Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CRYSTAL STRUCTURE OF SOME DICARBONYL ALLYL DERIVATIVES OF SUBSTITUTED CARBONYLS OF MOLYBDENUM

III. THE CRYSTAL STRUCTURE OF DICARBONYL-2,2'-BIPYRIDINE-PYRIDINE-π-ALLYLMOLYBDENUM TETRAFLUOROBORATE, $[(CO)_2(C_{10}H_8N_2)(C_5H_5N)(\pi\text{-}C_3H_5)Mo]^+[BF_4]^-$

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(Received October 11th, 1971)

SUMMARY

The crystal structure and molecular configuration of the complex dicarbonyl-2,2'-bipyridinepyridine-π-allylmolybdenum tetrafluoroborate $(CO)_2(C_{10}H_8N_2)(C_5H_5N)(\pi\text{-}C_3H_5)MoBF_4$ have been determined from three-dimensional data collected photographically at 22°C. The unit cell is monoclinic, spacegroup $P2_1/c$ with four formula units in a cell of dimensions $a=9.702\pm0.004$ Å, $b=13.632\pm0.001$ Å, $c=19.421\pm0.008$ Å, $\beta=117°8'\pm5'$. The structure has been refined to $R=0.0815$ by the application of an isotropic/anisotropic block-diagonal-approximation least-squares refinement using 2488 independent observed reflections.

The ligands form the apices of an approximate octahedron with the molybdenum at its centre. When viewed with the dicarbonyl ligands horizontal, the π-allyl and pyridine ligands lie axially, above and below (respectively) the dicarbonyl plane. The bipyridine plane lies 14.3° below the horizontal, dipping away from the π-allyl. The other inter-planar angles are π-allyl/dicarbonyl 13.8°, 2,2'-bipyridine/π-allyl 27.7°.

The three allyl carbon atoms are equidistant from the molybdenum atom. The Mo–C values all lie within $\pm1.5\ \sigma$ of the mean value of 2.292 ± 0.009 Å. The inter-carbon angle is $111.4\pm0.8°$ and the C–C bond lengths are 1.369 ± 0.013 Å and 1.471 ± 0.013 Å. The mean Mo–C and C–O bond lengths are 1.986 ± 0.008 Å and 1.187 ± 0.011 Å respectively and the Mo–C–O angles are near-linear. The bipyridine and pyridine ligands have each been shown to be planar with Mo–N contacts of 2.250 ± 0.011 Å (Bipy mean) and 2.320 ± 0.007 Å (Py).

Some disorder is evident associated with the BF_4 anion. This disorder appeared as distortion of the tetrahedral BF_4 configuration and as high thermal motion of the four fluorine atoms.

INTRODUCTION

This complex is the final structure in a series of three, taken from those pre-

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pared by Hull and Stiddard[1], studied to investigate the relative stereochemical positions of the various ligands present, the bonding schemes present for the allyl ligand, the thiocyanato ligands[2,3] and also, in this structure only, any ionic bonding. The first two structures solved, *viz.* (isothiocyanato)dicarbonyl-2,2'-bipyridine-π-allylmolybdenum (MCBAS), (isothiocyanato)dicarbonyl-1,10-phenanthroline(2-methylallyl)molybdenum (MCϕAS) both conclusively showed the thiocyanato ligand to be *N*-bonded and the allyl to be π-bonded.

This final complex, number 9 in Hull and Stiddard's[1] paper, dicarbonyl-2,2'-bipyridinepyridine-π-allylmolybdenum tetrafluoroborate will henceforth be referred to as MCPAB.

All computer programs used in the solution of this structure came from the Crystal '69 System written by Powell, Griffiths and Cross for an ICL 4130 computer.

CRYSTAL DATA

As with the MCBAS and MCϕAS complexes, very small crystals of the MCPAB complex, of approximately 0.06 mm in maximum dimension, were obtained from C. Hull of University College, London. The sample was recrystallised from a solution in pyridine and the new crystals appeared as orange/red prismatic crystals.

The densities of several crystals from the initial batch were measured by the method of flotation in a mixture of benzene and carbon tetrachloride and the density was found to be $D_{\text{obs}} = 1.507 \pm 0.015$ g/cm^3. Initially, the number of formula units per cell, *Z*, was obtained from the 010 oscillation and (*h*0*l*) Weissenberg photographs. These measurements and, later, the accurate cell parameters gave $Z=4$ and a calculated density of $D_{\text{calcd}} = 1.494 \pm 0.032$ g/cm^3.

From the (*hNl*) Weissenberg and (0*kl*) precession zones, for $N=0, 1, 2 \ldots 11$, the only systematic absences were: (*h*0*l*) reflections absent for $l=2n+1$; (0*k*0) reflections absent for $k=2n+1$. Thus the spacegroup was uniquely defined as $P2_1/c$.

The linear absorption coefficient, μ, was found to be 56.5 cm^{-1} and 6.6 cm^{-1} for Cu-$K\alpha$ and Mo-$K\alpha$ radiation, respectively. Assuming cylindrical-crystal absorption corrections the minimum and maximum values of the absorption coefficient, A^*, were 1.1 and 1.3 for the selected crystal of length 0.19 mm and cross-section 0.05 mm × 0.06 mm, Cu-$K\alpha$ radiation. In view of these values of A^* and the small size of the crystal no absorption corrections were made to the data, collected using Ni-filtered Cu-$K\alpha$ radiation.

The accurate cell parameters were obtained from the (*h*0*l*) and (0*kl*) Weissenberg zones using fine gold wire as a calibrating standard, Powell[4] and Graham[5], as described previously[2]. The data used[6] in this determination and the resulting cell parameters are as follows: cell constant for gold[7], $a=4.078504$ Å at 25°; copper radiation wavelengths $\lambda(\alpha_1)=1.54051$ Å, $\lambda(\alpha_2)=1.54433$ Å, $\lambda(\beta)=1.39217$ Å; coefficient of refraction 1.86×10^{-4} Å; coefficient of expansion $1.41 \times 10^{-5}/°$C; accurate cell parameters $a=9.702 \pm 0.004$ Å, $b=13.632 \pm 0.001$ Å, $c=19.421 \pm 0.008$ Å, $\beta= 117°8' \pm 5'$, at 22°.

The (*hNl*) data were collected using the equi-inclination Weissenberg arrangement, for $N=0, 1, 2 \ldots 11$, using Ni-filtered Cu-$K\alpha$ radiation ($\lambda=1.54178$ Å) at 30 kV and 25 mA. Each layer of data was collected in packs of five films. In total, 2488 independent non-zero reflections were recorded and the intensities estimated visually.

Initially, a further 679 accidentally absent reflections were included as "unobserveds", Hamilton[8], but these were removed after the initial stages of refinement. The usual Lorentz-polarisation and spot-distortion[9] corrections were applied to the intensities and the (hNl) layers of data were placed on a near absolute scale by the method of Wilson[10], giving an overall isotropic B of 1.43 Å^2. Individual layer scales were refined in the least-squares refinement. All data reduction was achieved using the Crystal '69 System of Powell, Griffiths and Cross on an ICL 4130 Computer.

STRUCTURE DETERMINATION

A three dimensional Patterson synthesis, using program POFOUR, gave the molybdenum site and this was used to phase the structure amplitudes, using PABLO, for the first electron-density distribution calculation using POFOUR.

Initially the full 3167 reflections were used and the first electron-density distribution gave both the 2,2'-bipyridine and dicarbonyl ligands very easily. However, the π-allyl and pyridine ligands were somewhat obscured by what appeared to be diffraction peaks. For these latter ligands, peaks were chosen at atomic sites, to give the expected ligand configuration. These sites were then included in three cycles of refinement, in which $\Sigma\omega\Delta^2 = \Sigma\omega|k \cdot F_o - F_c|^2$ was minimised, but, although $\Sigma\omega\Delta^2$ did reduce, the layer-scales and isotropic B values were shifting violently and $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ rose from 0.32 to 0.52.

In view of these effects it was decided to use only the observed data, and the 679 unobserved reflections, representing 21.4% of those used in the first refinement, were removed. These new Mo-phased reflections were then used to recalculate the previous electron-density distribution and the ligands were re-located. The bipyridine and dicarbonyl positions so obtained were not significantly different from those previously determined, the two sets of fractional parameters agreeing to better than ± 0.005. The regions around the allyl and pyridine ligands were still somewhat confused although almost half of the peaks previously observed were now absent. This reduction in the number of peaks still did not produce a sufficiently clear indication of the true atomic sites for these two ligands and no further attempt at their location was made at this stage. This only partial change in the confused state of these regions was thought to indicate either diffraction effects or bad phasing which had been based only on the molybdenum position. The molybdenum atom comprised only about 18.6% of the total scattering matter, so that the phasing was probably poor.

A second electron density distribution was then calculated using structure amplitudes phased using the atoms so far located in the $(CO)_2MoBipy$ ligands. In the allyl and pyridine regions only the expected three and six peaks, respectively, were observed and the location of these atoms was unambiguous. All previous "error" peaks had disappeared in these two regions but four peaks, of around $+1$ e/Å^3, were present close to the Mo site. These were similar to those observed in MCBAS[2] and MCϕAS[3] and were, at this stage, ignored. The boron and two of the expected four fluorine atoms were easily located but the two remaining fluorines appeared as rather extended peaks of about half the expected electron density, and no attempt at their location was made. Four cycles of isotropic refinement gave $R = 0.1645$, using the weighting scheme $\omega = |F_o|/F^*$ for $|F_o| < F^*$ and $\omega = F^*/|F_o|$ for $|F_o| > F^*$ with $F^* = 20$.

At this stage a difference-synthesis was calculated and three features were evident:

(*i*). The two remaining fluorine atoms appeared as greatly extended regions of half-weight electron density. This was taken to indicate that there might be some disorder present similar to that observed in $IrCl(CO)(NO)(P(C_5H_5)_3)_2BF_4$, Hodgson and Ibers[11], and that these two atoms would probably have large isotropic B values of about 10 Å^2.

(*ii*). All other atomic sites, except for one nitrogen and three carbon atoms, showed evidence of anisotropic thermal motion.

(*iii*). The residual electron-density peaks around the Mo site were of the same form as in MCBAS[2] and MCϕAS[3] but the peak values, of +0.5 e/Å^3 and −1.0 e/Å^3, were about half those previously observed.

The final four cycles of refinement, on x, y, z, b_{ij} (B_n for the four isotropic atoms) for all atoms and the layer scale factors, gave $R=0.0815$. The weighting scheme used was the same as in previous cycles but using $F^*=4F_{\min}$ (Hughes[12]) = 16 in order to obtain constant mean $\Sigma\omega\Delta^2$ for all ranges of $|F_o|$.

(*continued on p.* 143)

TABLE 1

THE FINAL FRACTIONAL POSITIONAL PARAMETERS AND STANDARD DEVIATIONS × 10^4

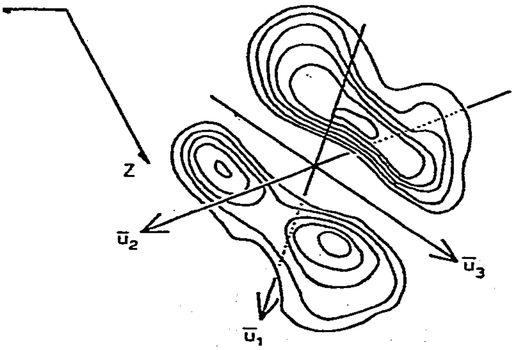
Atom	x	y	z
C32	0.2415(11)	0.1171(5)	0.4227(5)
C22	0.2548(8)	0.1655(7)	0.3608(4)
N2	0.0075(5)	0.1019(4)	0.2689(3)
C2	−0.3507(9)	0.0342(5)	0.1574(4)
Mo	−0.1898(0)	0.1005(0)	0.1452(0)
C1	−0.3819(9)	0.1352(7)	0.0433(4)
O1	−0.4903(7)	0.1408(7)	−0.0130(3)
O2	−0.4579(8)	−0.0065(6)	0.1655(4)
C3	−0.1332(11)	−0.0645(6)	0.1533(4)
C4	−0.0572(10)	−0.0185(8)	0.1179(5)
C5	−0.1666(13)	0.0274(6)	0.0448(5)
N1	0.0012(7)	0.1917(5)	0.1484(3)
C11	−0.0007(10)	0.2481(8)	0.0851(4)
C21	0.1033(11)	0.3047(8)	0.0839(6)
C31	0.2487(12)	0.3122(12)	0.1596(7)
C41	0.2594(10)	0.2624(9)	0.2252(6)
C51	0.1335(7)	0.2109(6)	0.2188(4)
C12	0.1297(7)	0.1601(5)	0.2840(3)
C42	0.1131(9)	0.0634(7)	0.4080(4)
C52	−0.0025(9)	0.0507(7)	0.3277(4)
N3	−0.2570(6)	0.2440(5)	0.1868(3)
C13	−0.2963(9)	0.3211(6)	0.1395(5)
C23	−0.3471(10)	0.4097(7)	0.1627(7)
C33	−0.3520(11)	0.4163(8)	0.2300(6)
C43	−0.3105(11)	0.3287(7)	0.2777(5)
C53	−0.2668(9)	0.2429(7)	0.2546(4)
B	−0.3342(10)	0.1076(8)	0.4091(5)
F1	−0.3821(9)	0.0794(8)	0.4615(4)
F2	−0.4418(8)	0.1082(5)	0.3340(3)
F3	−0.1938(14)	0.1535(13)	0.4263(6)
F4	−0.2305(20)	0.0282(12)	0.4191(7)

ABLE 2

IE FINAL THERMAL PARAMETERS

otropic motion defined by: exp $-(B\cdot\sin^2\theta/\lambda^2)$.
nisotropic motion defined by: exp $-(h^2\cdot b_{11}+k^2\cdot b_{22}+l^2\cdot b_{33}+h\cdot k\cdot b_{12}+k\cdot l\cdot b_{13}+k\cdot l\cdot b_{23})$.

tom	B (or b_{11})	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
32	3.531					
22	2.490					
2	1.357					
2	2.628					
Io	0.0042	0.0020	0.0011	−0.0006	−0.0003	0.0005
1	0.0099	0.0037	0.0016	0.0042	−0.0018	0.0025
1	0.0107	0.0113	0.0017	−0.0030	−0.0064	0.0013
2	0.0167	0.0092	0.0043	−0.0097	0.0068	−0.0049
3	0.0139	0.0008	0.0023	−0.0023	0.0036	0.0006
4	0.0101	0.0066	0.0027	0.0019	−0.0025	−0.0037
5	0.0259	0.0006	0.0030	−0.0040	0.0082	−0.0008
1	0.0070	0.0019	0.0017	0.0050	0.0002	0.0006
11	0.0109	0.0066	0.0011	−0.0030	0.0001	0.0029
21	0.0099	0.0091	0.0045	−0.0041	0.0044	0.0054
31	0.0102	0.0169	0.0048	−0.0041	0.0015	−0.0018
41	0.0080	0.0085	0.0049	−0.0017	−0.0022	0.0040
51	0.0039	0.0018	0.0031	−0.0002	0.0016	−0.0017
12	0.0033	0.0013	0.0015	−0.0001	−0.0022	−0.0010
42	0.0114	0.0038	0.0018	0.0023	0.0026	−0.0005
52	0.0083	0.0055	0.0020	0.0087	0.0022	0.0053
3	0.0057	0.0029	0.0019	0.0006	−0.0019	−0.0000
13	0.0100	0.0010	0.0030	−0.0029	0.0027	−0.0022
23	0.0087	0.0039	0.0082	−0.0004	0.0091	0.0041
33	0.0155	0.0060	0.0052	−0.0047	0.0077	−0.0005
43	0.0139	0.0038	0.0027	−0.0031	0.0064	−0.0018
53	0.0079	0.0065	0.0017	0.0034	0.0019	−0.0001
	0.0091	0.0053	0.0014	−0.0036	0.0016	0.0008
1	0.0223	0.0203	0.0049	0.0051	0.0134	0.0055
2	0.0242	0.0110	0.0025	−0.0117	0.0028	0.0017
3	0.0430	0.0563	0.0046	−0.0701	0.0130	−0.0141
4	0.0998	0.0312	0.0150	0.0756	0.0251	0.0131



g. 1. The section of the final difference synthesis through the molybdenum site at $y=0.1005$ and parallel the $x-z$-plane. The contours are positive in intervals of 0.1 e/Å^3.

TABLE 3

THE ROOT-MEAN-SQUARE DISPLACEMENTS, $\bar{U}$, AND THE DIRECTION COSINES l, m AND n, WITH RESPECT TO THE ORTHOGONAL AXES X, Y AND Z FOR THE ATOMS VIBRATING ANISOTROPICALLY

Atom	$\bar{U}$	l	m	n
Mo	0.0967	0.4001	−0.3654	0.8405
	0.1259	0.5490	0.8299	0.0955
	0.1937	−0.7339	0.4216	0.5326
C1	0.0984	0.3913	−0.4288	0.8142
	0.2019	0.0949	0.8989	0.4278
	0.2666	−0.9153	−0.0901	0.3925
O1	0.0760	0.4468	−0.0238	0.8943
	0.2997	−0.6338	−0.7139	0.2977
	0.3569	−0.6313	0.6999	0.3340
O2	0.1569	−0.6762	−0.6386	0.3673
	0.2496	0.4717	0.0077	0.8817
	0.3651	−0.5659	0.7695	0.2960
C3	0.0947	−0.1756	−0.9837	0.0377
	0.1874	0.1357	0.0137	0.9906
	0.2695	−0.9750	0.1791	0.1311
C4	0.1267	0.4751	−0.3067	0.8247
	0.2458	0.3793	0.9171	0.1226
	0.3079	−0.7940	0.2546	0.5521
C5	0.0481	0.1347	0.9890	0.0576
	0.2137	−0.1621	−0.0353	0.9861
	0.3225	0.9775	−0.1422	0.1556
N1	0.0692	0.4994	−0.7750	0.4249
	0.1612	0.1608	0.5627	0.8109
	0.2317	−0.8513	−0.3367	0.4024
C11	0.1060	0.0745	−0.3206	0.9443
	0.1973	0.7885	0.5986	0.1410
	0.2916	−0.6105	0.7431	0.2974
C21	0.1721	−0.8899	−0.4556	0.0238
	0.2110	0.2716	−0.4873	0.8299
	0.3561	−0.3665	0.7450	0.5574
C31	0.1836	0.7490	0.1065	0.6540
	0.3179	−0.6540	0.2165	0.7199
	0.3989	−0.0650	−0.9704	0.2324
C41	0.1524	0.7417	−0.0318	0.6700
	0.2576	−0.3410	−0.8781	0.3358
	0.3644	−0.5776	0.4775	0.6621
C51	0.1190	0.1248	0.9144	0.3850
	0.1217	0.8662	−0.2896	0.4072
	0.2454	−0.4839	−0.2827	0.8282
C12	0.0659	0.5233	0.4692	0.7114
	0.1048	0.3916	−0.8738	0.2882
	0.2258	−0.7568	−0.1278	0.6410
C42	0.1620	0.0133	0.2298	0.9731
	0.1805	0.5145	−0.8361	0.1904
	0.2308	−0.8574	−0.4981	0.1294
C52	0.0648	0.3675	−0.5809	0.7263
	0.2011	−0.9139	−0.0807	0.3979
	0.2750	0.1725	0.8099	0.5606
N3	0.1107	0.5954	−0.0784	0.7996

(continued)

TABLE 3 (*continued*)

Atom	$\bar{U}$	*l*	*m*	*n*
	0.1631	−0.0024	0.9950	0.0994
	0.2445	−0.8034	−0.0610	0.5923
C13	0.0739	0.1253	0.9312	0.3423
	0.1970	0.7552	−0.3133	0.5758
	0.2457	−0.6435	−0.1864	0.7424
C23	0.1490	−0.6719	−0.7406	0.0045
	0.1797	0.6944	−0.6278	0.3517
	0.3788	−0.2576	0.2394	0.9361
C33	0.1787	0.7738	0.5984	0.2078
	0.2516	0.5447	−0.7960	0.2640
	0.2940	−0.3233	0.0911	0.9419
C43	0.1661	−0.0321	0.8142	0.5797
	0.1959	−0.6739	−0.4460	0.5891
	0.2401	0.7382	−0.3718	0.5629
C53	0.1533	0.4957	−0.1479	0.8558
	0.1879	−0.7763	0.3663	0.5130
	0.2542	−0.3894	−0.9187	0.0668
B	0.1389	0.0699	−0.2174	0.9736
	0.1821	0.7898	0.6082	0.0791
	0.2422	−0.6093	0.7634	0.2143
F1	0.2113	−0.6995	−0.1437	0.7000
	0.2933	0.7142	−0.1735	0.6781
	0.4501	0.0240	0.9743	0.2240
F2	0.1902	0.0134	−0.1219	0.9925
	0.2540	0.6814	0.6814	0.7275
	0.3932	−0.7318	0.6752	0.0928
F3	0.2110	0.2583	0.2554	0.9317
	0.2948	−0.8639	−0.3706	0.3411
	0.7994	0.4324	−0.8930	0.1249
F4	0.3143	0.4878	−0.7276	0.4824
	0.5106	−0.3711	0.3274	0.8690
	0.7667	0.7902	0.6029	0.1103

A final difference synthesis gave no indication of any hydrogen sites, as had occurred in MCϕAS[3]. Also the residual Mo peaks were not situated along the axes of the Mo thermal ellipsoid and were thus taken to indicate some form of non-ellipsoidal thermal motion of the molybdenum and neighbouring atoms. Fig. 1 is the section, through the molybdenum site, of this difference synthesis and shows the positive residual peaks and the directions of the thermal ellipsoid axes. The two negative peaks occurred at about 1.15 Å from the molybdenum site, being one on either side of it in approximately the *b* direction.

Tables 1 and 2 give the final positional and thermal parameters for all atoms, together with their standard deviations. Table 3 lists the root-mean square displacements for the anisotropic atoms. Lists of the observed and calculated structure factors can be obtained by application to the authors.

THE MOLECULAR STRUCTURE

As may be seen from Fig. 2 the cation of this complex has an octahedral con-

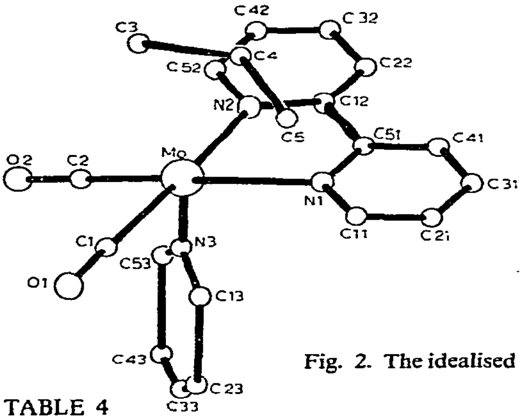


Fig. 2. The idealised MCPAB cation structure and atom designation.

TABLE 4

INTERATOMIC DISTANCES AND BOND ANGLES

Bond	Length (Å) and standard deviations (× 10^3)	Bonds	Angle and standard deviations (× 10)
Mo–C1	2.061(8)	C1 –Mo–C2	78.2(3)
Mo–C2	1.911(8)	N1 –Mo–N2	71.1(2)
Mo–C3	2.306(8)	C1 –Mo–N3	82.3(3)
Mo–C4	2.279(10)	C2 –Mo–N3	88.9(3)
Mo–C5	2.290(9)	N1 –Mo–N3	83.2(2)
Mo–N1	2.209(6)	N2 –Mo–N3	82.0(2)
Mo–N2	2.290(5)	N1 –C11–C21	129.3(8)
Mo–N3	2.320(7)	C11–C21–C31	114.7(10)
N1 –C11	1.443(10)	C21–C31–C41	120.1(11)
C11–C21	1.280(14)	C31–C41–C51	118.2(10)
C21–C31	1.507(16)	C41–C51–N1	124.4(7)
C31–C41	1.405(17)	C51–N1 –C11	112.3(6)
C41–C51	1.365(13)	N2 –C12–C22	120.2(6)
C51–N1	1.409(9)	C12–C22–C32	119.6(7)
N2 –C12	1.343(9)	C22–C32–C42	119.9(8)
C12–C22	1.433(9)	C32–C42–C52	118.3(7)
C22–C32	1.428(12)	C42–C52–N2	120.9(7)
C32–C42	1.358(13)	C52–N2 –C12	120.5(5)
C42–C52	1.458(11)	N3 –C13–C23	118.3(8)
C52–N2	1.380(10)	C13–C23–C33	122.0(10)
C51–C12	1.458(10)	C23–C33–C43	116.5(9)
N3 –C13	1.332(10)	C33–C43–C53	121.7(8)
C13–C23	1.452(13)	C43–C53–N3	118.0(8)
C23–C33	1.334(16)	C53–N3 –C13	123.4(8)
C33–C43	1.452(14)	C3 –C4 –C5	111.4(8)
C43–C53	1.386(13)	Mo–C1 –O1	170.6(8)
C53–N3	1.363(10)	Mo–C2 –O2	178.1(6)
C1 –O1	1.123(10)	F1 –B –F2	116.9(8)
C2 –O2	1.251(11)	F1 –B –F3	125.5(8)
C3 –C4	1.369(13)	F1 –B –F4	98.6(9)
C4 –C5	1.471(13)	F2 –B –F3	116.4(8)
B –F1	1.352(12)	F2 –B –F4	107.3(9)
B –F2	1.353(10)	F3 –B –F4	75.7(11)
B –F3	1.395(16)		
B –F4	1.431(19)		

figuration comparable with the MCBAS^2 and MCϕAS^3 complexes. The allyl, dicarbonyl and bipyridine ligands occupy the same relative positions around the molybdenum as in MCBAS^2 with the pyridine ligand replacing the isothiocyanate.

The 2,2′-bipyridine ligand is defined by the plane $0.5789X-0.7952Y-0.1802Z+3.369=0$, where X, Y and Z are orthogonal axes, as defined in Table 5. The

TABLE 5

EQUATIONS OF THE BEST-FIT PLANES AND MEAN ATOMIC DEVIATIONS

I 2,2′-bipyridine ligand	IV pyridine ligand
II pyridyl-1 ring	V allyl carbon atoms
III pyridyl-2 ring	VI dicarbonyl atoms

Planes defined by $l\cdot X+m\cdot Y+n\cdot Z+d=0$ where $X=a\cdot x+c\cdot z\cdot\cos\beta$, $Y=b\cdot y$, $Z=c\cdot z\cdot\sin\beta$

DIRECTION COSINES OF PLANES

Plane	l	m	n	d
I	0.5789	−0.7952	−0.1802	3.3369
II	0.5695	−0.7899	−0.2275	3.4380
III	0.5951	−0.7911	−0.1414	3.1432
IV	0.8312	0.3107	0.4609	0.9480
V	0.2175	−0.8439	−0.4905	1.1344
VI	0.4277	−0.8214	−0.3773	3.5055

ATOMIC DEVIATIONS

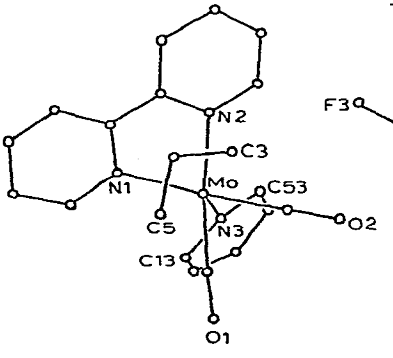
Plane	Atom	Deviation	Atom	Deviation
I	Mo	−0.016		
	N1	0.043	C11	−0.059
	C21	−0.078	C31	0.033
	C41	0.093	C51	−0.003
	N2	0.058	C12	−0.011
	C22	0.001	C32	−0.059
	C42	−0.078	C52	0.072
II	Mo	0.003		
	N1	0.048	C11	−0.003
	C21	−0.026	C31	0.017
	C41	0.024	C51	0.059
III	Mo	−0.169		
	N2	0.002	C12	−0.036
	C22	0.036	C32	0.003
	C42	−0.046	C52	0.043
IV	Mo	−0.069		
	N3	0.022	C13	0.003
	C23	−0.017	C33	0.012
	C43	0.004	C53	−0.021
V	Mo	−1.934		
	N1	−2.613	N2	−2.821
	C1	−1.678	C2	−1.638
VI	Mo	0.095		
	C1	−0.041	O1	0.027
	C2	0.044	O2	−0.029

mean deviation of the bipyridine atoms from this plane is ±0.049 Å and the molybdenum lies 0.016 Å out of the plane, away from the allyl. The bond lengths, Table 4, have been found to be C–N (mean) = 1.394±0.010 Å; C–C (ring) in the range 1.280± 0.014 Å to 1.507±0.016 Å; C–C (bridging) = 1.458±0.010 Å. The interbond angles again approach the expected 120°, for hexagonal rings, but lie in the range 114.7° to 129.3°. It has been noted that the atoms C11, C21, C31 have larger thermal amplitudes than their neighbours in the ring and these may explain the extremes for the bonds and angles associated with these atoms[13]. The planarity of the two individual rings was investigated because of the large deviations from the mean bipyridine plane (*e.g.* C41 at 0.093 Å) and the two rings were found to be twisted about the bridging C–C bond by 5.1°. The atom deviations from their corresponding rings are given in Table 5.

The four atoms of the dicarbonyl are again[2,3] co-planar, the mean deviation being 0.037 Å, Table 5. The best-fit plane is $0.4277X - 0.8214Y - 0.3773Z + 3.5055 = 0$ and the molybdenum is situated 0.095 Å out of this plane towards the allyl. The Mo–C and C–O bond lengths, listed in Table 4, have mean values of 1.986±0.008 Å and 1.187±0.011 Å. The Mo–C–O angles, Table 4, are 170.6±0.8° and 178.1±0.6°, *i.e.* only the latter appears to be significantly linear.

The pyridine ligand, in this complex replacing the previous[2,3] isothiocyanato ligand has been shown, as expected, to be planar with a mean atom deviation of 0.013 Å. The equation of the plane is $0.812X + 0.3107Y + 0.4609Z + 0.9480 = 0$. The mean C–N and C–C bond lengths at 1.348± 0.010 Å and 1.406±0.014 Å, respectively, agree favourably with the corresponding mean values for pyridine and for the pyridine ligand in $Mo(CO)_3Py(Bipy)$, Griffiths[14]. If the cation is projected onto the N–N(Bipy)/C–C(dicarb) plane the pyridine ligand is seen to approximately bisect the C(dicarb)–Mo–N(Bipy) angle and not the N(Bipy)–Mo–N(Bipy) angle. Thus in this projection the pyridine plane is seen to be normal to the apparent 2-fold axis of the cation and not parallel to it. This orientation is identical with that observed by Griffiths[14] for $Mo(CO)_2Py(Bipy)$. Fig. 3 shows the projection onto the bipyridine plane which was plotted using a program written by Cross.

The π-allyl ligand is absolutely defined by the plane through its three carbon atoms and has the equation $0.2175X - 0.8439Y - 0.4905Z + 1.1344 = 0$. With respect



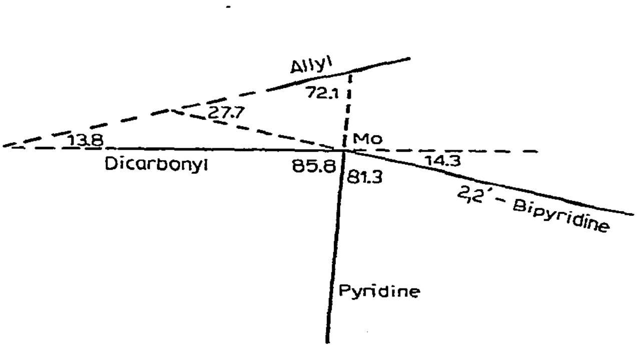


Fig. 3. The final MCPAB structure projected onto the 2,2'-bipyridine ligand plane.

Fig. 4. A schematic representation of the interplanar angles for the various MCPAB ligands.

to the dicarbonyl and bipyridine ligands the π-allyl has the identical orientation as in MCBAS[2] and the methylallyl in MCϕAS[3]. Within the ligand the mean C–C bond length is 1.420±0.013 Å and the inter-bond angle is 111.4±0.8°.

The resulting interplanar angles are dicarbonyl/allyl 13.8°; dicarbonyl/bipyridine 14.3°; bipyridine/allyl 27.7° as shown schematically in Fig. 4 and pyridine/dicarbonyl 85.8°; pyridine/bipyridine 81.3° and pyridine/allyl 72.1°.

The BF_4 anion has an approximately tetrahedral arrangement of fluorines around the central boron. The mean B–F bond length and F–B–F angle have been found to be 1.366±0.015 Å and 106.7±0.9° respectively. These values, particularly the angles, have no doubt been greatly affected by the large thermal motion of the fluorines, whose mean isotropic *B* value is 11.0 Å^2. Hodgson and Ibers[11] have investigated an $IrBF_4$ complex in which there was a disordered BF_4 anion. They refined this anion as a central boron and two rigid tetrahedral F_4 groups in the ratio 0.82 to 0.18. The mean isotropic *B* values for each of these tetrahedra were 8.6 and 7.8 Å^2, respectively, which are reasonably close to those values observed here in MCPAB. As refinement of rigid tetrahedra is not possible with PABLO the anion was not treated in this way but was assumed to contain four independent fluorine atoms of large anisotropic thermal motion. The bond lengths and angles, Table 4, obtained agree with the values obtained in $NaBF_3OH$[15] in which the hydroxyl group was refined as a fourth fluorine, MBF_4 (with M = K, Rb, Cs, NH_4)[16], $Cu(PyO)_4(BF_4)_2$[17], $CuEn_2(BF_4)_2$[18] and $NaBF_4$[19].

THE THERMAL MOTION

The thermal motion of the MCPAB atoms is best described by reference to Fig. 3 and Table3. From Fig. 5 it can be seen that carbon atoms bonded to hydrogen atoms of the bipyridine ligand are vibrating mostly in a direction roughly perpendicular to the bipyridine plane. The remaining atoms of the bipyridine ligand being more strongly bound appear more random in their vibrations. Similar observations are made in the pyridine. In the carbonyl and BF_4^- groups the consituent atoms have maximum vibrations perpendicular to the respective bonds, and the very large r.m.s. displacements of the fluorine atoms are highly evident.

TABLE 6

THE INTER-IONIC DISTANCES < 3.7 Å (E.S.D. IN PARENTHESIS × 10^2)

Atoms labelled (a), (b) and (c) are related to those in Table 1 by: (a) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (b) $(x-1), y, z$; (c) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Atoms	Distance	Atoms	Distance
F1–C22(b)	3.36(1)	F3–C42	2.74(2)
F1–C32(b)	3.41(1)	F3–C52	2.93(2)
F1–C13(a)	3.44(1)	F4–C21(c)	3.29(2)
F2–C41(b)	3.42(1)	F4–C31(c)	3.29(2)
F2–C22(b)	3.31(1)	F4–C42	3.25(2)
F3–C11(a)	3.09(1)	F4–C52	3.27(2)
F3–C21(a)	3.16(2)		

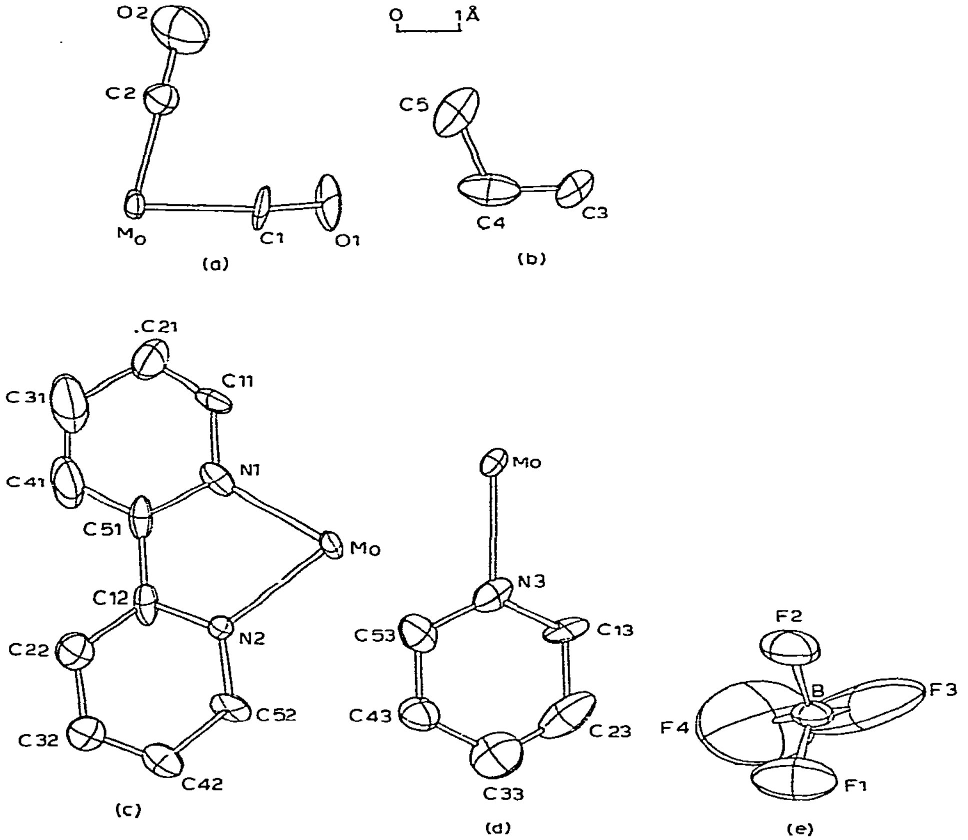


Fig. 5. The thermal vibration ellipsoids for the various ligands: (a) dicarbonyl, (b) allyl, (c) 2,2'-bipyridine, (d) pyridine, (e) BF_4.

THE BONDING

Table 6 gives the inter-ionic distances < 3.7 Å. It will be seen from the table that the cation–anion closest contacts lie between 3.09 Å and 3.45 Å. The closest contact between two cations is 3.68 Å between the carbonyl oxygen O1 at (x,y,z) and the bipyridine carbon C22 at $(x-1, \frac{1}{2}-y, z-\frac{1}{2})$. Fig. 6 shows the bonding scheme as viewed from the 010-direction.

THE CRYSTAL '69 SYSTEM OF STRUCTURE ANALYSIS PROGRAMS

1 PODAR

This is a data reduction program intended for the processing of raw data collected by either Weissenberg or Precession methods. It calculates the mean intensity for a set of equivalent reflections and applies the Phillips distortion, Lorentz and polarization corrections. (J. H. Cross)

2 POSCALE

This deduces an overall absolute scale using a least-squares best-fit procedure

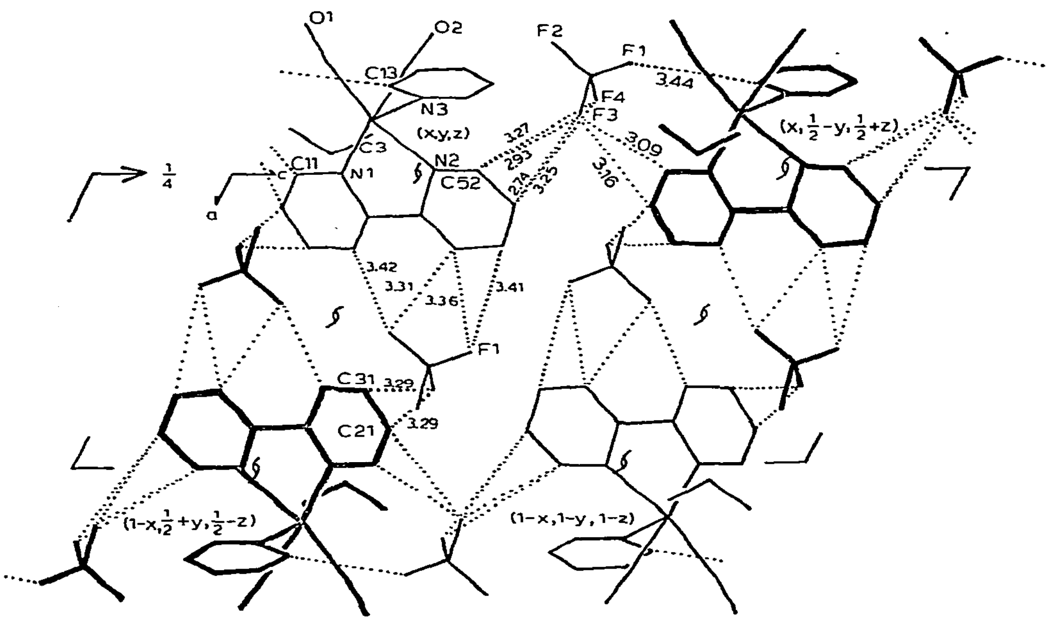


Fig. 6. The ionic-bonding scheme in MCPAB. All BF_4 anions are present but the ($\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) and ($\bar{x}$, $\bar{y}$, $\bar{z}$) cations have been omitted and replaced by those at ($1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) and ($1-x$, $1-y$, $1-z$) to avoid the confusion of overlap.

in the Wilson[10] method, adopting a parabola as the best-fit curve. An overall isotropic temperature factor is also deduced. (M. T. G. Powell)

3 POFOUR

This is a fast general purpose Fourier synthesis program using the Beevers–Lipson method of summation for space groups 1 to 74[6], excluding *Fdd2* and *Fddd*. (M. T. G. Powell and A. Griffiths)

4 PABLO

A block-diagonal structure-factor/least-squares program in which up to 90 atoms, fully anisotropic, and 20 layer scale-factors may be refined. Several weighting schemes are available and an analysis of the scheme is output. Individual damping factors may be applied to the variables to speed up convergence. (A. Griffiths and M. T. G. Powell)

5 PADI

A molecular geometry program calculating variances, co-variances, mean-square thermal displacements, intra- and inter-molecular bond lengths and angles, least-squares best-fit planes defined by up to 20 atoms and molecular projection onto any given plane. (M. T. G. Powell and A. Griffiths).

ACKNOWLEDGEMENTS

We are grateful to the Governors of Portsmouth Polytechnic for providing the facilities, to Drs. C. G. Hull and M. H. B. Stiddard for the crystals, Dr. N. P. Johnson for his help in the recrystallisation and to Dr. A. Griffiths and Messrs. M. T. G. Powell, and J. H. Cross for the use of their computer programs.

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