of the type $Mo_2(NCS)_4[O_2CCH(NH_3)R]_2 \cdot nH_2O$ containing neutral zwitterionic amino acids [9], and $Mo_2(NCS)_4(dppm)_2$ [10].

Two structural features of the present compound deserve comment. The twist of 11.0° away from an eclipsed conformation probably results from internal repulsions between the phenyl groups of Ph_2Ppy and the thiocyanate ions. The twisted structure appears to lessen the repulsive contacts somewhat.

The other notable feature is the long Mo–Mo bond, 2.191(1) Å. This is about equal to that in $Mo_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$ [6], both of which are the longest Mo–Mo quadruple bond distances known. While a tendency for long Mo–Mo bonds to be associated with the presence of NCS^- ligands has been noted in several other cases (distances of 2.16–2.18 Å [7, 10]) there are also thiocyanato compounds in which the Mo–Mo distances are normal [6, 9], and no simple correlation can be said to exist.

Supplementary Material

Tables of fractional coordinates, all bond distances and angles, anisotropic displacement parameters, and observed and calculated structure factors, are available from author F.A.C.

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