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Structures of Tetracarbonyl(di-2-pyridylamine)chromium(0), -molybdenum(0) and -tungsten(0)

Crystallographic and Spectroscopic Evidence for an Intermolecular NH----OC Hydrogen Bond

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The complexes [M(CO)$_4$·dipyam] [M = Cr, Mo, W; dipyam: di-2-pyridylamine, (C$_5$H$_4$N)$_2$NH] are triclinic, space group P$\bar{1}$, Z = 2. The molybdenum and tungsten complexes are isostructural. Cell dimensions (Cr, Mo, W) are a *= 8.436(2), 6.919(1), 6.951(1);* b *= 8.893(2), 13,385(2), 13.352(2);* c *= 10.382(2), 8.504(1), 8.455(1) Å; α = 88.8(1), 81.0(1), 81.0(1); β = 82.1(1), 68.3(1), 68.3(1); γ = 65.4(1), 86.1(1), 85.9(1)°. A single crystal structure determination for [Mo(CO)$_4$·dipyam] (1266 reflections, R = 0.062) shows the complex to be octahedral and mononuclear, but with an intermolecular contact between the uncoordinated NH group and a carbonyl oxygen atom in an adjoining molecule which is close enough (H---O calc., 2.23 Å) to satisfy the usual criterion for a weak hydrogen bond. The NH and B$_2$-carbonyl stretching frequencies in the crystal are 55 cm^{-1} and about 40 cm^{-1}, respectively, lower than in solution, consistent with the proposed hydrogen-bonded structure. The tungsten complex is similar with perhaps a marginally stronger hydrogen bond, but the infrared and structural data for [Cr(CO)$_4$·dipyam] indicate that in this case hydrogen-bonding is minimal or non-existent.*

Introduction

In preliminary studies [1] of reactions between di-2-pyridylamine [dipyam, (C$_5$H$_4$N)$_2$NH] and Group VI metal hexacarbonyls we observed that the crystal and solution i.r. spectra of the complex [Mo(CO)$_4$·dipyam] are sufficiently different to suggest a significant perturbation of the molecule, or a possible intermolecular interaction, in the crystalline phase. Specifically, the lowest-frequency CO stretching mode shifts by 41 cm^{-1}, from 1822 cm^{-1} in CH$_2$Cl$_2$ solution [2] to 1781 cm^{-1} in the crystal, whereas in the corresponding 2,2′-bipyridyl complex the crystal and solution CO stretching frequencies are virtually coincident. Similar effects occur in the spectrum of the tungsten complex [W(CO)$_4$·dipyam] but in the chromium complex [Cr(CO)$_4$·dipyam] the differences between the crystal and solution spectra are much smaller. Any intermolecular association in the crystal is likely to involve the initially uncoordinated secondary nitrogen atom of the di-2-pyridylamine ligand, but none of the more obvious model structures is immediately convincing [1]. We have now carried out crystal-structure analyses for the three [M(CO)$_4$·dipyam] complexes, and have correlated these results with further studies of their vibrational spectra in the crystal and solution phases.

Experimental

Preparative

The complexes were obtained from the reactions of equimolar quantities of di-2-pyridylamine and the appropriate metal carbonyl in refluxing toluene under nitrogen (Mo 1½ hours [2]; Cr, W, 3 hours). The molybdenum and tungsten complexes separated from the cold reaction mixtures as small, bright yellow parallelpipeds in better than 90% yield; the chromium complex as brown plates in 30–40% yield. The crystalline complexes are indefinitely air-stable. Solubility in non-coordinating organic solvents is poor and decreases markedly in the order Cr > Mo > W. The solutions tend to discolour if exposed to the atmosphere for prolonged periods.

Analytical data: Found (Calc.): {Cr(CO)$_4$·[(C$_5$H$_4$N)$_2$NH]}: Cr, 50.4 (50.2); H, 2.5 (2.7); N, 12.3 (12.5)%. {Mo(CO)$_4$·[(C$_5$H$_4$N)$_2$NH]} : C, 44.7 (44.4); H, 2.5 (2.4); N, 11.0 (11.1)%. {W(CO)$_4$·[(C$_5$H$_4$N)$_2$NH]}: C, 36.4 (36.0); H, 2.0 (1.9); N, 8.8 (9.0)%.

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TABLE I. Crystal Data.*

Space Group	$[Cr(CO)_4 \cdot dipyam]$ Triclinic $P\bar{1}$	$[Mo(CO)_4 \cdot dipyam]$ Triclinic $P\bar{1}$	$[W(CO)_4 \cdot dipyam]$ Triclinic $P\bar{1}$
a (Å)	8.436(2)	6.919(1)	6.951(1)
b	8.893(2)	13.385(2)	13.352(2)
c	10.382(2)	8.504(1)	8.455(1)
α (°)	88.8(1)	81.0(1)	81.0(1)
β	82.1(1)	68.3(1)	68.3(1)
γ	65.4(1)	86.1(1)	85.9(1)
V (Å^3)	701.3(6)	721.1(5)	718.3(5)
M	335.2	379.2	467.1
d (g cm^{-3})	1.59	1.75	2.16
Approx. single-crystal dimensions (mm)	0.3 × 0.3 × 0.03	0.3 × 0.15 × 0.15	0.3 × 0.2 × 0.15
2θ max (°)	30	40	50
Independent observed reflections	520	1266	2501
R final	0.080	0.062	0.070

*Mo/Kα radiation, λ = 0.7107 Å.

Physical Measurements

I.r. spectra were obtained using a Perkin-Elmer 457 spectrophotometer.

Structure Determinations

The crystals of the three complexes were well-formed but were generally rather small: the experimental products contained only a few specimens of a suitable minimal size for single-crystal intensity measurement. The chromium complex crystallised as very thin plates (<0.03 mm) and yielded reliably measurable intensities, with the chosen crystal, only at values of 2θ lower than 30°.

The intensity data were collected using a Nicolet P3 automatic four-circle diffractometer with graphite-monochromated Mo/Kα radiation (λ = 0.7107 Å). Lattice constants were determined from the diffractometer setting angles for 10–15 accurately-centred high-angle reflections ($20° < 2\theta < 30°$). Full details of the unit-cell dimensions and related parameters are given in Table I. All three complexes are triclinic, space group $P\bar{1}$, $Z = 2$. The molybdenum and tungsten complexes are clearly isostructural (all unit cell dimensions identical to within 1%) but have no obvious crystallographic relationship with the chromium complex.

Intensities were measured using the θ–2θ scan technique: appropriate reference reflections monitored at intervals showed no significant changes in intensity as a function of time. Lorentz- and polarisation-corrected intensities for which $I > 3\sigma(I)$ were classified as 'observed'.

$[Mo(CO)_4 \cdot dipyam]$

The structure of the molybdenum complex was solved [3] by conventional Patterson and Fourier synthesis followed by block-diagonal least-squares refinement to a final value of R = 0.062 (1266 reflections, Mo atom anisotropic). At this point, the shifts in all parameters were <0.25 e.s.d. A difference Fourier synthesis revealed no significant areas of electron density and yielded no direct evidence of the hydrogen atom positions. All reflections were given unit weight throughout the calculations, and none were rejected in the course of the refinement.

$[W(CO)_4 \cdot dipyam]$

An initial structure-factor calculation using the positional parameters obtained for the molybdenum complex yielded an R-value of 0.132 (2501 reflections). Refinement from this point with all atoms anisotropic converged at R = 0.070. The e.s.d.'s in the final positional parameters are appreciably higher than those for the corresponding atoms in the molybdenum complex (Table II), presumably as a result of the greater absorption effects associated with the tungsten atom. The data for the two complexes are identical within the usual uncertainty limit of 3 × e.s.d.

$[Cr(CO)_4 \cdot dipyam]$

The structure of the chromium complex was solved by Patterson and Fourier techniques, using the 520 available observed reflections, and refined with all atoms isotropic to a final value of R = 0.080. Given the limited data set, there are inevitably

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) (e.s.d. in last significant figure(s).

	[Cr(CO)$_4$·dipyam]			[Mo(CO)$_4$·dipyam]			[W(CO)$_4$·dipyam]		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
M	2218(4)	1017(3)	2394(3)	1527(2)	2501(1)	3060(1)	1535(1)	2508(1)	3060(1)
C(1)	4021(21)	−736(20)	1567(16)	−763(19)	3223(9)	4443(16)	−813(29)	3237(15)	4485(22)
C(2)	1030(24)	−257(22)	2513(17)	2177(21)	1992(10)	5070(17)	2228(34)	2001(16)	5103(26)
C(3)	1410(21)	1686(20)	844(16)	3228(18)	3697(9)	2806(15)	3237(25)	3669(15)	2783(19)
C(4)	2937(22)	175(21)	3933(17)	−390(20)	1345(10)	3661(16)	−330(30)	1369(15)	3628(22)
C(5)	−1033(19)	3008(19)	4316(15)	4936(19)	804(9)	1885(15)	4908(31)	793(15)	1905(26)
C(6)	−2576(20)	4341(19)	4873(15)	6729(20)	320(9)	1000(16)	6718(32)	320(17)	972(27)
C(7)	−2861(21)	5937(20)	4462(16)	7853(21)	755(10)	−679(17)	7840(33)	746(17)	−682(28)
C(8)	−1683(21)	6187(20)	3533(16)	7126(19)	1635(9)	−1376(16)	7143(31)	1635(17)	−1398(25)
C(9)	−156(19)	4793(19)	3023(15)	5268(17)	2068(8)	−389(14)	5269(26)	2068(14)	−376(22)
C(10)	5507(20)	1695(20)	2180(15)	−902(20)	3416(9)	689(15)	−920(28)	3415(17)	666(26)
C(11)	6568(21)	2556(20)	1860(16)	−1329(20)	4016(10)	−652(16)	−1273(31)	3999(17)	−705(27)
C(12)	5773(20)	4244(19)	1584(15)	344(19)	4246(9)	−2184(16)	359(31)	4245(16)	−2230(25)
C(13)	3982(19)	5047(18)	1663(15)	2309(18)	3900(9)	−2356(15)	2359(30)	3899(15)	−2397(24)
C(14)	2879(20)	4222(19)	2017(15)	2606(17)	3296(8)	−930(14)	2602(26)	3298(14)	−939(22)
O(1)	5204(14)	−1878(14)	984(11)	−2237(14)	3646(7)	5326(11)	−2262(23)	3669(12)	5335(18)
O(2)	300(15)	−1158(14)	2631(11)	2642(16)	1707(7)	6262(12)	2663(31)	1707(14)	6292(21)
O(3)	893(15)	1959(15)	−183(11)	4132(15)	4395(7)	2826(12)	4178(25)	4394(13)	2747(21)
O(4)	3318(15)	−455(15)	4920(11)	−1630(17)	709(8)	4220(13)	−1546(30)	701(15)	4151(24)
N(1)	144(15)	3207(14)	3345(11)	4199(14)	1681(7)	1245(11)	4195(22)	1695(11)	1240(19)
N(2)	3671(15)	2535(14)	2233(11)	1029(14)	3087(7)	578(12)	1057(21)	3090(12)	567(17)
N(3)	1074(15)	5014(14)	2091(11)	4602(14)	2962(7)	−1128(11)	4649(23)	2987(13)	−1152(19)

TABLE III. [Mo(CO)$_4$·dipyam]. Bond Lengths and Selected Bond Angles (e.s.d. in last significant figure).

Bond Lengths (Å)		Bond Angles (°)	
Mo–C(1)	1.896(12)	C(1)MoC(2)	88.9(6)
Mo–C(2)	1.936(14)	C(1)MoC(3)	86.5(5)
Mo–C(3)	1.988(12)	C(1)MoC(4)	86.9(6)
Mo–C(4)	1.987(14)	C(1)MoN(1)	175.9(5)
Mo–N(1)	2.269(9)	C(1)MoN(2)	95.0(5)
Mo–N(2)	2.274(9)	C(2)MoC(3)	86.7(6)
		C(2)MoC(4)	86.2(6)
C(1)–O(1)	1.19(2)	C(2)MoN(1)	95.2(5)
C(2)–O(2)	1.18(2)	C(2)MoN(2)	175.6(5)
C(3)–O(3)	1.17(2)	C(3)MoC(4)	171.2(5)
C(4)–O(4)	1.17(2)	C(3)MoN(1)	93.9(4)
		C(3)MoN(2)	91.5(4)
N(1)–C(5)	1.36(2)	C(4)MoN(1)	93.1(5)
C(5)–C(6)	1.37(2)	C(4)MoN(2)	94.1(5)
C(6)–C(7)	1.40(2)	N(1)MoN(2)	80.9(3)
C(7)–C(8)	1.38(2)		
C(8)–C(9)	1.39(2)	Mo C(1)O(1)	177.8(1.1)
C(9)–N(1)	1.35(1)	Mo C(2)O(2)	177.3(1.2)
		Mo C(3)O(3)	173.5(1.0)
N(2)–C(10)	1.35(2)	Mo C(4)O(4)	171.1(1.2)
C(10)–C(11)	1.40(2)		
C(11)–C(12)	1.39(2)	Mo N(1)C(5)	118.5(8)
C(12)–C(13)	1.37(2)	Mo N(1)C(9)	123.7(8)
C(13)–C(14)	1.42(2)	Mo N(2)C(10)	117.5(8)
C(14)–N(2)	1.34(1)	Mo N(2)C(14)	123.0(8)
N(3)–C(9)	1.39(1)	N(1)C(9)N(3)	120.5(1.0)
N(3)–C(14)	1.38(2)	N(2)C(14)N(3)	120.8(1.1)
		C(9)N(3)C(14)	129.3(1.0)

appreciable residual errors in some of the lighter atom parameters, but the results are adequate to define the gross molecular structure and to illustrate the molecular packing in the crystal.

Details of the calculated fractional coordinates for the three complexes are given in Table II; Supplementary Tables listing the observed and calculated structure factors and thermal vibrational parameters are available on request*.

Discussion

Full details of the bond lengths and angles in [Mo(CO)$_4$·dipyam] are listed in Table III and some selected bond lengths and angles for [Cr(CO)$_4$·

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*Supplementary Tables available on request from the Editor or from the authors.

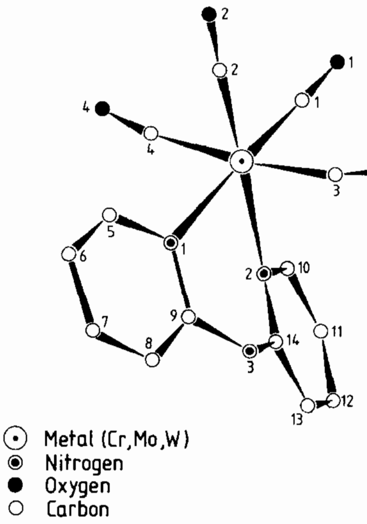

Fig. 1. Molecular structure and atomic numbering system. Diagram illustrates [Mo(CO)$_4$·dipyam].

dipyam] and [W(CO)$_4$·dipyam] are given in Table IV. A complete listing of bond length and angle data for the latter two complexes is included in the Supplementary Tables*. The atomic numbering system is indicated in Fig. 1.

All three complexes have 'normal' mononuclear octahedral structures, with chelate rather than bridging di-2-pyridylamine ligands. The differences between the chromium complex and the molybdenum or tungsten complexes are associated with the packing of the molecules in the crystal rather than with the internal molecular structure.

The salient features of the structure are illustrated in the molybdenum complex. The central secondary nitrogen atom N(3) does not interact with the metal atom [Mo–N(3) = 3.39 Å] and retains the planar conformation [$C(9)\hat{N}(3)C(14)$ = 129.3°] found in the free ligand [$C\hat{N}C$ = 131.1°] [4] and other di-2-pyridylamine complexes [5]. The perpendiculars to the planes containing the pyridyl rings intersect at an angle of 27°. The *trans* carbonyl groups C(3)O(3) and C(4)O(4) are quite noticeably bent away from the ligand pyridyl rings, with $O\hat{C}M$ and $C\hat{M}C$ angles between 171.1 and 173.5°. Similar crowding effects of di-2-pyridylamine ligands have been noted elsewhere [6].

Intermolecular Contacts

The shortest intermolecular distance, not involving hydrogen atoms, in [Mo(CO)$_4$·dipyam] is 3.04(1) Å between the secondary nitrogen atom N(3) and a carbonyl oxygen O(1)′ in an adjoining molecule**. This distance is approximately equal to the van der Waals radius sum for oxygen and nitrogen and is short enough, if the NH bond is appropriately oriented, to be compatible with significant NH---O hydrogen bonding [7–9] (Fig. 2).

The hydrogen atoms were not directly located in the structure determination: given the usual uncer-

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*Supplementary Tables available on request from the Editor or from the Authors.

**Parameters for O(1)′ are (1 + x, y, z – 1).

TABLE IV. Selected Bond Lengths and Angles for [Cr(CO)$_4$·dipyam] and [W(CO)$_4$·dipyam] (e.s.d. in last significant figure).

	[Cr(CO)$_4$·dipyam]	[W(CO)$_4$·dipyam]
Bond Lengths (Å)		
M–C(1)	1.79(2)	1.94(2)
M–C(2)	1.79(2)	1.97(2)
M–C(3)	1.83(2)	1.95(2)
M–C(4)	1.82(2)	1.95(2)
M–N(1)	2.15(1)	2.26(1)
M–N(2)	2.16(1)	2.26(2)
C(1)–O(1)	1.19(2)	1.17(2)
C(2)–O(2)	1.19(2)	1.16(3)
C(3)–O(3)	1.19(2)	1.20(3)
C(4)–O(4)	1.18(2)	1.19(3)
Bond Angles (°)		
C(3)MC(4)	173.8(8)	173.1(8)
MC(3)O(3)	173.1(1.5)	174.6(1.6)
MC(4)O(4)	173.9(1.6)	172.9(1.8)
C(9)N(3)C(14)	126.4(1.3)	126.2(1.6)

TABLE V. N(3)H···O(1)′ Distances (Å) and N(3)HO(1)′ angles (°) in [Mo(CO)$_4$·dipyam] as a Function of N(3)H Bond Length for Different Orientations of the N(3)H Bond (e.s.d.s are 0.02 Å, 1.0°).

NH bond length, Å	*0.90*	*1.00*	*1.10*
i) Planar, symmetrical C_2NH	2.30(139)	<u>2.23(137)</u>	2.16(135)
ii) NH bent from i) by 5° towards O(1)′	2.26(145)	2.18(144)	2.10(142)
iii) NH bent from i) by 10° towards O(1)′	2.22(152)	2.13(151)	2.04(149)
iv) NH bent from i) by 5° away from O(1)′	2.36(132)	2.29(130)	2.23(129)
v) NH bent from i) by 10° away from O(1)′	2.42(126)	2.36(124)	2.31(122)

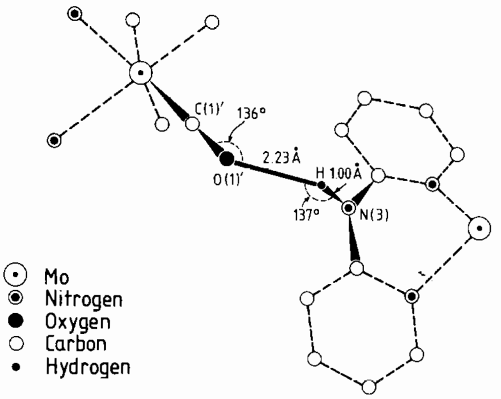

Fig. 2. Intermolecular hydrogen bond in crystalline [Mo(CO)$_4$·dipyam].

tainties in the hydrogen-atom parameters in heavy-metal complexes, it is unlikely that the existence of a weak hydrogen bond could be conclusively established, or disproved, using the X-ray data alone. However, if we assume a physically reasonable NH bond length of 1.00 Å, with planar symmetrical C_2NH geometry [*i.e.* with the NH bond direction bisecting the C(9)$\hat{N}$(3)C(14) angle] we obtain a calculated N(3)H----O(1)′ distance of 2.23 Å, with an N(3)-$\hat{H}$O(1)′ angle of 137°. The usual criterion [7, 8] for NH----O hydrogen bonding requires an O----H distance of less than about 2.4–2.6 Å, with a moderately obtuse NHO angle. The calculated parameters are thus appreciably within the limits for a weak hydrogen bond. The data in Table V illustrate the effects of variations in the model structure on the NH----O interaction. To increase the H----O(1)′ distance to 2.4 Å, or more, it is necessary to reduce the NH bond length to 0.9 Å and to displace the bond by at least 10° out of the planar symmetrical conformation, directly away from the O(1)′ atom. If the NH bond length is maintained at 1.00 Å, a correspondingly greater displacement of the bond is necessary. There is no evidence, in the structural or spectroscopic data (see below) to suggest that any such displacement occurs. Conversely, any hydrogen-bonding interaction will tend marginally to lengthen the NH bond and cause it to bend towards O(1)′, so that the actual N(3)H----O(1)′ distance is likely to be somewhat less than the calculated value of 2.23 Å. Thus, while the crystallographic data, taken on their own, do not ncessarily prove the existence of an intermolecular NH----O hydrogen bond in [Mo(CO)$_4$·dipyam], they are clearly fully consistent with such a structure, if supporting evidence can be provided from other sources.

The closest intermolecular contacts involving the N(3) atom in [Cr(CO)$_4$·dipyam] are N(3)----O(2)″, 3.24 Å and N(3)----O(3)″″, 3.30 Å, yielding H----O(2)″ and H----O(3)″″ distances, calculated on the same basis as before, of 2.50 Å and 2.92 Å, respectively*. Even with relatively large residual errors in the atomic coordinates, there is obviously no need to postulate any appreciable hydrogen bonding in the crystalline chromium complex. The greater solubility of [Cr(CO)$_4$·dipyam] relative to [Mo(CO)$_4$·dipyam] or [W(CO)$_4$·dipyam] is consistent with the development of intermolecular hydrogen bonds in the latter two complexes.

NH Stretching Vibrations

The NH stretching frequency in free, non-hydrogen-bonded di-2-pyridylamine is 3425 cm^{-1}

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*Parameters for O(2)″ are (x, y – 1, z) and for O(3)″″ are (–x, 1 – y, –z).

TABLE VI. NH and CO Stretching Frequencies (cm^{-1}).

	Medium	νNH	νCO			
			A_1 (1)	B_1	A_1 (2)	B_2
dipyam	CCl_4	3425				
$[Cr(CO)_4\cdot$dipyam$]$	mull	3382w	2011ms	1903s	1861sh	1797s
	CH_2Cl_2	3406mw[a]	2007m	1889s	1869sh	1819s
$[Mo(CO)_4\cdot$dipyam$]$	mull	3351mw	2011m	1902m	1867ms	1781s
	CH_2Cl_2	3406vw[b]	2014m	1897s	1872s	1822s
$[W(CO)_4\cdot$dipyam$]$	mull	3337mw	2004s	1892s	1860s	1777s
	CH_2Cl_2	3400?vvw[b]	2005ms	1883s	1860s	1822ms

[a] Saturated solution in 0.5 mm cell. [b] Saturated solution in 3 mm cell. s = strong, m = medium, w = weak, sh = shoulder, v = very.

[10]. The compound is strongly hydrogen-bonded in the crystal (νNH ~ 3300 cm^{-1}, br) and in polar solvents (νNH in dioxan = 3324 cm^{-1}) and it associates, to some extent, in non-polar solvents [10]. The pronounced tendency of the molecule to hydrogen-bond does not always seem to have been appreciated by other authors and in particular the work of Sobczyk, Koll and Malarski, [10] leading to the identification of the genuinely non-hydrogen-bonded NH stretching vibration, has been almost universally ignored.

Complex formation, via the pyridyl nitrogen atoms, with metal acceptors in positive oxidation states should promote a drift of electrons away from the central NH bond, leading to a marginal weakening of the bond and hence to a reduction in the NH stretching frequency. Thus, the highest NH stretching frequencies reported for complexes of di-2-pyridylamine with M^{2+} or M^{3+} acceptors are about 3340–3350 cm^{-1}, [11–13]. In the carbonyl complexes, σ-electron transfer to the metal(0) atoms should occur less easily than to positively charged acceptors, and the free NH stretching frequencies should therefore be higher than those in 'classical' complexes, possibly not much different from that in the uncoordinated ligand.

Vibrational data for the $[M(CO)_4\cdot$dipyam$]$ complexes are listed in Table VI. The NH stretch in $[Cr(CO)_4\cdot$dipyam$]$ is readily identifiable at 3406 cm^{-1} in dichloromethane solution, and a corresponding weak i.r. band appears at 3406 cm^{-1} in the spectrum of the less soluble molybdenum complex. The tungsten complex is less soluble still, and in this case the NH stretch can be located only approximately, as a very weak absorption around 3400 cm^{-1}. These frequencies are at least 50 cm^{-1} higher than any previously reported for coordinated di-2-pyridylamine, and following the discussion in the preceding paragraph we take them as characteristic of the non-hydrogen-bonded ligand bound to metal(0) acceptor atoms. The NH absorption intensities are very sensitive to traces of moisture and are considerably diminished or even completely suppressed (in solutions of the molybdenum and tungsten complexes) if the solvents are not properly dried. This is presumably because hydrogen-bonding between the NH group and adventitious water molecules lowers the NH stretching frequency and causes it to be completely obscured, in the long-path samples necessary for these measurements, by the intense solvent absorptions below ~3300 cm^{-1}.

The NH stretching absorptions in the crystal i.r. spectra are well-defined and readily detectable: the bandwidths at half-height are about 15 cm^{-1} (Cr complex) or 25–30 cm^{-1} (Mo, W complexes). The observed frequencies are all below 3400 cm^{-1}. In the case of $[Cr(CO)_4\cdot$dipyam$]$ the shift from the solution frequency (-24 cm^{-1}) is fairly small and can probably be attributed to essentially non-bonded NH----O contacts in the crystal, but the corresponding shifts of -55 cm^{-1} and -69 cm^{-1}, respectively, in $[Mo(CO)_4\cdot$dipyam$]$ and $[W(CO)_4\cdot$dipyam$]$ are clearly more significant and are fully consistent with the hydrogen-bonded structures indicated for these complexes by the X-ray analyses.

The difference of 14 cm^{-1} between the NH stretching frequencies in the molybdenum and tungsten complexes suggests that the N(3)----O(1)′ distance may be slightly shorter in the latter case. The structural data for $[W(CO)_4\cdot$dipyam$]$ yield an N(3)----O(1)′ distance of 2.99(2) Å, 0.05 Å shorter than in the molybdenum complex, with a corresponding H···O(1)′ distance of 2.19 Å and an $N(3)\hat{H}O(1)'$ angle of 137°. Given the uncertainties in the atomic coordinates for $[W(CO)_4\cdot$dipyam$]$, the precise numerical values are probably of little significance,

TABLE VII. Intermolecular Contacts Closer than 3.35 Å Involving Carbonyl Oxygen Atoms.

	$Cr(CO)_4 \cdot$dipyam[a]		[$Mo(CO)_4 \cdot$dipyam][b]
O(1)–O(3)'	3.26(2) Å	O(1)–N(3)'	3.04(1) Å
O(1)–C(3)'	3.27(2)	O(1)–O(3)''	3.22(1)
O(1)–C(13)''	3.33(2)		
O(1)–N(2)'	3.34(2)	O(2)–C(13)'''	3.29(2)
O(1)–C(12)''	3.34(2)		
		O(3)–O(1)''	3.22(1)
O(2)–O(3)'''	3.06(2)	O(3)–C(13)'''	3.35(2)
O(2)–N(3)''	3.24(2)		
		O(4)–O(4)''''	3.36(2)
O(3)–O(2)'''	3.06(2)		
O(3)–O(1)'	3.26(2)		
O(3)–N(3)''''	3.30(2)		
O(4)–O(4)''''	3.28(2)		
O(4)–C(10)'''''	3.32(2)		

[a] Coordinates of primed atoms are: '(1 – x, –y, –z); ''(x, y – 1, z); '''(–x, –y, –z); ''''(–x, 1 – y, –z); '''''(1 – x, –y, 1 – z).
[b] Coordinates of primed atoms are: '(x – 1, y, 1 + z); ''(–x, 1 – y, 1 – z); '''(x, y, 1 + z); ''''(–x, –y, 1 – z).

but the result nevertheless is consistent with the spectroscopic observations.

CO Stretching Vibrations

The assignments for the CO stretching modes given in Table VI are based on those of Cotton and Kraihanzel [14] for the corresponding 2,2'bipyridyl complexes and are justified by the virtual identity of the [$M(CO)_4 \cdot$bipy] and [$M(CO)_4 \cdot$dipyam] solution spectra. Strictly, the assignments refer only to the solution spectra: for the crystalline compounds, with two molecules in the $P\bar{1}$ cell, the eight CO stretching modes transform as 4Ag(R) + 4Au(IR). However, it is convenient to use the C_{2v} symmetry labels as a starting point for discussion of the crystal spectra.

The normal modes $A_1(1)$ and B_1 are essentially the symmetrically- and antisymmetrically-coupled stretches of the *trans* O(3)C(3)–M–C(4)O(4) group. The $A_1(2)$ and B_2 modes are the corresponding symmetric and antisymmetric stretches of the *cis*-carbonyls C(1)O(1) and C(2)O(2). The putative intermolecular hydrogen bonds in the molybdenum and tungsten complexes involve the *cis*-carbonyl group C(1)O(1) and hence should most directly affect the $A_1(2)$ and B_2 modes in the crystal spectra.

The B_2 modes in [$Mo(CO)_4 \cdot$dipyam] and [$W(CO)_4 \cdot$dipyam] are about 40 cm^{-1} lower in the crystal than in dichloromethane solution. Shifts in the other three vibrations are all less than 10 cm^{-1}. To the extent that any hydrogen-bonding interaction involving O(1) will tend to remove the equivalence of C(1)O(1) and C(2)O(2), the "$A_1(2)$" and "B_2" modes in the crystal will begin to take on the character of isolated bond-stretching vibrations. The low frequencies of the "B_2" modes can therefore be accounted for if we consider them to be predominantly stretching vibrations of the C(1)O(1) carbonyls, somewhat weakened by hydrogen-bond formation at the O(1) atoms.

Carbonyl stretching frequencies in crystalline metal carbonyl complexes are notoriously unpredictable and the preceding discussion is in no way rigorous. However, it is instructive to compare the environments of the carbonyl groups in [$Mo(CO)_4 \cdot$dipyam] with those in [$Cr(CO)_4 \cdot$dipyam]. The B_2 carbonyl stretching vibration in the latter complex is 22 cm^{-1} lower in the crystal than in solution, and the B_1 mode is also shifted by 14 cm^{-1}, even though there appears to be very little possibility of significant hydrogen-bonding in this case. In Table VII we list the intermolecular distances closer than 3.35 Å, involving carbonyl oxygen atoms, in the two complexes. The Table clearly illustrates the crowded environment of the carbonyl groups in [$Cr(CO)_4 \cdot$dipyam] relative to those in the molybdenum complex. In particular, the oxygen atom O(1) has five near neighbours (compared with only two, one of these being N(3)', in [$Mo(CO)_4 \cdot$dipyam]), and there are additional close contacts, with no counterpart in the molybdenum complex, of 3.06 Å between the atoms O(2) and O(3) in adjoining molecules. Given these results, the differences between the crystal and solution spectra of [$Cr(CO)_4 \cdot$dipyam] are in no way remarkable. Equally, there is little if anything to suggest that the large shift in the B_2 carbonyl mode in [$Mo(CO)_4 \cdot$dipyam] could be caused by a non-bonded contact: on the contrary, the data support the attribution of this shift to a hydrogen-bonded structure in the crystal.

Conclusion

Taken together, the structural and spectroscopic data point consistently to the presence of weak but significant intermolecular hydrogen bonds in the crystalline [Mo(CO)$_4$·dipyam] and [W(CO)$_4$·dipyam] complexes. Metal carbonyl oxygen atoms are not ideal hydrogen-bond acceptors, and examples of authenticated hydrogen-bonded complexes are rare and have often proved elusive in the past. In their early work on complexes of Group VI metal carbonyls with ethylenediamine and diethylenetriamine, Kraihanzel and Cotton [14] suggested that differences between the crystal and solution carbonyl stretching spectra might be caused by hydrogen-bonding effects in the crystal, but this was not substantiated by subsequent X-ray analyses [15, 16]. It is worth noting that the di-2-pyridylamine ligand is ideally designed for intermolecular hydrogen-bond formation: the relative acidity of the central NH group, and its marked tendency to form hydrogen bonds, has been amply demonstrated, and the geometry of the ligand is such that when the two pyridyl nitrogen atoms are coordinated to a metal acceptor, the NH bond is on the periphery of the complex molecule, directed away from the centre and free from any problems of steric interference with the hydrogen-bonding interaction. In addition the relatively poor π-acceptor character of the donor nitrogen atoms will tend to promote the development of a fractional negative charge on the carbonyl oxygen atoms (and especially those *trans* to nitrogen) thereby enhancing their ability to interact with the hydrogen atom. There is no obvious reason why other ligands, selected with these considerations in mind, should not form similar or more strongly hydrogen-bonded carbonyl complexes.

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