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Molybdenum Carbonyl-di-2-pyridylamine Complexes

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The di-2-pyridylamine complexes [M(CO)$_4$·dipyam] [M = Cr, Mo, W; dipyam = $(C_5H_4N)_2NH$] have solution IR spectra, in the CO stretching region, which are to all intents and purposes identical with those of the corresponding 2,2′-bipyridyl(bipy) complexes [1, 2]. In repeating the preparation of [Mo(CO)$_4$·dipyam] we have observed that its spectrum in the crystal is significantly different from that obtained in solution: in particular, the lowest-frequency CO stretch falls by about 40 cm^{-1} from its solution value (Table I). In [Mo(CO)$_4$·bipy], in contrast, the CO stretching frequencies do not differ appreciably between the solid and solution spectra. The di-2-pyridylamine complex, unlike [Mo(CO)$_4$·bipy] dissolves only to a very limited extent in most organic solvents: a saturated solution in dichloromethane is barely adequate to provide a satisfactory solution spectrum. Similar effects are observed in the corresponding chromium and tungsten complexes. The molybdenum carbonyl-di-2-pyridylketone complex [Mo(CO)$_4$·dipyco] in general resembles [Mo(CO)$_4$·bipy] and shows no significant frequency shift between the solid and solution spectra.

The reaction of [Mo(CO)$_4$·dipyam] with pyridine yields the trisubstituted product [Mo(CO)$_3$·dipyam·py]. This complex, unlike its 2,2′-bipyridyl and 1,10-phenanthroline analogues [3] (Table I) displays three distinct and clearly separated CO stretching vibrations, the lowest being at 1730 cm^{-1}. The complex is almost totally insoluble in common organic solvents. The donor properties of the pyridyl nitrogen atoms in di-2-pyridylamine should be very similar to those in 2,2′-bipyridyl or 1,10-phenanthroline; using the arguments of Houk and Dobson [3, 4], we would therefore expect the spectrum of unperturbed *fac*-[Mo(CO)$_3$·dipyam·py] to resemble those of [Mo(CO)$_3$·bipy·py] and [Mo(CO)$_3$·phen·py], with only two distinct CO stretching vibrations (A + E). The appearance of three CO stretching vibrations in the spectrum of the solid compound thus suggests an appreciable distortion of the molecule from C_{3v} symmetry. The solubility data, taken together with the differences between the solid and solution spectra of [Mo(CO)$_4$·dipyam], are consistent with some form of intermolecular interaction in the solid leading to an associated or polymeric structure.

As these effects appear to be confined to the di-2-pyridylamine complexes, it is tempting, at first sight, to implicate the central secondary >NH group in any associative interaction. However, in numerous other complexes the ligand binds only through the two pyridyl nitrogen atoms (see, *e.g.* [5, 6]) moreover, any direct formal >NH → Mo interaction would imply a seven-coordinate Mo(0) atom and would raise electroncounting problems in terms of the 18-electron rule. (All of the complexes are diamagnetic). An alternative possibility may be a direct >NH → OC interaction. A structure containing bridging, rather than chelate, di-2-pyridylamine is certainly possible, but the IR data for [Mo(CO)$_4$·dipyam] indicate that in solution at least the molecule functions as a 'normal' bidentate chelate ligand. Definitive structural data are clearly desirable for these complexes.

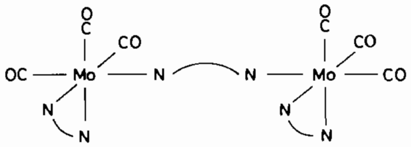
The reaction of [Mo(CO)$_4$dipyam] over several hours with an excess ofdi-2-pyridylamine gives an almost quantitative yield of a bright yellow, microcrystalline, highly insoluble complex with the analy-

TABLE I. IR Active CO Stretching Frequencies (cm^{-1}).

Compound	νCO				Medium	Ref.
[Mo(CO)$_4$·bipy]^a	2017 m	1909 vs	1882 m	1830 s	$CHCl_3$	1
[Mo(CO)$_4$·dipyam]	2018 m	1904 s	1873 ms	1822 ms	CH_2Cl_2	2
	2013 ms	1905 m	1867 s	1782 s	mull	
[Mo(CO)$_4$·dipyco]^a	2008 ms	1892 m	1850 s	1820 s	mull	
[Mo(CO)$_3$·dipyam·py]	1893 ms	1760 vs	1730 s, br		mull	
[Mo(CO)$_3$·bipy·py]^a	1908 s	1777 s			py	3
[Mo(CO)$_3$·phen·py]^a	1902 s	1782 s			py	3
[Mo$_2$(CO)$_6$·dipyam$_3$]	1900 s, br	1854 w	1796 s, br	1738 s, br	mull	

^{a}For these complexes νCO absorptions are broadened in the solid but not significantly shifted from their solution frequencies.

tical composition [$Mo_2(CO)_6$·$dipyam_3$]. The vibrational spectrum is broadly comparable with that of [$Mo(CO)_3$·dipyam·py], with the lowest-frequency CO stretch at 1738 cm^{-1}. In the mass spectrum, a molecular ion peak appears at m/e = 873, corresponding to [$Mo_2(CO)_6$·$dipyam_3$]$^{+}_{3}$, with decarbonylated fragments down to [Mo_2·$dipyam_3$]$^+$. The most probable structure thus appears to be one involving both bridging and chelate di-2-pyridylamine ligands (*e.g.* I).



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Analogous reactions of [$Mo(CO)_4$·bipy], [$Mo(CO)_4$·phen], [$Mo(CO)_4$·dipyco] and [$Mo(CO)_4$·diphos] with di-2-pyridylamine all show evidence of further substitution, particularly in the case of [$Mo(CO)_4$·bipy], but proceed more slowly than the [$Mo(CO)_4$·dipyam]–dipyam reaction and we have so far been unable to isolate analytically pure di-2-pyridylamine bridged binuclear products from these systems*. The [$Mo(CO)_4$·dipyam]-bipy or dipyco systems (leading in principle to 2,2′-bipyridyl or di-2-pyridylketone-bridged products) yield only the unreacted starting materials. The ability of di-2-pyridylamine to form complexes of this type presumably is a result of the flexibility of the molecule about the central amino group.

Crystallographic and further synthetic studies on these and related complexes are now in progress.

Experimental

[$Mo(CO)_4$·dipyam] was obtained as yellow crystals from the reaction of $Mo(CO)_6$ (0.01 mole) with $(C_5H_4N)_2NH$ (0.01 mole) in refluxing toluene (1½ hours). Yield 95%. *Anal.* Found, (Calc.): C, 44.7 (44.4); H, 2.5 (2.4); N 11.0 (11.1)%. *[$Mo(CO)_4$·dipyco]* was obtained similarly, as dark brown crystals, from refluxing xylene. Yield 92%. *Anal.* Found (Calc): C, 46.8 (45.9); H, 2.7 (2.1); N, 9.2 (9.0)%. *[$Mo(CO)_3$·dipyam·py]*. A solution of [$Mo(CO)_4$·dipyam] was refluxed in 1:1 pyridine:toluene for 1½ hours. The orange-yellow complex progressively settled from the reaction solution. Yield 72%. *Anal.* Found (Calc): C, 50.2 (50.2); H, 3.7 (3.3); N, 12.0 (13.0)%. *[$Mo_2(CO)_6$·$dipyam_3$]* A mixture of [$Mo(CO)_4$·dipyam] (0.001 mole) and dipyam (0.05 mole) was refluxed in toluene for 3 hours. The complex separated as lemon-yellow crystals. Yield >95%. *Anal.* Found (Calc): C 49.5 (49.5); H 3.0 (3.1); N 14.8 (14.4)%. All reactions were carried out under nitrogen. The crystalline products are indefinitely air-stable.

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*We have recently obtained the pure complex [$W_2(CO)_6$-$(bipy)_2$(dipyam)], which is presumably binuclear with chelate 2,2′-bipyridyl and bridging di-2-pyridylamine, from the reaction of [$W(CO)_4$(bipy)] with di-2-pyridylamine.