Trisubstituted Group 6 Metal Carbonyl Complexes with Di-2-pyridylamine Ligands. Crystal Structures of (2,2'-Bipyridyl-*N,N'*)tricarbonyl(di-2-pyridylamine-*N'*)-molybdenum(0) and -tungsten(0)†

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Reactions of [M(CO)$_4$(bipy)] (M = Mo or W; bipy = 2,2'-bipyridyl) with di-2-pyridylamine, $(C_5H_4N)_2NH$ (dipyam), yield the isostructural mixed-ligand complexes [M(CO)$_3$(bipy)(dipyam)]. Both complexes crystallise in the monoclinic space group $P2_1/c$ with, Mo [W], a = 10.620(15) [10.564(6)], b = 12.915(12) [12.925(6)], c = 16.524(26) [16.508(12)] Å, β = 107.81(11) [107.83(6)]°, and Z = 4. The complexes have *fac*-octahedral structures with bidentate 2,2'-bipyridyl and monodentate di-2-pyridylamine ligands. Substitution of monodentate heterocyclic amines, L, in [M(CO)$_4$(dipyam)] (M = Cr, Mo, or W) yields the mixed-ligand complexes [M(CO)$_3$(dipyam)L] which have three well resolved ν(CO) stretching absorptions in their i.r. spectra. This contrasts with the two ν(CO) bands characteristically observed in the analogous *fac*-[M(CO)$_3$(bipy)L] or *fac*-[M(CO)$_3$(phen)L] (phen = 1,10-phenanthroline) complexes and raises the possibility that the [M(CO)$_3$(dipyam)L] complexes may have the relatively unusual *mer*-octahedral geometry. Binuclear di-2-pyridylamine-bridged complexes are readily obtained from the reactions of [M(CO)$_4$(dipyam)] with di-2-pyridylamine.

In an earlier study[1] of the metal–carbonyl–di-2-pyridylamine complexes [M(CO)$_4$(dipyam)] [M = Cr, Mo, or W; dipyam = $(C_5H_4N)_2NH$] we observed that in two cases (M = Mo or W) the crystal structures involved intermolecular NH $\cdots$ OC contacts close enough to suggest the formation of weak hydrogen bonds. Supporting evidence for hydrogen bonding in these two crystalline compounds was found in perturbations of their solid-state NH and CO stretching frequencies relative to those in solution, to the ν(NH) frequency in the free ligand, and to the ν(NH) and ν(CO) frequencies in crystalline [Cr(CO)$_4$(dipyam)], in which there are no comparable intermolecular contacts. At best, hydrogen bonding to a carbonyl oxygen atom will be very weak and difficult to establish or disprove in any entirely conclusive way; however, it seemed likely that further substitution of the complexes, by increasing the π^* electron density on the remaining carbonyl ligands, would tend to enhance the ability of the terminal oxygen atoms to act as hydrogen-bond acceptors. We now report some preparative, structural, and spectroscopic studies on a series of tricarbonyl complexes containing di-2-pyridylamine ligands.

Experimental

Preparations.—All reactions were carried out in a dry nitrogen atomosphere. Details of reaction times, yields, and elemental analyses are listed in Table 1. The molybdenum compounds consistently formed more rapidly, and in better yield, than their chromium or tungsten analogues.

[M(CO)$_3$(bipy)(dipyam)] (M = Mo *or* W). These complexes were obtained from the reactions of the tetracarbonyl complexes [M(CO)$_4$(bipy)] (bipy = 2,2'-bipyridyl) with di-2-pyridylamine (typically in 1:5 mole ratio) in refluxing toluene. The reaction mixtures rapidly became very dark and the deep red, almost black complexes crystallised on cooling. The compounds were washed with light petroleum (b.p. 60—80 °C throughout) and dried *in vacuo*. Attempts to isolate further products from the reaction mixtures yielded amorphous black solids with no detectable carbonyl stretching absorptions. The reaction of [Cr(CO)$_4$(bipy)] with di-2-pyridylamine resulted in extensive decomposition with the precipitation of a small amount of a pyrophoric black solid of unknown composition.

[M$_2$(CO)$_6$(dipyam)$_3$] (M = Cr, Mo, *or* W). These complexes were prepared from the reactions of [M(CO)$_4$(dipyam)] with a five-molar excess of di-2-pyridylamine in refluxing toluene. In the case of the tungsten and chromium complexes, the progress of the reaction was indicated by a colour change to orange or orange-red in the solution and suspended solid. The yellow molybdenum complex reacted with no detectable colour change but the conversion, monitored by the disappearance of the [Mo(CO)$_4$(dipyam)] ν(CO) band at 2 011 cm^{-1}, was almost quantitative and appeared to be complete after *ca.* 3 h. The microcrystalline products were filtered off from the hot reaction mixtures, washed well with toluene and light petroleum, and dried *in vacuo*.

[M(CO)$_3$(dipyam)L] [L = *pyridine* (py), 4-*methyl-* (4Me-py) *or* 2,6-*dimethyl-pyridine* (2,6Me$_2$-py), *quinoline* (quin) *or* 4-*methylquinoline* (4Me-quin); M = Cr, Mo, *or* W]. The tetracarbonyl complexes [M(CO)$_4$(dipyam)] were heated to reflux in a 1:1 ligand:toluene mixture. In most cases the mixed-ligand tricarbonyl complexes began to separate from the boiling reaction mixtures. The amorphous or microcrystalline products were filtered off from the cooled reaction mixtures, washed well with toluene and light petroleum, and dried *in vacuo*. Identifiable py and 2,6Me$_2$-py complexes were obtained only with molybdenum as the metal atom. Prolonged reactions of [Cr(CO)$_4$(dipyam)] or [W(CO)$_4$(dipyam)] with pyridine yielded amorphous brown products with very variable elemental analyses.

The complexes listed in Table 1 are all air-stable and can be handled without difficulty under normal laboratory conditions. Evidence of decomposition begins to appear only after several months of exposure to air and light.

Physical Measurements.—Infrared spectra were recorded for the solid complexes (Nujol mulls) using a Perkin-Elmer 457

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† *Supplementary data available* (No. SUP 56457, 8 pp.): thermal parameters, full lists of bond lengths and angles, atomic co-ordinates for W complex. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical (%) and preparative data

Complex	Found (calc.) C	H	N	Reaction time (h)	Yield (%)	Colour
[Mo(CO)$_3$(bipy)(dipyam)]	56.0 (56.4)	3.5 (3.4)	13.8 (13.8)	15	20	Red-black
[W(CO)$_3$(bipy)(dipyam)]	45.8 (46.4)	2.7 (2.9)	12.0 (11.8)	15	15	Red-black
[Mo(CO)$_3$(dipyam)(py)]	50.2 (50.2)	3.6 (3.3)	12.1 (13.0)	1.5	75	Orange-yellow
[Mo(CO)$_3$(dipyam)(2,6Me$_2$-py)]	51.6 (52.4)	3.9 (4.0)	11.6 (12.2)	2	20	Yellow-brown
[Cr(CO)$_3$(dipyam)(4Me-py)]	56.1 (57.0)	3.9 (4.0)	13.8 (14.0)	4	55	Orange
[Mo(CO)$_3$(dipyam)(4Me-py)]	50.9 (51.4)	3.8 (3.6)	12.5 (12.6)	1.5	85	Yellow
[W(CO)$_3$(dipyam)(4Me-py)]	43.0 (42.9)	3.4 (3.0)	10.3 (10.5)	2	45	Yellow
[Cr(CO)$_3$(dipyam)(quin)]	60.7 (60.6)	3.9 (3.7)	11.9 (12.8)	4	30	Brown
[Mo(CO)$_3$(dipyam)(quin)]	55.1 (55.0)	3.6 (3.4)	11.8 (11.7)	1.5	85	Orange
[W(CO)$_3$(dipyam)(quin)]	45.6 (46.5)	2.9 (2.8)	9.9 (9.9)	2	60	Red
[Cr(CO)$_3$(dipyam)(4Me-quin)]	60.6 (61.3)	4.2 (4.0)	12.2 (12.4)	2	65	Red
[Mo(CO)$_3$(dipyam)(4Me-quin)]	55.6 (55.9)	4.0 (3.8)	11.4 (11.3)	1.5	90	Yellow-orange
[W(CO)$_3$(dipyam)(4Me-quin)]	46.6 (47.4)	3.1 (3.1)	10.2 (9.6)	3	65	Orange
[Cr$_2$(CO)$_6$(dipyam)$_3$]	55.8 (55.0)	3.7 (3.5)	16.3 (16.0)	4	60	Orange-red
[Mo$_2$(CO)$_6$(dipyam)$_3$][a]	49.5 (49.5)	3.0 (3.1)	14.8 (14.4)	3	95	Yellow
[W$_2$(CO)$_6$(dipyam)$_3$][b]	40.1 (41.2)	2.5 (2.6)	11.2 (12.0)	10	75	Orange-yellow

[a] Molecular-ion peak at m/z = 873. [b] Weak molecular-ion peaks in the range m/z = 1 045—1 053 (^{182}W, ^{184}W, ^{186}W).

spectrophotometer. The complexes are less soluble than their corresponding [M(CO)$_3$(bipy)L] complexes[2] and attempts to obtain satisfactory solution spectra were unsuccessful. Mass spectra (20 eV) of the [M$_2$(CO)$_6$(dipyam)$_3$] complexes were obtained using an AEI MS30 instrument, with the samples volatilised at *ca.* 200 °C.

Crystal Structure Determinations of [M(CO)$_3$(bipy)(dipyam)] (M = Mo *or* W).—*Crystal data for* [Mo(CO)$_3$(bipy)(dipyam)]. $C_{23}H_{17}MoN_5O_3$, M = 507.4, monoclinic, space group $P2_1/c$, a = 10.620(15), b = 12.915(12), c = 16.524(26) Å, β = 107.81(11)°, U = 2 157.8 Å^3, D_c = 1.56 g cm^{-3}, Z = 4, F(000) = 1 024 electrons, μ(Mo-K_α) = 6.4 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

Data collection and processing. Intensity data for tabular crystal 0.5 × 0.2 × 0.1 mm, Nicolet P3 automatic four-circle diffractometer, graphite-monochromated Mo-K_α radiation. Cell dimensions from setting angles for 15 reflections, $20 < 2\theta < 30°$. θ—2θ scan technique, variable scan speed, room temperature; 5 806 unique reflections measured (h 0 $\longrightarrow$ 14, k 0 $\longrightarrow$ 18, l $-22 \longrightarrow +22$, $0 < 2\theta < 60°$), 5 601 treated as observed [$I > 2\sigma(I)$]. Lorentz and polarisation corrections, not corrected for absorption or extinction. Three reference reflections monitored at intervals showed no sign of significant crystal movement or decomposition.

Structure analysis and refinement. Solved using MULTAN 80,[3] refined by block-diagonal least squares,[4] all atoms anisotropic, to R = 0.088, $\Delta/\sigma < 0.1$. Final difference map had no significant features, hydrogen atoms not located. Normal distribution of F *vs.* $|F_o|$ or $\sin^2\theta$. Weighting scheme $w = \{1 + [(|F_o| - 60)/30]^2\}^{-1}$, function minimised $\Sigma w(|F_o| - |F_c|)^2$. Neutral-atom scattering factors from International Tables.[5] Final atomic parameters listed in Table 2, selected bond lengths and angles in Table 3.

Crystal data for [W(CO)$_3$(bipy)(dipyam)]. $C_{23}H_{17}N_5O_3W$, M = 595.3, monoclinic, space group $P2_1/c$, a = 10.564(6), b = 12.925(6), c = 16.508(12) Å, β = 107.83(6)°, U = 2 145 Å^3, D_c = 1.84 g cm^{-3}, Z = 4, F(000) = 1 152 electrons, μ(Mo-K_α) = 57.4 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å. Unit-cell dimensions from 14 reflections, $20 < 2\theta < 30°$; isomorphous with [Mo(CO)$_3$(bipy)(dipyam)]. The structure determination (R = 0.095, 2 581 reflections) yielded a result identical with that for Mo compound but with significantly larger estimated standard deviations in the final calculated parameters, presumably arising from uncorrected absorption errors or crystal imperfections. Full details are included in SUP 56457.

Table 2. Fractional atomic co-ordinates with estimated standard deviations in parentheses for [Mo(CO)$_3$(bipy)(dipyam)]

Atom	X/a	Y/b	z/c
Mo	0.793 28(6)	0.254 67(5)	0.062 84(4)
N(1)	0.591 0(6)	0.210 2(5)	−0.038 1(4)
N(2)	0.521 7(7)	0.120 8(6)	0.060 4(5)
N(3)	0.501 8(11)	0.040 3(8)	0.187 2(6)
N(4)	0.747 4(7)	0.417 0(5)	0.014 7(4)
N(5)	0.875 1(6)	0.276 4(5)	−0.046 5(4)
O(1)	0.896 5(9)	0.035 2(6)	0.124 6(6)
O(2)	0.695 8(8)	0.273 1(6)	0.221 0(4)
O(3)	1.059 7(8)	0.322 1(8)	0.187 2(5)
C(1)	0.852 9(9)	0.114 5(7)	0.099 6(6)
C(2)	0.729 3(8)	0.264 1(7)	0.160 4(5)
C(3)	0.959 5(9)	0.296 8(7)	0.140 6(6)
C(4)	0.567 5(7)	0.245 4(7)	−0.118 6(4)
C(5)	0.446 3(9)	0.232 6(7)	−0.181 1(5)
C(6)	0.344 8(9)	0.183 1(8)	−0.162 6(6)
C(7)	0.365 5(8)	0.143 6(7)	−0.081 0(6)
C(8)	0.490 7(7)	0.159 8(6)	−0.020 5(5)
C(9)	0.440 0(9)	0.089 1(6)	0.107 3(6)
C(10)	0.310 5(8)	0.105 0(7)	0.077 9(6)
C(11)	0.233 5(12)	0.073 9(11)	0.123 3(8)
C(12)	0.282 8(14)	0.019 9(10)	0.200 0(8)
C(13)	0.417 0(13)	0.006 4(9)	0.231 8(8)
C(14)	0.671 0(10)	0.482 9(7)	0.046 4(6)
C(15)	0.658 9(12)	0.586 8(8)	0.021 7(8)
C(16)	0.709 2(11)	0.620 2(8)	−0.040 8(8)
C(17)	0.777 8(14)	0.552 4(7)	−0.077 7(7)
C(18)	0.797 0(9)	0.450 1(6)	−0.046 3(6)
C(19)	0.874 5(8)	0.374 1(6)	−0.078 5(5)
C(20)	0.940 4(10)	0.398 2(8)	−0.136 8(6)
C(21)	1.011 0(10)	0.320 2(9)	−0.163 1(6)
C(22)	1.008 3(9)	0.221 6(7)	−0.132 3(6)
C(23)	0.942 5(8)	0.202 1(7)	−0.074 6(5)

Results and Discussion

The complexes fall into three groups: (*i*) [M(CO)$_3$(bipy)(dipyam)] (M = Mo or W), (*ii*) [M(CO)$_3$(dipyam)L] (M = Cr, Mo, or W; L = monodentate heterocyclic amine), and (*iii*) [M$_2$(CO)$_6$(dipyam)$_3$] (M = Cr, Mo, or W). Vibrational frequency data [ν(NH) and ν(CO)] are listed in Table 4.

Table 3. Selected bond lengths (Å) and angles * with estimated standard deviations in parentheses for [Mo(CO)$_3$(bipy)(dipyam)]

Mo–N(1)	2.352(6)	N(3)–C(9)	1.43(1)
Mo–N(4)	2.243(6)	C(9)–C(10)	1.33(1)
Mo–N(5)	2.249(6)	C(10)–C(11)	1.33(2)
Mo–C(1)	1.952(9)	C(11)–C(12)	1.40(2)
Mo–C(2)	1.936(8)	C(12)–C(13)	1.37(2)
Mo–C(3)	1.917(9)	C(13)–N(3)	1.40(2)
C(1)–O(1)	1.148(12)		
C(2)–O(2)	1.165(11)	N(4)–C(14)	1.38(1)
C(3)–O(3)	1.154(12)	C(14)–C(15)	1.40(1)
		C(15)–C(16)	1.37(2)
N(1)–C(4)	1.35(1)	C(16)–C(17)	1.39(2)
C(4)–C(5)	1.39(1)	C(17)–C(18)	1.41(1)
C(5)–C(6)	1.37(1)	C(18)–N(4)	1.34(1)
C(6)–C(7)	1.40(1)		
C(7)–C(8)	1.41(1)	C(18)–C(19)	1.48(1)
C(8)–N(1)	1.35(1)		
		N(5)–C(19)	1.37(1)
N(2)–C(8)	1.37(1)	C(19)–C(20)	1.39(1)
N(2)–C(9)	1.39(1)	C(20)–C(21)	1.40(2)
		C(21)–C(22)	1.38(2)
		C(22)–C(23)	1.37(1)
		C(23)–N(5)	1.36(1)

N(1)–Mo–N(4)	85.7(2)	Mo–C(1)–O(1)	175.0(8)
N(1)–Mo–N(5)	87.4(2)	Mo–C(2)–O(2)	176.7(8)
N(1)–Mo–C(1)	97.6(3)	Mo–C(3)–O(3)	179.8(8)
N(1)–Mo–C(2)	97.4(3)		
N(1)–Mo–C(3)	176.7(3)	Mo–N(1)–C(4)	118.0(5)
N(4)–Mo–N(5)	72.2(2)	Mo–N(1)–C(8)	125.0(5)
N(4)–Mo–C(1)	172.7(3)	N(1)–C(8)–N(2)	114.6(7)
N(4)–Mo–C(2)	98.2(3)	C(7)–C(8)–N(2)	122.0(7)
N(4)–Mo–C(3)	91.6(3)	C(8)–N(2)–C(9)	130.3(7)
N(5)–Mo–C(1)	101.4(3)	N(2)–C(9)–C(10)	120.3(8)
N(5)–Mo–C(2)	169.0(3)	N(2)–C(9)–N(3)	117.1(8)
N(5)–Mo–C(3)	90.0(3)		
C(1)–Mo–C(2)	87.9(4)	Mo–N(4)–C(14)	121.9(6)
C(1)–Mo–C(3)	84.9(4)	Mo–N(4)–C(19)	118.2(5)
C(2)–Mo–C(3)	84.8(4)	Mo–N(5)–C(18)	118.0(5)
		Mo–N(5)–C(23)	124.0(5)

* Angles between normals to planes: N(1)–C(8)/N(3)–C(12) (dipyam), 24.8°; N(4)–C(18)/N(5)–C(23) (bipy), 4.2°; N(1)–C(8)/N(4)–C(18), 82.1°; N(1)–C(8)/N(5)–C(23), 82.6°; N(3)–C(12)/N(4)–C(18), 57.6°; and N(3)–C(12)/N(5)–C(23), 58.7°.

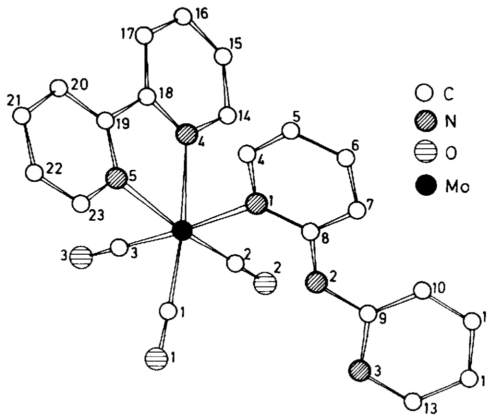


Figure 1. Molecular structure of [Mo(CO)$_3$(bipy)(dipyam)] showing the atom-labelling scheme

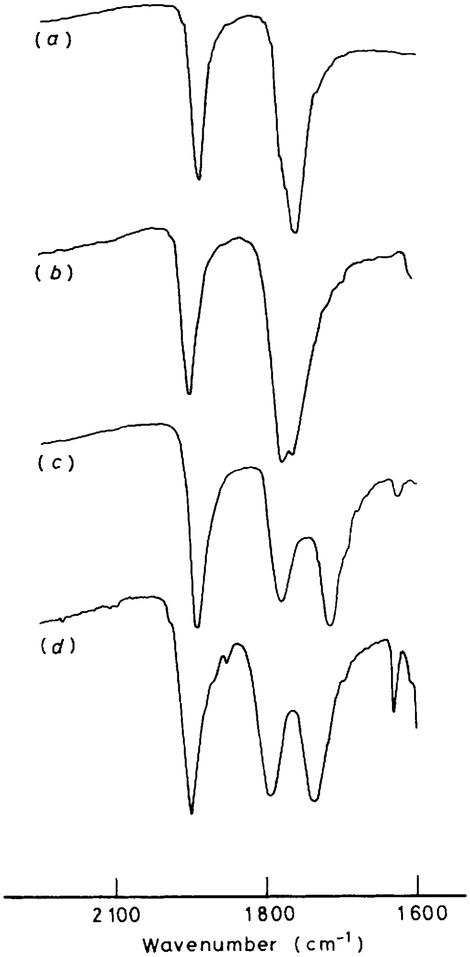


Figure 2. ν(CO) stretching vibrations in (*a*) [Mo(CO)$_3$(bipy)(py)], (*b*) [Mo(CO)$_3$(bipy)(dipyam)], (*c*) [Mo(CO)$_3$(dipyam)(py)], and (*d*) [Mo$_2$(CO)$_6$(dipyam)$_3$] (Nujol mulls)

(*i*) [Mo(CO)$_3$(bipy)(dipyam)] *and* [W(CO)$_3$(bipy)(dipyam)].—These two isostructural complexes contain bidentate 2,2′-bipyridyl and mondentate di-2-pyridylamine, the latter ligand being bound to the metal through one of the two pyridyl nitrogen atoms (Figure 1). The complexes are mononuclear, with *fac*-octahedral geometry at the metal atoms. The non-bonded molybdenum–nitrogen distances Mo ··· N(2) and Mo ··· N(3) are 3.25 and 4.49 Å, respectively, and the M–C–O and C–M–C angles reveal no abnormal perturbations of the Mo(CO)$_3$ grouping. Interchange of the atoms N(3) and C(10) leads to a small but significant increase in the value of *R*.

The secondary nitrogen atom N(2) makes no intermolecular N ··· N or N ··· O contacts closer than 4.0 Å. The possibility of intermolecular hydrogen bonding therefore does not arise in these compounds. The closest intramolecular N ··· O distance [N(2) ··· O(2)] is 3.37 Å, again too great for hydrogen bonding to be seriously considered. An intramolecular interaction between N(2) and the unco-ordinated pyridyl nitrogen atom N(3) is feasible in principle [the N(2) ··· N(3) distance is only 2.41 Å] but would require a severe distortion of the NH bond and should lead to a large shift in the NH stretching frequency. In fact, the NH stretching frequencies in [Mo(CO)$_3$(bipy)(dipyam)] and [W(CO)$_3$(bipy)(dipyam)] ($\sim$3 320 cm^{-1}) are to all intents and purposes identical with those in the [M(CO)$_3$(dipyam)L] complexes (Table 4) in which the pyridyl nitrogen atoms are all co-ordinated and intramolecular NH ···N interactions would not be possible. There is therefore no need to postulate any form of hydrogen bonding in the two [M(CO)$_3$-

Table 4. NH and CO stretching frequencies (cm^{-1})[a]

Complex	ν(NH)	ν(CO)		
		A_1[b]	E[b]	
[Cr(CO)$_3$(bipy)(py)][c]		1 897s	1 781s	
[Mo(CO)$_3$(bipy)(py)][d]		1 908s	1 777s	
[W(CO)$_3$(bipy)(py)][c]		1 892s	1 773s	
[Cr(CO)$_3$(phen)(py)][c]		1 898s	1 780s	
[Mo(CO)$_3$(phen)(py)][d]		1 902s	1 782s	
[W(CO)$_3$(phen)(py)][c]		1 894s	1 780s	
[Mo(CO)$_3$(bipy)(dipyam)]	3 310w	1 899ms	1 777s, 1 761s(sh)	
[W(CO)$_3$(bipy)(dipyam)]	3 320w	1 890s	1 773s, 1 758ms(sh)	
		$A_1(2)$[e]	B_1[e]	$A_1(1)$[e]
[Mo(CO)$_3$(dipyam)(py)]	3 319mw	1 891s	1 780s	1 715s
[Mo(CO)$_3$(dipyam)(2,6Me$_2$-py)]	~3 320w,br	1 897s	1 782ms	1 730s,br
[Cr(CO)$_3$(dipyam)(4Me-py)]	3 324w	1 893s	1 780s	1 720s
[Mo(CO)$_3$(dipyam)(4Me-py)]	3 320w	1 894ms	1 782s	1 719s
[W(CO)$_3$(dipyam)(4Me-py)]	~3 320w	1 883s	1 761s	1729s,br
[Cr(CO)$_3$(dipyam)(quin)]	3 325w	1 885ms	1 770ms	1 725ms
[Mo(CO)$_3$(dipyam)(quin)]	3 321w	1 892ms	1 780w	1 725ms
[W(CO)$_3$(dipyam)(quin)]	~3 320w,br	1 878ms	1 771s	1 720vs,br
[Cr(CO)$_3$(dipyam)(4Me-quin)]	3 321w	1 893s	1 780s	1 719s
[Mo(CO)$_3$(dipyam)(4Me-quin)]	~3 320w,br	1 898s	1 787s	1 725s
[W(CO)$_3$(dipyam)(4Me-quin)]	~3 320w	1 888s	1 782s	1 715s,br
[Cr$_2$(CO)$_6$(dipyam)$_3$]	~3 325w	1 894s (1 852w)	1 783s	1 730s
[Mo$_2$(CO)$_6$(dipyam)$_3$]	3 339mw	1 898s (1 850w)	1 790s	1 735s
[W$_2$(CO)$_6$(dipyam)$_3$]	3 319w	1 890s (1 843w)	1 779s	1 725s

[a] Nujol mulls. [b] *fac* Complexes, C_{3v} M(CO)$_3$ symmetry. [c] Ref. 2. [d] Ref. 9. [e] Provisional assignments for *mer*-octahedral geometry, with local C_{2v} M(CO)$_3$ symmetry; see ref. 12.

(bipy)(dipyam)] complexes. This observation is directly relevant to the earlier work[1] as the NH stretching frequencies in these two complexes are lower than those in [Mo(CO)$_4$(dipyam)] (3 351 cm^{-1}) or [W(CO)$_4$(dipyam)] (3 337 cm^{-1}), and 100 cm^{-1} lower than the free-ligand frequency of 3 425 cm^{-1}.[6] Thus, the shifts of 74 and 88 cm^{-1} from the free-ligand frequency, observed in the two crystalline tetracarbonyl complexes[1] cannot be adduced as evidence for the presence of intermolecular hydrogen bonds in these compounds.

The two [M(CO)$_3$(bipy)(dipyam)] complexes appear to be the first fully authenticated examples of compounds containing monoco-ordinated di-2-pyridylamine ligands. The difficulty of substituting a fourth carbonyl ligand to form the bis-chelate complexes [M(CO)$_2$(bipy)(dipyam)] is illustrated by the separation of the [M(CO)$_3$(bipy)(dipyam)] complexes as the only identifiable products from the preparative reactions after periods of up to 24 h in boiling toluene. However it is worth noting that our yields are invariably low, suggesting that more highly-substituted species may also be formed in the reaction mixtures. The bis-bipy dicarbonyl complexes [M(CO)$_2$(bipy)$_2$] are air- and light-sensitive:[7] similar [M(CO)$_2$(bipy)(dipyam)] complexes would be unlikely to survive under the conditions of our preparative reactions, which were designed primarily to yield pure crystalline samples of the air- and light-stable tricarbonyl compounds.

In an early reaction[8] between [W(CO)$_4$(bipy)] and di-2-pyridylamine we obtained a small amount of an amorphous material corresponding analytically to [W$_2$(CO)$_6$(bipy)$_2$(dipyam)], which presumably would be binuclear with bridging di-2-pyridylamine. Attempts to repeat this reaction, using [W(CO)$_4$(bipy)] : dipyam ratios as high as 5 : 1, have consistently yielded [W(CO)$_3$(bipy)(dipyam)] as the only product. Equimolar mixtures of [W(CO)$_3$(bipy)(dipyam)] and [W(CO)$_4$(bipy)] (or the analogous molybdenum compounds) showed no evidence of reaction, other than slight decomposition, after 15—20 h in boiling toluene. The original result therefore appears to be fortuitous and there is no convincing evidence for the formation of binuclear complexes.

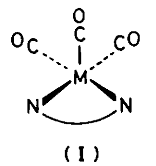
(*ii*) [M(CO)$_3$(dipyam)L] *Complexes*.—The trisubstitued mixed-ligand complexes [M(CO)$_3$(dipyam)L] (L = monodentate heterocyclic amine) superficially resemble their well known 2,2′-bipyridyl and 1,10-phenanthroline (phen) analogues[2,9,10] [M(CO)$_3$(bipy)L] and [M(CO)$_3$(phen)L], but have strikingly different i.r. spectra in the carbonyl stretching region, with three strong, well separated ν(CO) absorptions instead of the two bands characteristically observed in the latter complexes (Table 4, Figure 2). The [M(CO)$_3$(bipy)(py)] and [M(CO)$_3$(phen)(py)] complexes are typical examples[2,9–12] of *fac*-octahedral [M(CO)$_3$(L–L)L′] molecules in which the donor atoms in the bidentate ligand L–L and the monodentate ligand L′ are chemically very similar in character. The metal atom has effective local C_{3v} symmetry and two ν(CO) bands (A_1 + E) appear in the i.r. spectrum. Even when the monodentate amine ligand L′ is unusually bulky and highly asymmetric, as in the [M(CO)$_3$(bipy)(dipyam)] complexes, the degeneracy of the E species mode is only partially lifted and the spectrum still has recognisable 'C_{3v}' character (Figure 2). As a general rule, complete resolution into three well defined ν(CO) modes occurs in *fac*-octahedral complexes only when there is a clearly non-equivalent donor-atom set (*e.g.* N$_2$P) reducing the local symmetry to C_s, or less.

It is clearly not possible to attribute the differences between the spectra of the [M(CO)$_3$(bipy)L] and [M(CO)$_3$(dipyam)L] complexes simply to inequivalences in the N$_3$ donor-atom set in the latter molecules. There is ample evidence to confirm that the donor behaviour of the pyridyl nitrogen atoms in di-2-pyridylamine differs only marginally, at the most, from those in 2,2′-bipyridyl or 1,10-phenanthroline. The most significant observation in the present context is that the CO stretching vibrations of [M(CO)$_4$(dipyam)] in solution are found at frequencies virtually identical with those in [M(CO)$_4$(bipy)] or

$[M(CO)_4(phen)]$.[8] Thus, if we consider only the local environment of the metal atom, we would expect *fac*-$[M(CO)_3(dipyam)L]$ to display only two ν(CO) absorptions ($A_1 + E$) at frequencies very close to those in the analogous *fac*-$[M(CO)_3(bipy)L]$ or *fac*-$[M(CO)_3(phen)L]$ complexes. When the internal geometry of the ligand is taken into account, the most obvious difference between the di-2-pyridylamine and the 2,2′-bipyridyl or 1,10-phenanthroline complexes arises in the orientation of the pyridyl rings, which will lie at an angle to the $M(CO)_2N_2$ plane (defined by the two co-ordinated nitrogen atoms and the carbonyl groups *trans* to them) in *fac*-$[M(CO)_3(dipyam)L]$, but will lie in the plane in *fac*-$[M(CO)_3(bipy)L]$ or *fac*-$[M(CO)_3(phen)L]$. However, the idealised molecular symmetry is the same (C_s) in all three cases, so that here again no dramatic differences in the spectra seem likely.

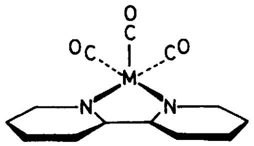
An alternative and in some ways more satisfactory interpretation of the vibrational data is obtained if we assume that the di-2-pyridylamine complexes have the relatively uncommon *mer*-octahedral geometry, with local C_{2v} symmetry giving rise to three i.r.-active CO stretching modes ($2A_1 + B_1$). The tentative frequency assignments listed in Table 4 are based on those proposed by Cotton[12] for *mer*-$[M(CO)_3L_3]$ complexes. The main problem which arises in this treatment of the $[M(CO)_3(dipyam)L]$ spectra concerns the intensities of the '$A_1(2)$' modes, which derive from the symmetric stretch of the *trans* pair of CO ligands, and should normally be rather weak. In our experimental spectra, obtained using solid samples at room temperature, all three ν(CO) peaks are strong, with the (approximate) integrated intensities of the $A_1(2)$ absorptions usually *ca.* 65—90% of those due to the B_1 or $A_1(1)$ modes. Because of the very poor solubilities of the complexes, even in the pure amine ligands, we have been unable to obtain more reliable intensity data from solution spectra. If the proposed *mer* structures are correct, the '$A_1(2)$' intensities must be enhanced by resonances with the other ν(CO) modes. In the C_1 molecular point group, rather than the C_{2v} idealised local group, there are no symmetry-imposed restrictions on interactions between the three CO stretching vibrations, and the unusually low $A_1(1)$ frequencies, down to 1 715 cm^{-1} in some cases, would also be consistent with the occurrence of fairly strong resonance effects.

The commonly accepted mechanism[13—17] for substitution reactions in $[M(CO)_4(L–L)]$ complexes, where the bidentate ligand L–L is a poorer acceptor than CO, involves the dissociation of a *cis*-CO ligand, in a rate-determining step, to yield a square-pyramidal intermediate (**I**).* According to the principle of 'quasi-microscopic reversibility' as enunciated by Dobson[15,16] for reactions under kinetic control (*i.e.* where there are no steric interferences), the stereochemistry of the reaction product $[M(CO)_3(L–L)L']$ obtained from the addition of a monodentate ligand L′ to the intermediate $[M(CO)_3(L–L)]$ will 'mirror the site of the initial M–CO bond breaking,' even when the intermediate is itself fluxional. The kinetic product is therefore exclusively the *fac* isomer. However, in cases where formation of the *fac* isomer would lead to congestion along an edge or face of the co-ordination octahedron, the reaction comes under thermodynamic control and the more stable (*i.e.* less hindered) *mer* isomer may be obtained.

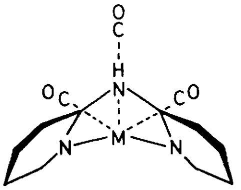


(I)

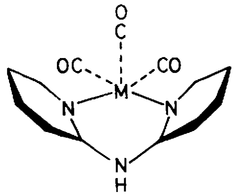
The intermediates $[M(CO)_3(bipy)]$ and $[M(CO)_3(dipyam)]$, formed by dissociation of *cis*-CO ligands from $[M(CO)_4(bipy)]$ and $[M(CO)_4(dipyam)]$, respectively, are illustrated by (**II**), (**IIIa**), and (**IIIb**). In (**II**), the rigidly co-ordinated 2,2′-bipyridyl is held coplanar, or very nearly so, with the basal plane of the intermediate and offers no significant obstacle to a ligand approaching the vacant co-ordination site. The $[M(CO)_3(bipy)L]$ complexes are therefore characteristically *fac*-octahedral with all except the most heavily hindered ligands. The $[M(CO)_3(dipyam)]$ intermediates (**IIIa**) or (**IIIb**), however, have structures in which the pyridyl rings, or the central NH group, project below the basal plane and, particularly in the case of (**IIIb**), appreciably shield the vacant co-ordination site. In this case it is feasible that a developing steric interaction between an approaching ligand and the co-ordinated di-2-pyridylamine could lead to a concerted rearrangement to yield the thermodynamically more stable *mer* isomer as the reaction product. It is worth noting here that the di-2-pyridylamine ligand, being less highly conjugated than 2,2′-bipyridyl, is less rigid, and is free to undergo internal rotations about the bonds to the central nitrogen atom and also, to some extent, to vary the central C–N–C angle. Structure determinations for numerous di-2-pyridylamine complexes show that the dihedral angle between the pyridyl rings can vary from *ca.* 0 to 45°, enabling the ligand to adjust itself to a variety of co-ordination geometries and chelate bite angles.[18—21] This internal flexibility means that any energy barrier to the *fac–mer* rearrangement in the carbonyl complexes or intermediates should be small and easily surmounted.



(II)



(IIIa)



(IIIb)

Complete structure determinations for representative examples of these complexes are obviously needed, but our efforts to obtain suitable specimens for *X*-ray analysis have so far been singularly unrewarded.

(*iii*) $[M_2(CO)_6(dipyam)_3]$ *Complexes*.—The binuclear structures of these complexes are indicated by the elemental analyses and confirmed by the identification of appropriate molecular-ion peaks in the mass spectra. The i.r. spectra clearly resemble those of the $[M(CO)_3(dipyam)L]$ complexes. Given the preparative method used, the most probable structure would involve two chelate and one bridging di-2-pyridylamine ligands, as illustrated in (**IV**), below, rather than a structure with

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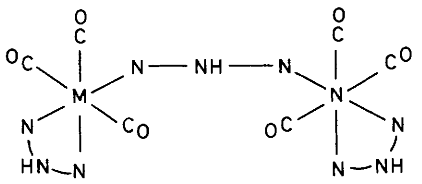
* A concurrent mechanism following a bimolecular dissociative–interchange pathway is also possible and may occur in some cases.[16,17] Without detailed kinetic information it would be pointless to speculate on the involvement of such mechanisms in the reactions under consideration here. Stereochemically the result would be the same in either case.

three bridging di-2-pyridylamines. The reactions leading to these binuclear complexes must involve the initial formation of mononuclear $[M(CO)_3(dipyam)_2]$, analogous to $[M(CO)_3(bipy)(dipyam)]$, with one bidentate and one monodentate di-2-pyridylamine, but the onward reactions to the binuclear products appear to occur very rapidly and we have not yet been able to isolate the intermediate compounds. There is no evidence of intramolecular substitution to yield $[M(CO)_2(dipyam)_2]$.



(IV)

The contrast between $[M(CO)_4(dipyam)]$ and $[M(CO)_4(bipy)]$ is again very marked. In the latter case, as we have previously discussed, the addition of di-2-pyridylamine yields stable mononuclear *fac*-$[M(CO)_3(bipy)(dipyam)]$ with little or no evidence of further reactions to form binuclear species; if the second pyridyl nitrogen atom of the di-2-pyridylamine ligand reacts at all, it does so intramolecularly to yield the rather reactive or unstable $[M(CO)_2(bipy)(dipyam)]$. It is very tempting to ascribe these differences between the $[M(CO)_4(dipyam)]$ and $[M(CO)_4(bipy)]$ systems entirely to differences in the stereochemistry of the carbonyl substitution reactions. It is certainly true that *mer*, *mer* geometries for the metal atoms in $[M_2(CO)_6(dipyam)_3]$ would greatly facilitate the formation of the binuclear complexes, but it is also possible to construct a model of a hypothetical *fac*,*fac*-$[M_2(CO)_6(bipy)_2(dipyam)]$ complex in which there appear to be no intolerably close intramolecular contacts. More detailed structural information on complexes containing bridging di-2-pyridylamine ligands, particularly with regard to the relative orientations of the two pyridyl rings, would be highly desirable.

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