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MIXED AMINEMOLYBDENUM TRICARBONYLS

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SUMMARY

Some substituted molybdenum carbonyl derivatives containing two different non-carbonyl ligands have been synthesised. The CO stretching force constants and stretch–stretch interaction constants have been evaluated from the infra-red spectra.

INTRODUCTION

Substituted derivatives of Group VIA metal carbonyls containing two different non-carbonyl groups have been known since 1935[1]. Recently[2-8] they have been the subject of renewed attention because of their importance in structural and mechanistic studies. To our knowledge, only two papers[2,3] deal with the structure of such derivatives in relation to the CO stretching force constant, k, and stretch–stretch (CO–CO) interaction constant k_i. We have derived the values of k and k_i from infrared spectra of such complexes synthesised in our laboratory. These mixed ligand molybdenum carbonyls contain one monodentate nitrogen donor ligand, Am, (Am = ethylamine, isopropylamine, n-butylamine, cyclohexylamine, benzylamine, allylamine, piperidine, morpholine, ethylenediamine, and 2-picoline) and one bidentate nitrogen donor ligand, B, (B = *o*-phenanthroline, or 2,2′-bipyridine).

RESULTS AND DISCUSSION

Mixed aminemolybdenum tricarbonyls, $[Mo(CO)_3BAm]$, containing ethylamine or isopropylamine as Am, were prepared by heating hexacarbonylmolybdenum and B (1/1 molar ratio) with the excess of the appropriate amine Am, in evacuated sealed tubes. The other compounds were synthesised by refluxing under nitrogen equimolecular mixtures of hexacarbonylmolybdenum and B in n-butylamine, cyclohexylamine, benzylamine, allylamine, piperidine, morpholine, ethylenediamine, or 2-picoline. In the case of allylamine and diethylamine it was advantageous to use xylene as solvent. Better yields of $[Mo(CO)_3BAm]$ having Am = ethylamine or isopropylamine were obtained by heating $[Mo(CO)_4B]$ and the corresponding amine in an evacuated sealed tube. With triethylamine, quinoline, or acridine as Am, $[Mo(CO)_3BAm]$ complexes were not isolated. Similarly employing 2,2′-biquinoline as B a mixed aminemolybdenum tricarbonyl was not obtained, but $[Mo(CO)_4$-

(2,2'-Biquinoline)] was isolated. Preliminary accounts of the work are given in ref. (9). The mixed aminemolybdenum tricarbonyls are black crystalline solids, insoluble in water, or aliphatic and aromatic hydrocarbons; they are sparingly soluble in diethyl ether or methanol. They dissolve in acetone or dichloromethane but decompose immediately to produce an ash-like residue. Some of the complexes decompose even under dry nitrogen. Since most of the above complexes decompose rapidly in solution, their infrared spectra were measured as Nujol mulls. One of the CO bands lay between 1888–1894 cm^{-1}(s) and the other between 1754–1760 cm^{-1}(s).

Since the molecular geometry of these derivatives is consistent with C_s symmetry, the following modified secular equations: (terms are defined in ref. 10) are applicable:

$$\begin{array}{l} A'(1) \\ A'(2) \end{array} \begin{vmatrix} \mu\cdot k_1-\lambda & \sqrt{2}\cdot\mu\cdot k_{i(ba)} \\ \sqrt{2}\cdot\mu k_{i(ba)} & \mu\cdot(k_2+k_{i(bb)}-\lambda \end{vmatrix} = 0$$

$$A''=\mu\cdot(k_2-k_{i(bb)}) \qquad \text{where } k_{i(ba)}=c\cdot k_{i(bb)}\,.$$

Three carbonyl bands, due to $2A'+A''$ modes, are expected. The term $k_{i(bb)}$ involves the coupling of two carbonyls, each *trans* to a nitrogen of ligand B; $k_{i(ba)}$ may be attributed to the coupling of one carbonyl *trans* to a nitrogen of B and the second *trans* to the nitrogen of Am. We evaluated the ratio of the interaction constants $k_{i(ba)}/k_{i(bb)}$ to a good approximation for our seven compounds (B = *o*-Phen, Am = $C_2H_5NH_2$, i-$C_3H_7NH_2$, $C_6H_5CH_2NH_2$; B = 2,2'-Bipy, Am = $C_2H_5NH_2$, i-$C_3H_7NH_2$, $C_4H_9NH_2$, and $C_6H_{11}NH_2$). We used the k_i value of 0.65 mdyne/Å [termed $k_{i(b)}$ here] of $[Mo(CO)_3Py_3]$[2] (Pyridine is very similar to B in bonding properties) and the k_i values [termed $k_{i(a)}$ here] of *cis*-$[Mo(CO)_3Am_3]$ (Am = $C_2H_5NH_2$, i-$C_3H_7NH_2$, $C_4H_9NH_2$, $C_6H_{11}NH_2$, and $C_6H_5CH_2NH_2$), which are 0.73 mdyne/Å for first four and 0.79 mdyne/Å for the last compound[11]. The value of c was determined by substituting the values of $k_{i(b)}$ and $k_{i(a)}$ in the following equation:

$$c=k_{i(ba)}/k_{i(bb)}=\tfrac{1}{2}(k_{i(b)}+k_{i(a)})/k_{i(b)}$$

This was found to be 1.06 for six mixed aminemolybdenum tricarbonyls, $[Mo(CO)_3$-BAm] (Am = $C_2H_5NH_2$, i-$C_3H_7NH_2$, n-$C_4H_9NH_2$, $C_6H_{11}NH_2$), and 1.10 for $[Mo(CO)_3$(*o*-Phen)$(C_6H_5CH_2NH_2)]$. This small deviation from 1 in the c value justifies the assumption that the interaction constants $k_{i(ba)}$ and $k_{i(bb)}$ are nearly equal in such complexes. From this observation it may be concluded that the two physically different *cis* CO–CO interactions are indistinguishable, and the bonding properties of the ligands B and Am will also be indistinguishable. Under these circumstances, the splitting of the E mode (C_{3v} symmetry) into A' and A'' modes (C_s symmetry) is not to be expected to an appreciable extent, in agreement with our results. In almost all the spectra, the two close-lying bands due to A' and A'' modes are unsplit, and only two carbonyl bands due to A_1+E modes (C_{3v} symmetry) are recorded. The position of *o*-phenanthroline and 2,2'-bipyridine in the spectrochemical series is very close to that of other amines which is also an indication of near equivalence in their bonding properties. In view of these facts, C_{3v} symmetry may be inferred for the local symmetry of the carbonyl groups undisplaced from the hexacarbonylmolybdenum octahedron, and hence the Cotton–Kraihanzel secular equations for C_{3v} symmetry[10] are applicable for the calculation of CO stretching and interaction force constants.

TABLE 1

CO STRETCHING FREQUENCIES, CO FORCE CONSTANT AND CO–CO INTERACTION CONSTANT IN MIXED AMINE-MOLYBDENUM TRICARBONYLS

Complex	$\nu(CO)^a$ (cm^{-1})		k (mdynes/Å)	k_i (mdynes/Å)
	A_1	E		
cis-$[Mo(CO)_3(o\text{-Phen})(C_2H_5NH_2)]$	1888	1754	13.08	0.66
cis-$[Mo(CO)_3(o\text{-Phen})(i\text{-}C_3H_7NH_2)]$	1888	1754	13.08	0.66
cis-$[Mo(CO)_3(o\text{-Phen})(C_5H_{11}N)]$	1890	1758	13.12	0.65
cis-$[Mo(CO)_3(o\text{-Phen})(C_4H_9NO)]$	1892	1754	13.09	0.67
cis-$[Mo(CO)_3(o\text{-Phen})(C_6H_5CH_2NH_2)]$	1888	1754	13.08	0.66
cis-$[Mo(CO)_3(o\text{-Phen})(2\text{-}C_5H_4NCH_3)]$	1892	1760	13.16	0.64
cis-$[Mo(CO)_3(o\text{-Phen})(CH_2NH_2)_2]$	1888	1756	13.10	0.65
cis-$[Mo(CO)_3(2,2'\text{-Bipy})(C_2H_5NH_2)]$	1888	1754	13.08	0.66
cis-$[Mo(CO)_3(2,2'\text{-Bipy})(iso\text{-}C_3H_7NH_2)]$	1888	1754	13.08	0.66
cis-$[Mo(CO)_3(2,2'\text{-Bipy})(C_4H_9NH_2)]$	1888	1760	13.14	0.63
cis-$[Mo(CO)_3(2,2'\text{-Bipy})(C_6H_{11}NH_2)]$	1888	1756	13.10	0.65
cis-$[Mo(CO)_3(2,2'\text{-Bipy})(C_4H_9NO)]$	1890	1754	13.09	0.67
cis-$[Mo(CO)_3(2,2'\text{-Bipy})(C_5H_{11}N)]$	1892	1756	13.11	0.66
cis-$[Mo(CO)_3(2,2'\text{-Bipy})(C_2H_5)_2NH]$	1894	1760	13.17	0.66
cis-$[Mo(CO)_3(2,2'\text{-Bipy})(C_3H_5NH_2)]$	1888	1754	13.08	0.66

[a] All of strong intensity; accuracy ± 5 cm^{-1}.

Dobson and Houk[4] report the symmetry of a similar compound, *cis*-$[Mo(CO)_3(Diphos)(C_6H_5)_3Sb]$, as C_{3v}, according to the carbonyl bands 1948(s) and 1857(vs), assigned to A_1+E modes.

Comparing the values of k and k_i in the mixed aminemolybdenum tricarbonyls of Table 1 with those for the trisubstituted derivatives of the type *cis*-$[Mo(CO)_3Am_3]$[11], it is observed that the CO stretching force constants increase in the compounds $[Mo(CO)_3BAm]$, due to the presence of B ligands, which are feeble π-acceptors. The values of interaction constants decrease indicating lesser CO–CO interaction than in *cis*-$[Mo(CO)_3Am_3]$.

EXPERIMENTAL

Hexacarbonylmolybdenum (Climax Molybdenum Co.) was sublimed before use. Ethylamine and isopropylamine were used as aqueous (50% and 70%, respectively) solutions, but other amines were used neat. All the experiments were performed under dry nitrogen or *in vacuo*. Infrared spectra were measured on a Perkin–Elmer Spectrophotometer model 521.

o-Phenanthrolinetetracarbonylmolybdenum(0) was obtained by the method given in ref. 1, and 2,2'-bipyridinetetracarbonylmolybdenum(0) by that in ref. 12.

Preparation of o-phenanthroline(ethylamine)tricarbonylmolybdenum(0)

o-Phenanthrolinetetracarbonylmolybdenum(0) (0.2 g) and ethylamine (1.5 ml of 50% aqueous solution) were heated in an evacuated sealed pyrex tube at 110° for 3 h. The red colour gradually changed to black. The tube was cooled to room temperature and the black product was removed from the tube and washed thoroughly with benzene to remove unreacted *o*-phenanthrolinetetracarbonylmolybdenum(0). The product (0.159 g) was recrystallised from a mixture (1/1) of methanol and acetone under nitrogen, and was dried *in vacuo*. (Found: C, 50.5; H, 3.6; N, 10.5. $C_{15}H_{17}MoN_3O_3$ calcd.: C, 50.3; H, 3.7; N, 10.3%.) It was insoluble in hydrocarbons, carbon tetrachloride, and light petroleum, but dissolved in acetone or dichloromethane to give a beautiful violet solution; this decomposed very rapidly in air. The compound was also air-sensitive in the solid state.

TABLE 2

MIXED AMINEMOLYBDENUM TRICARBONYLS PREPARED

Compound	Method and conditions	Yield (%)	Analysis, found (calcd.) (%)		
			C	H	N
[Mo(*o*-Phen)(CO)$_3$(i-C$_3$H$_7$NH$_2$)][a]	Sealed tube,	87.0	51.7	3.9	10.0
black	120°, 4 h		(51.5)	(4.0)	(10.0)
[Mo(2,2′-Bipy)(CO)$_3$(C$_2$H$_5$NH$_2$)][a]	Sealed tube,	88.0	46.7	3.9	10.9
black	110°, 4 h		(47.2)	(3.9)	(11.0)
[Mo(2,2′-Bipy)(CO)$_3$(i-C$_3$H$_7$NH$_2$)][c]	Sealed tube,	83.8	48.4	4.2	10.4
black	120°, 4 h		(48.6)	(4.3)	(10.6)
[Mo(*o*-Phen)(CO)$_3$(C$_5$H$_{11}$N)][b]	Reflux,	80.1	53.7	4.3	9.6
black	45 min		(53.9)	(4.2)	(9.4)
[Mo(*o*-Phen)(CO)$_3$(C$_4$H$_9$NO)][b]	Reflux,	56.3	50.8	3.7	9.4
violet black	2½ h		(51.1)	(3.8)	(9.3)
[Mo(*o*-Phen)(CO)$_3$(C$_6$H$_5$CH$_2$NH$_2$)][b]	Reflux,	66.0	61.9	4.3	7.4
violet black	2 h		(62.4)	(4.1)	(7.5)
[Mo(*o*-Phen)(CO)$_3$(2-C$_5$H$_4$NCH$_3$)][b]	Reflux,	50.2	54.8	3.1	9.3
violet	2½ h		(55.6)	(3.3)	(9.2)
[Mo(*o*-Phen)(CO)$_3$(CH$_2$NH$_2$)$_2$][b]	Reflux,	72.2	48.2	3.7	13.3
violet black	2 h		(48.5)	(3.8)	(13.3)
[Mo(2,2′-Bipy)(CO)$_3$(C$_4$H$_9$NH$_2$)][b]	Reflux,	91.9	49.8	4.5	10.1
shining black	45 min		(49.8)	(4.6)	(10.2)
[Mo(2,2′-Bipy)(CO)$_3$(C$_6$H$_{11}$NH$_2$)][b]	Reflux,	89.9	51.7	4.3	9.8
shining black	45 min		(52.4)	(4.8)	(9.6)
[Mo(2,2′-Bipy)(CO)$_3$(C$_4$H$_9$NO)][b]	Reflux,	66.0	47.9	3.8	9.9
violet black	3 h		(48.2)	(4.0)	(9.9)
[Mo(2,2′-Bipy)(CO)$_3$(C$_5$H$_{11}$N)][b]	Reflux,	88.0	50.9	4.3	9.8
shining black	45 min		(51.3)	(4.5)	(9.9)
[Mo(2,2′-Bipy)(CO)$_3$(C$_2$H$_5$)$_2$NH][b]	Reflux,	43.3	49.7	4.3	9.9
violet	3 h, xylene		(49.8)	(4.6)	(10.2)
[Mo(2,2′-Bipy)(CO)$_3$(C$_3$H$_5$NH$_2$)][b]	Reflux,	68.4	48.6	3.6	10.4
violet	3 h, xylene		(48.8)	(3.8)	(10.5)

[a] Starting materials were [Mo(CO)$_4$B] and the appropriate amines. [b] An equimolar mixture of hexacarbonylmolybdenum and B was refluxed in the amines (Am) without using any other solvent, unless otherwise stated.

Other products are shown in Table 2.

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