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Crystal and molecular structure of tetracarbonyl (6,6′-dimethyl-2,2′-bipyridine)molybdenum benzene solvate

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Abstract

The crystal structure of the complex *cis*-[Mo(CO)$_4$(6,6′-dimethyl-2,2′-bipyridine)]·C_6H_6 has been determined by X-ray diffraction. The structure shows that repulsion between the methyl groups and the carbonyl ligands in the equatorial plane is principally responsible for the geometric distortion observed. Within the asymmetrically bound ligand the two pyridine rings suffer distortions in the same direction to pseudo-boat conformations so as to optimise molybdenum–nitrogen binding. The benzene solvent molecules are in narrow channels which lie between the axial carbonyl ligands. There are no significant short intermolecular contacts between the benzene and complex molecules.

Introduction

Chelation of a metal ion by 2,2′-bipyridine results in isomerisation of the ligand to the *cis* conformation. The (metal + ligand) unit is planar, or very nearly planar, which optimises binding. Substitution on the ligand at the 4,4′- or 5,5′-ring positions does not affect this planarity. However, substitution at the 6,6′-ring positions, adjacent to the donor atom is expected to cause distortion of the coordination sphere of the metal. This distortion is expected to be more significant as the coordination number of the metal increases because of repulsive non-bonded interactions.

We report the preparation and structure of [Mo(CO)$_4$(6,6′-dimethyl-2,2′-bipyridine)] · C_6H_6. This forms part of a wider study of the coordination chemistry of 3,3′- and 6,6′-disubstituted-2,2′-bipyridines. The influence of different solvents on the electronic absorption spectra of metal complexes of α-diimine ligands has been

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studied for many years [1], but structural information about the solvent–solute interaction is very sparse.

Experimental

6,6′-Dimethyl-2,2′-bipyridine [2] (0.10 g, 0.54 mmol) and [Mo(CO)$_4$(η^2,η^2-bicyclohepta[2.2.1]diene)] [3] (0.234 g, 0.78 mmol) were mixed together as solids under dinitrogen and then dry, dinitrogen-saturated, de-oxygenated benzene (8 ml) was added. The mixture was stirred at room temperature for six days in an inert atmosphere in the dark. The complex (0.11 g, 51% yield) was isolated as orange needles from benzene/petrol. Microanalysis. Found: C, 48.5; H, 2.9; N, 7.1. $C_{16}H_{12}MoN_2O_4$ calc.: C, 49.0; H, 3.1; N, 7.1%. Spectroscopic measurements (IR, NMR, UV-vis) all consistent with expectation. X-Ray measurements were made using an Enraf-Nonius CAD-4 diffractometer with Mo-K_α radiation (λ = 0.71069 Å), operating in the ω–2θ scan mode. The structure was solved and developed *via* standard heavy atom methods using SHELXS-86 [4] and refined by full-matrix least-squares analyses with SHELX-76 [5]. Molecular geometry calculations were made with PLATON-91 [6]. $C_{16}H_{12}MoN_2O_4 \cdot C_6H_6$ $M = 470.27$, monoclinic, a = 15.163(2), b = 9.949(4), c = 15.282(2) Å, β = 115.80(1)°, V = 2075.6 Å^3, space group $P2_1/a$, $Z = 4$, $D_c = 1.51$ g cm^{-3}, $F(000) = 784$, μ(Mo-K_α) = 5.7 cm^{-1}. Total observed data = 3142 [$I \geq 3\sigma(I)$]. Refinement with anisotropic atomic displacement parameters for non-hydrogen atoms of the complex. Data were corrected for absorption using DIFABS [7]. Hydrogen atoms on the complex were located and refined. The benzene molecule was located in two orientations (*ca.* 3:2) which have a common centre and are related to each other by rotation of ~ 30° about the D_6 axis and their carbon atoms refined with isotropic displacement parameters. The benzene hydrogen atom positions were calculated and assigned a fixed isotropic displacement parameter (0.1). Final R; R_w = 0.030; 0.031 for 331 variables with weights, $w = [\sigma^2(F_o) + 0.0001(F_o^2)]^{-1}$.

Lists of thermal parameters and structure factors and a complete table of bond lengths and angles are available from the authors.

Results and discussion

The molecular structure of the complex is illustrated in Figs. 1–3 with the full atomic numbering scheme in Fig. 1. The fractional atomic coordinates for the refined structure and a selection of the resulting bond angles and lengths are given in Tables 1 and 2. The crystal packing is illustrated in Fig. 4 which shows the position of the benzene solvent molecules.

The methyl groups in the 6,6′-positions of the bipyridine ring system introduce a source of steric congestion as a result of the interaction with the carbonyl groups in the same (equatorial) plane of the six-coordinate complex. The π-delocalisation in planar 6,6′-dimethyl-2,2′-bipyridine is largely retained in the complex. The steric distortion of the complex manifests itself in four ways. First, the bipyridine ligand is tilted with respect to the plane of the equatorial carbonyl ligands. The best plane through the bipyridine ring system makes an angle of 19° with the plane defined by the molybdenum atom and the two equatorial carbonyls. The methyl groups are clearly placed to one side of the equatorial plane (Figs. 2 and 3), but by unequal

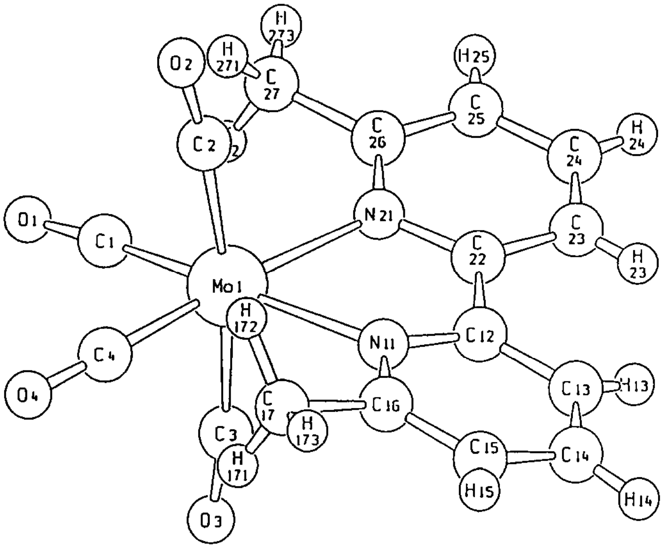

Fig. 1. Molecular structure of [$Mo(CO)_4(6,6'-Me_2-2,2'-bipy)$] with atom numbering scheme [12].

amounts. The perpendicular distance from C17 to the Mo–C1–C4 plane is 0.39 Å; from C27 to the same plane, the perpendicular distance is 0.63 Å. An unusual feature of this structure is the slight asymmetry in the binding of the bipyridine ligand to the metal. This is most clearly seen in Fig. 3, where the bond (C12–C22) linking the pyridine rings is not parallel to the equatorial $Mo(CO)_2$ plane. This feature is similar to that observed in pseudo-square planar [$PdCl_2$(6,6'-dimethyl-

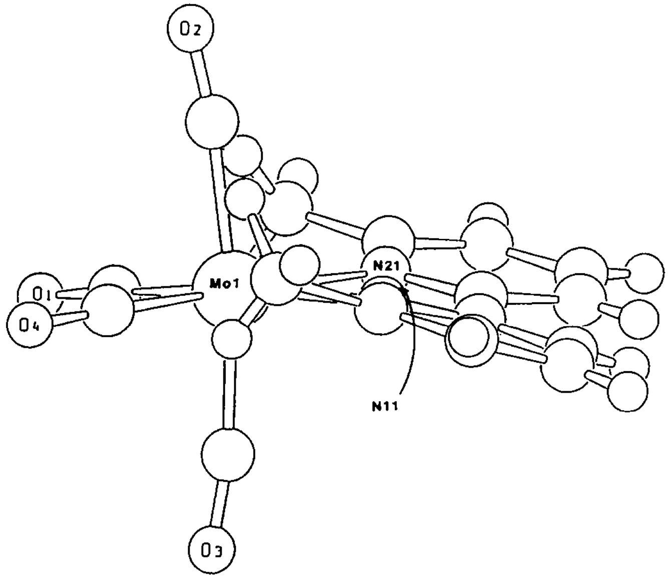

Fig. 2. View of [$Mo(CO)_4(6,6'-Me_2-2,2'-bipy)$] showing the orientation of ligand relative to {$Mo(CO)_4$} group [12].

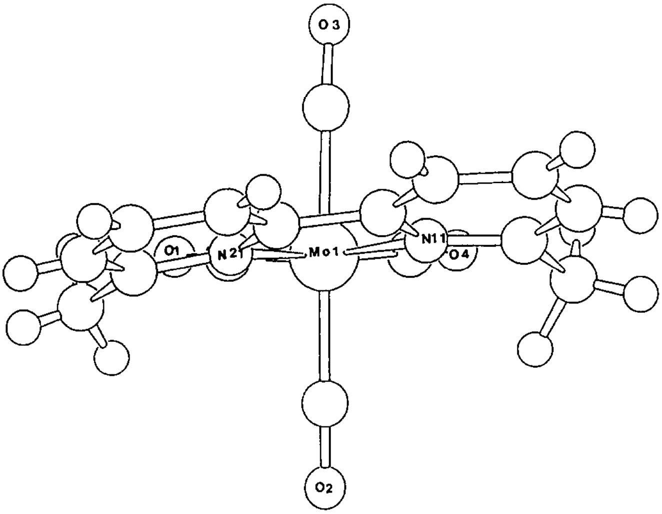

Fig. 3. View of [Mo(CO)$_4$(6,6′-Me$_2$-2,2′-bipy)] through the equatorial {Mo(CO)$_2$} plane [12].

2,2′-bipyridine], which is the only other known structure [8] of a complex of this ligand.

Second, the Mo–N bonds are significantly longer than those in comparable systems such as [Mo(CO)$_4$(phen)] 2.243(2) Å [9], *cis*-[Mo(CO)$_2$(bipy)$_2$] 2.143(6), 2.239(5) Å [10] and [Mo(CO)$_4$(3,3′-dimethyl-2,2′-bipyridine] 2.258(3), 2.263(4) Å [11]. Third, the angle C1–Mo–C4 between the equatorial Mo–CO bonds (81.4(1)°) is significantly compressed when compared with the corresponding angle in [Mo(CO)$_4$(phen)] (93.2(1)°) [9]. The non-bonded C · · · H contacts between equatorial carbonyl carbons and adjacent methyl groups lie in the range 2.64–2.79 Å, indicating van der Waals contact between these groups. Last, a detailed examination of the geometry of the coordinated bipyridine ligand shows that both pyridine rings are slightly distorted into shallow pseudo-boat forms with apices at the nitrogen (N11, N21) and the *para* carbon (C14, C24) atoms in each ring. Both rings are puckered in the same sense. The effect of this slight puckering of the pyridine rings is to optimise bonding between the nitrogen lone pairs and the molybdenum atom as a consequence of their pointing away from the methyl groups and into the equatorial Mo(CO)$_2$ plane. The pyridine rings in [PdCl$_2$(6,6′-dimethyl-2,2′-bipyridine)] are also slightly distorted, but our calculations on data retrieved show that the deformation produces pseudo-boats rather than the pseudo-chair conformations reported [8].

The distortion of the coordination polyhedron follows a familiar pattern. The axial carbonyl ligands are both bent (Mo–C2–O2 : 173.8(3)° and Mo–C3–O3 : 171.4(3)° respectively) and are both bent away from the bipyridine ligand (C2–Mo–C3 171.6(1)°). The equatorial Mo–C bonds (1.935(2), 1.942(3) Å) are shorter than the axial Mo–C bonds (2.035(4), 2.007(4) Å) as was found in [Mo(CO)$_4$(phen)] [9]. The compression of the C1–Mo–C4 angle has been discussed above. Judged by the Mo–C and C–O bond lengths as indices of π-bonding, it would appear that the Mo–N interaction in this complex is surprisingly similar to that in [Mo(CO)$_4$(phen)] [9].

Table 1

Fractional atomic coordinates and equivalent isotropic displacement factors (Å^2) with esd's in parentheses

Atom	x	y	z	U_{eq} [a]
Mo1	0.03100(2)	0.19328(2)	0.19690(2)	0.0415(2) *
O1	0.1333(2)	−0.0023(3)	0.3695(2)	0.080(1) *
O2	0.1945(2)	0.1135(3)	0.1290(2)	0.077(2) *
O3	−0.1349(2)	0.1977(3)	0.2683(2)	0.102(2) *
O4	−0.0704(2)	−0.0766(2)	0.1082(2)	0.077(1) *
N11	−0.0491(2)	0.3522(2)	0.0799(2)	0.045(1) *
N21	0.0986(2)	0.3976(2)	0.2595(2)	0.044(1) *
C1	0.0977(2)	0.0742(3)	0.3062(3)	0.055(2) *
C2	0.1358(3)	0.1497(3)	0.1518(2)	0.053(2) *
C3	−0.0744(3)	0.2071(3)	0.2426(2)	0.058(2) *
C4	−0.0339(2)	0.0265(3)	0.1373(2)	0.055(2) *
C12	−0.0362(2)	0.4807(3)	0.1134(2)	0.048(1) *
C13	−0.0953(3)	0.5827(4)	0.0587(3)	0.064(2) *
C14	−0.1682(3)	0.5568(4)	−0.0319(3)	0.071(2) *
C15	−0.1775(3)	0.4293(4)	−0.0675(3)	0.067(2) *
C16	−0.1181(3)	0.3293(3)	−0.0113(2)	0.054(2) *
C17	−0.1272(4)	0.1891(4)	−0.0522(3)	0.071(2) *
C22	0.0479(2)	0.5051(3)	0.2090(2)	0.049(2) *
C23	0.0752(3)	0.6348(4)	0.2433(3)	0.069(2) *
C24	0.1548(4)	0.6558(4)	0.3282(3)	0.079(2) *
C25	0.2078(3)	0.5494(4)	0.3784(3)	0.068(2) *
C26	0.1799(2)	0.4200(3)	0.3436(2)	0.052(2) *
C27	0.2400(3)	0.3047(4)	0.3995(3)	0.067(2) *
H13	−0.088(3)	0.661(4)	0.082(3)	0.087(5)
H14	−0.215(3)	0.623(4)	−0.074(3)	0.087(5)
H15	−0.216(3)	0.411(4)	−0.127(3)	0.087(5)
H171	−0.166(3)	0.141(4)	−0.032(3)	0.086(5)
H172	−0.051(3)	0.149(3)	−0.033(3)	0.086(5)
H173	−0.164(3)	0.199(3)	−0.124(3)	0.086(5)
H23	0.037(3)	0.700(4)	0.206(3)	0.087(5)
H24	0.176(3)	0.740(4)	0.354(3)	0.087(5)
H25	0.263(3)	0.563(4)	0.433(3)	0.087(5)
H271	0.254(3)	0.239(4)	0.362(3)	0.086(5)
H272	0.204(3)	0.259(4)	0.432(3)	0.086(5)
H273	0.295(3)	0.329(4)	0.445(3)	0.086(5)
C31	0.1457(7)	0.401(1)	0.669(1)	0.092(3)
C32	0.1207(8)	0.284(2)	0.7051(7)	0.085(3)
C33	0.072(1)	0.187(1)	0.644(2)	0.108(4)
C34	0.0391(8)	0.202(1)	0.541(1)	0.097(3)
C35	0.0641(8)	0.317(2)	0.5090(8)	0.091(3)
C36	0.1153(8)	0.411(1)	0.572(1)	0.088(3)
C31A	0.134(1)	0.356(2)	0.703(1)	0.075(3)
C32A	0.096(1)	0.222(2)	0.688(1)	0.089(4)
C33A	0.052(1)	0.171(1)	0.594(2)	0.084(4)
C34A	0.052(1)	0.249(3)	0.520(1)	0.090(4)
C35A	0.087(2)	0.369(3)	0.532(2)	0.120(6)
C36A	0.131(1)	0.437(1)	0.626(2)	0.097(4)
H31	0.1878(0)	0.4803(0)	0.7175(0)	0.1000(0)
H32	0.1413(0)	0.2731(0)	0.7818(0)	0.1000(0)
H33	0.0564	0.0941(0)	0.6716(0)	0.1000(0)
H34	−0.0041(0)	0.1251(0)	0.4912(0)	0.1000(0)
H35	0.0420(0)	0.3317(0)	0.4322(0)	0.1000(0)

Table 1 (continued)

Atom	x	y	z	U_{eq} [a]
H36	0.1339(0)	0.5012(0)	0.5436(0)	0.1000(0)
H31A	0.1654(0)	0.3973(0)	0.7754(0)	0.1000(0)
H32A	0.1024(0)	0.1606(0)	0.7488(0)	0.1000(0)
H33A	0.0195(0)	0.0722(0)	0.5801(0)	0.1000(0)
H34A	0.0191(0)	0.2083(0)	0.4476(0)	0.1000(0)
H35A	0.0844(0)	0.4213(0)	0.4693(0)	0.1000(0)
H36A	0.1581(0)	0.5392(0)	0.6353(0)	0.1000(0)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j\Sigma_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$ for atoms denoted by asterisks, and U_{iso} for the remaining atoms.

In the crystal (Fig. 4), the complex molecules are stacked along the *a* axis, with the main axis of the molecule at *ca.* 20° to the *a* axis. Neighbours within the stack are related by the *a* glide plane. Adjacent stacks in the $\pm c$ direction are related by the 2_1 axes, and in the $\pm b$ direction by unit cell translations. Each benzene molecule has two orientations differing by *ca.* 30° about a common D_6 axis; only the more common one is illustrated. These solvent molecules are located in narrow channels parallel to the *b* axis which lie in between the axial carbonyl ligands of the complexes. Within a channel, neighbours are related by a centre of symmetry. There are no significant short intermolecular contacts between benzene and

Table 2

Bond lengths (Å) and angles (°) with esd's in parentheses

Bond lengths					
Mo1-N11	2.299(2)	O4-C4	1.159(4)	C15-C16	1.366(5)
Mo1-N21	2.290(2)	N11-C12	1.359(4)	C16-C17	1.510(5)
Mo1-C1	1.935(3)	N11-C16	1.349(4)	C22-C23	1.387(4)
Mo1-C2	2.035(4)	N21-C22	1.346(4)	C23-C24	1.350(6)
Mo1-C3	2.007(4)	N21-C26	1.358(4)	C24-C25	1.349(5)
Mo1-C4	1.942(3)	C12-C13	1.371(4)	C25-C26	1.386(4)
O1-C1	1.163(4)	C12-C22	1.482(4)	C26-C27	1.483(5)
O2-C2	1.146(4)	C13-C14	1.369(5)		
O3-C3	1.149(4)	C14-C15	1.363(5)		
Bond angles					
N11-Mo1-N21	72.7(1)	Mo1-N11-C12	114.4(2)	C14-C15-C16	120.1(3)
N11-Mo1-C1	173.4(1)	Mo1-N11-C16	126.7(2)	N11-C16-C15	121.9(3)
N11-Mo1-C2	96.2(1)	C12-N11-C16	117.9(3)	N11-C16-C17	118.3(3)
N11-Mo1-C3	89.6(1)	Mo1-N21-C22	115.2(2)	C15-C16-C17	119.8(3)
N11-Mo1-C4	103.6(1)	Mo1-N21-C26	126.8(2)	N21-C22-C12	117.8(2)
N21-Mo1-C1	102.2(1)	C22-N21-C26	117.9(3)	N21-C22-C23	121.4(3)
N21-Mo1-C2	93.3(1)	Mo1-C1-O1	176.1(3)	C12-C22-C23	120.7(3)
N21-Mo1-C3	94.2(1)	Mo1-C2-O2	173.8(3)	C22-C23-C24	120.1(4)
N21-Mo1-C4	176.1(1)	Mo1-C3-O3	171.4(3)	C23-C24-C25	119.2(3)
C1-Mo1-C2	88.3(1)	Mo1-C4-O4	175.2(3)	C23-C24-C25	119.2(3)
C1-Mo1-C3	86.4(1)	N11-C12-C13	121.2(3)	N21-C26-C25	121.0(3)
C1-Mo1-C4	81.4(1)	N11-C12-C22	116.5(3)	N21-C26-C27	119.7(3)
C2-Mo1-C3	171.6(1)	C13-C12-C22	122.2(3)	C25-C26-C27	119.3(3)
C2-Mo1-C4	88.3(1)	C12-C13-C14	120.2(3)		
C3-Mo1-C4	84.5(1)	C13-C14-C15	118.4(3)		

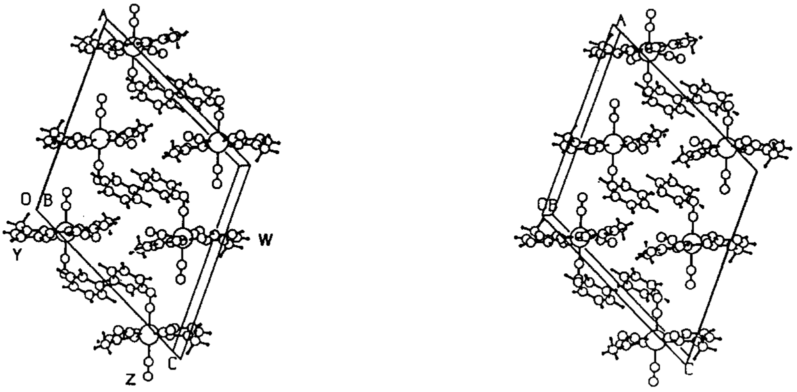

Fig. 4. Stereoscopic view down the *b* axis of the crystal packing in [Mo(CO)$_4$(6,6′-Me$_2$-2,2′-bipy)]. Only the major orientation of the benzene ring is displayed. The relations of labelled complex molecules to the shaded benzene ring are discussed in the text.

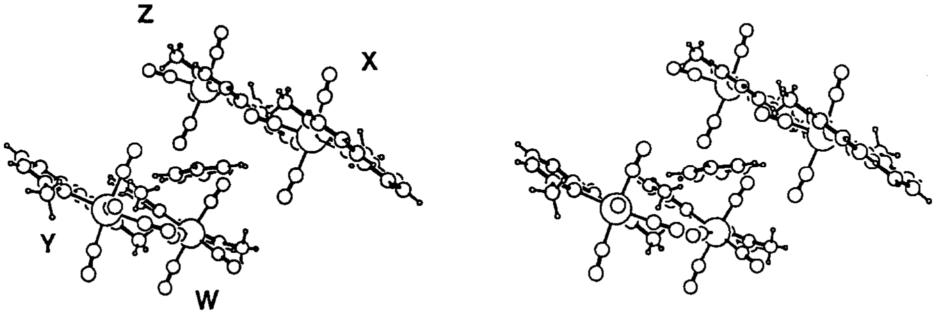

Fig. 5. Stereoview of nearest neighbour interactions of a benzene ring with [Mo(CO)$_4$(6,6′-Me$_2$-2,2′-bipy)] molecules in the crystal.

complex molecules. There is no especially favoured orientation between the complex molecules and the benzene rings; the closest approaches of a benzene ring are to an axial CO ligand of complex molecule W (Fig. 5), to an equatorial CO ligand of complex molecule X, to an axial carbonyl carbon and a methyl group of complex molecule Y, and to the outer edge (C23) of complex molecule Z.

Acknowledgements

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