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Some π Complexes Involving Metal Carbonyls and the Triple Bond of Diethylaminoacetonitrile[1]

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Received December 17, 1968

Some new compounds of the type $[M(CO)_3 . L{-}L]_2$, *A,* $[Mn(CO)_2 . L{-}L]_3$, *B, and* $[Fe(CO)_3 . L{-}L]$, *C, (where* $M = Cr$, *Mo, W and* $L{-}L = (C_2H_5)_2NCH_2C{\equiv}N$) *have been prepared. The elemental analysis and the molecular weight determinations show that the A compounds are dimers and the B compounds is a trimer. On the basis of different results obtained, structures involving metal-metal bonding and coordination of the cyano group through the triple bond are proposed.*

Introduction

In our previous work[2] with the complexes of group IV halides and diethylaminoacetonitrile, the results had strongly suggested that the triple bond of the nitrile group was the possible site of coordination to the metal atom. In order to add evidence in support of coordination through the triple bond of the cyano group, it was considered interesting to extend the same work to metal carbonyls which give well defined substitution reactions with Lewis bases. Since the metal carbonyls are known to form simple substitution monomers[3,4,5] as well as polynuclear substitution compounds[6-11] it was decided to investigate the possibility of obtaining polynuclear complexes of the type obtained by Hayter, King or Abel *et al.*[9,10,11]

Experimental Section

The ligand and the metal carbonyls were obtained from the K & K Laboratories and Alfa Inorganics Inc. respectively. The solvents were purified and dried by conventional methods. The compounds were prepared as detailed below.

Preparation of $[Mo(CO)_3 . (C_5H_5)_2NCH_2C{\equiv}N]_2$. A mixture of 3.51 g. (13.3 mmoles) of molybdenum hexa-carbonyl, 1.51 g. (13.4 mmoles) of diethylaminoacetonitrile, and 40 ml of tetrahydrofuran was refluxed ~24 hours with magnetic stirring under nitrogen atmosphere. After cooling to room temperature the dark red-brown solution was filtered and to the filtrate was added 25 ml n-hexane. 2.0 g (yield 50%) dark red-brown compound was obtained as a precipitate on subjecting the filtrate to partial evaporation and drying the precipitate *in vacuo* for 8 hours at room temperature.

Preparation of $[W(CO)_3 . (C_2H_5)_2NCH_2C{\equiv}N]_2$. A mixture of 4 g (11.4 mmoles) of tungsten hexacarbonyl, 1.32 g (11.7 mmoles) of diethylaminoacetonitrile, and 40 ml tetrahydrofuran was refluxed for about 72 hours with magnetic stirring. After cooling to room temperature the dark brown reaction mixture was filtered under reduced pressure. To the filtrate was added 25 ml. n-hexane and the resulting solution subjected to partial evaporation. A dark brown compound separated out which was dried *in vacuo* for 24 hours at room temperature (1.8 g, yield 41%).

Preparation of $[Cr(CO)_3 . (C_2H_5)_2NCH_2C{\equiv}N]_2$. The method of preparation was very similar to that described above. The reactants were taken in the following proportion: $Cr(CO)_6$, 2 g (9.1 mmoles); ligand, 1.04 g (9.2 mmoles)solvent THF, 40 ml; time of reaction ~96 hours, dark brown compound 0.4 g (yield 18%).

Preparation of $[Fe(CO)_3 . (C_2H_5)_2NCH_2C{\equiv}N]$. A mixture of freshly distilled 4.38 g (22.4 mmoles) of $Fe(CO)_5$, 2.52 g (22.4 mmoles) of diethylaminoacetonitrile, 25 ml tetrahydrofuran was refluxed for ~48 hours with magnetic stirring in nitrogen atmosphere. The red reaction mixture remained clear on cooling to room temperature. A red thick layer separated out from the reaction mixture on partial evaporation and on adding 25 ml n-hexane. The red viscous product was repeatedly dissolved in THF precipitated with n-hexane and finally dried *in vacuo* at 60°C giving a brown solid.

Preparation of $[Mn(CO)_2 . (C_2H_5)_2NCH_2C{\equiv}N]_3$. A mixture of 2 g (5.1 mmoles) of $Mn_2(CO)$, 1.2 g (10.7 mmoles) of diethylaminoacetonitrile, and 40 ml of tetrahydrofuran was refluxed ~24 hours as described

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(1) Paper presented at the X International Conference on Coordination Chemistry, Tokyo, Japan, September 13, 1967. (See Proceedings X I.C.C.C., p. 32).
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previously. The pale wellow reaction mixture gradually became golden brown. After cooling to room temperature the volume of the solution was reduced by abour half under reduced pressure. To the resulting solution was added 25 ml of n-hexane. A yellewish brown compound separated out which was dried *in vacuo* at room temperature.

Preparations of $[Cr(CO)_3 . (C_2H_5)_2NCH_2C{\equiv}N]Na$ *and* $[W(CO)_3 . (C_2H_5)_2NCH_2C{\equiv}]I$. These compounds were prepared by the methods described by Abel, Singh, and Wilkinson.[16]

Conductivity measurements on a 0.0061 molar solution of $[Cr(CO)_3Na . (C_2H_5)_2NCH_2C{\equiv}N]$ in tetrahydrofuran, using a Metrohm conductoscope type E 365 B, gave a molar conductance of 1.32 ohm^{-1} cm^2 at room temperature.

The N.M.R. spectra of the ligand diethylaminoacetonitrile, L–L and the compounds $[Cr(CO)_3L{-}L]_2$ and $[Mo(CO)_3L{-}L]_2$ were taken in d_6 acetone solution. The spectrum of the ligand gave very sharp peaks but the spectra of the compounds gave broad bands in essentially the same region, so that no meaning-full information could be obtained.

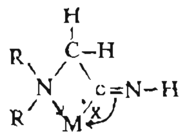
Micro elemental analysis for the compounds was performed by Galbraith Laboratories Inc., Knoxville, Tennessee (U.S.A.) The molecular weight determinations were carried out in nitrobenzene solutions by a cryoscopic methods. The analytical results are included in Table I.

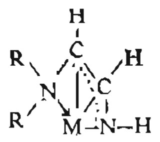
The infrared spectra of the complexes were recorded on a Perkin-Elmer Spectrophotometer, Model 621, in Nujol mulls using caesium iodide plates. In the $\nu(C{\equiv}N)$ and $\nu(C{\equiv}O)$ regions the spectra were also recorded in tetrahydrofuran solution using NaCl cells and the bands observed were found identical to the bands in Nujol mulls. The infrared spectra results in the normal and the far infrared regions are reported in Table II and III respectively.

The magnetic susceptibility measurements on the freshly prepared compounds showed a very weak paramagnetism. This weak paramagnetism, however, seemed to increase on keeping the compounds exposed for a few days. The compounds were found sensitive to light and atmosphere but could be stored in dark under nitrogen atmosphere. The traces of impurity seem to cause low paramagnetism in the compounds.

Results and Discussion

The ligand diethylaminoacetonitrile can interact with metal carbonyls in a number of ways. As a monodentate ligand it can either coordinate through the amino nitrogen or through the cyano nitrogen depending on their basicity. As a bidentate ligand it can coordinate either to two different metal atoms or to the same metal atom forming a chelate. The nature of interaction can also involve the abstraction of a hydrogen atom from the tetrahydrofuran solvent to give a $(C_2H_5)_2NCH_2C{=}NH$ ligand which could chelate as a 5-electron donor to the metal atom. Interaction can also involve a transfer of one hydrogen from the CH_2 carbon atom to the other carbon atom to give an allylic-like 3-electron donating system. These two possible structures resulting from the transfer of hydrogen atoms can be shown as below:





Another less likely possibility may involve the loss of a hydrogen atom to give the system in which the formally positively charged ligand could donate four electrons to the negatively charged metal atom:

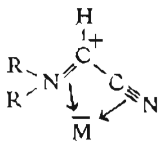


Table I. Analytical results

Compound	Color	Melting point °C	Metal % Theor. Found	Carbon % Theor. Found	Hydrogen % Theor. Found	Nitrogen % Theor. Found	Mol. wt. Theor. Found
$[Cr(CO)_3 . L{-}L]_2$	dark	~120 D	20.95	43.51	4.84	11.29	496
	brown		20.8	43.2	5.2	11.2	462
$[Mo(CO)_3 . L{-}L]_2$	dark	112-15	32.84	36.98	4.10	9.59	584
	brown		32.6	36.3	3.6	9.0	580
$[W(CO)_3 . L{-}L]_2$	dark	95-8	48.40	28.42	3.16	7.37	760
	brown		47.7	30.3	3.4	8.0	750
$[Mn(CO)_3 . L{-}L]_3$	yellowish	170-2	24.63	43.03	5.38	12.55	669
	brown		24.3	41.4	4.3	12.7	680
$[Fe(CO)_3 . L{-}L]_2$*	brown	115-18	22.15	42.8	4.76	11.1	—
			20.90	40.5	4.34	10.3	
$[Cr(CO)_3 . L{-}L]Na$	brown	95-100	19.17	39.81	4.43	—	271
			19.0	39.1	5.0	—	263
$[W(CO)_3 . L{-}L]I$**		~200D	—	21.3	2.37	5.52	—
				19.3	2.45	4.33	—
** Iodine %:	Theor. 25.05 Found 24.7						

L–L = $(C_2H_5)_2NCH_2C{\equiv}N$; D = Decomposed by turning black; * Compound could not be purified due to poor solubility.

Table II. Infrared Spectral Results (cm^{-1})

$(C_2H_5)_2NCH_2C{\equiv}N$ L–L	$Cr(CO)_6$	$\begin{bmatrix}Cr(CO)_3\\ L{-}L\end{bmatrix}_2$	$Mo(CO)_6$	$\begin{bmatrix}Mo(CO)_3\\ L{-}L\end{bmatrix}_2$	$W(CO)_6$	$\begin{bmatrix}W(CO)_3\\ L{-}L\end{bmatrix}_2$	$Mn_2(CO)_{10}$	$\begin{bmatrix}Mn(CO)_2\\ L{-}L\end{bmatrix}_3$	$Fe(CO)_5$	$\begin{bmatrix}Fe(CO)_3\\ L{-}L\end{bmatrix}_2$	$\begin{bmatrix}Cr(CO)_3\\ L{-}L\end{bmatrix}Na$	Band Assignments
2220 m w		2118 m		21110 m		2120 m		2145 m 2120 m		2110 m	2110 m	$\nu(C{\equiv}N)$
	1999 ms 1986 vs 1975 sh 1953 m	2055 s 1985 m 1936 sb	1995 s 1975 sb 1940 sb	2065 s 1985 m 1908 vsb	1970 s 1945 m 1918 s	2060 s 1970 sh 1910 vsb	2055 s 2050 sh 2021 s 2012 sh 1982 s 1975 s 1965 sh	2030 s 2015 s 1935 sb	2022 s 2000 s 1965 s	2080 sh 2040 s 1960 sh 1930 s	2055 s 1980 s 1918 sb	$\nu(C{\equiv}O)$

s = strong; m = medium; w = weak; b = broad; sh = shoulder.

Table III. Far Infrared Spectral Results (700-200 cm^{-1}) in Nujol Mulls

L–L neat	$Cr(CO)_6$	$\begin{bmatrix}Cr(CO)_3\\ L{-}L\end{bmatrix}_2$	$\begin{bmatrix}Cr(CO)_3\\ L{-}L\end{bmatrix}Na$	$Mo(CO)_6$	$\begin{bmatrix}Mo(CO)_3\\ L{-}L\end{bmatrix}_2$	$W(CO)_6$	$\begin{bmatrix}W(CO)_3\\ L{-}L\end{bmatrix}_2$	$Mn_2(CO)_{10}$	$\begin{bmatrix}Mn(CO)_2\\ L{-}L\end{bmatrix}_3$
	668 s sh	672 m sh	672 s sh	690 s	680 s	685 m	670 s	640 v s	678 m
									648 v s
	650 v s	655 s	655 s	590 s	587 s	570 s	590 sh		645 sh
					580 sh		580 s	555 sh	562 w
	600 m sh								545 w
									530 sh
	560 m sh	565 m b	550 m b			527 sh			
		512 m	508 m sh		487 w b		455 sh		455 m
475 m		465 v w	462 w sh		465 w b				475 sh
	442 s	450 m	450 m	465 s		398 sh	455 mb	440 m	430 w
				362 s b	422 w b	377 sh	420 sh		
						367 s b	386 sh	399 m	
385 m		392 w	390 w		372 sh				
		300 m			364 s b		377 s		
		275 s					367 sh		
		262 s	250 w						285 w
		242 m s	235 wb						269 w
		220 s							260 v w
									237 v w

s = strong; m = medium; w = weak; sh = shoulder; v = very.

Table IV. The infrared active normal vibrational species in different type of Complexes Studies [a]

Molecule	Symmetry	(M—C), (C=O) species	(M—C—O) species	No. of IR active bands in far IR region	(C≡N)	Remarks
$M(CO)_6$	O_h [b]	$A_{1g}+E_g+\underline{T_{1u}}$	$T_{1g}+T_{2g}+\underline{T_{1u}}+{}_{2u}$	2	---	
$[M(CO)_3LL]_2$	C_1	$\underline{6A}$	$\underline{12A}$	18	$\underline{2A}$	LL not symmetrcally attached
	C_2	$\underline{3A}+\underline{3B}$	$\underline{6A}+\underline{6B}$	18	$\underline{A}+\underline{B}$	LL symmetrically attached but non-planar
	C_{2v}	$\underline{2A_1}+A_2+\underline{2B_1}+\underline{B_2}$	$\underline{3A_1}+3A_2+\underline{3B_1}+\underline{3B_2}$	11	$\underline{A_1}+\underline{B_1}$	LL symmetrically attached *cis & trans* to each other assuming planar configuration of LL
	C_{2h} [b]	$2A_g+B_g+\underline{A_u}+\underline{2B_u}$	$3A_g+3B_g+\underline{3A_u}+\underline{3B_u}$	9	$A_g+\underline{B_u}$	
$Na[M(CO)_3LL]$	C_1 [b]	$\underline{3A}$	$\underline{6A}$	9	$\underline{A}$	
$[Mn(CO)_2LL]_3$	C_1	$\underline{6A}$	$\underline{12A}$	18	$\underline{2A}$	LL not symmetrically attached
	C_3 [b]	$\underline{2A}+\underline{2E}$	$\underline{4A}+\underline{4E}$	12	$\underline{A}+\underline{E}$	LL symmetrically attached

[a] Underlined are the infrared active species. [b] The most probable configurational symmetry.

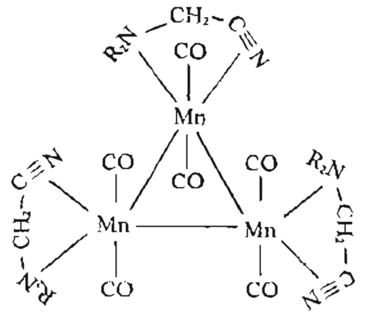
In fact the absence of new bands in the NH and the —C=N— stretchin regions in the IR spectra of these compounds makes these possibilities very unlikely.

The analytical results and the molecular weight determination (Table I) indicate that the A compounds are dimers and the B compound is a trimer. The infrared spectral studies on these compounds clearly show that the C≡N stretching frequencies have shifted to a lower region by about 100 cm^{-1}. This unusual behaviour showing a negative shift of the $\nu(C\equiv N)$ strongly suggests that in such cases the bonding of the $C\equiv N$ to the metal is not by way of the nitrogen atom through its available electron pair. Farona and Bremer[12] have recently reported the preparation of a compound of succinonitrile with an halogenated manganese carbonyl where a bathochrome effect of 90 cm^{-1} was noticed for the cyano stretching frequency. Bock and Dieck,[13] while working with dialkylcyanamide and nickel tetracarbonyl, obtained the compound $Ni_2(CO)_2(R_2NCN)_2$ an infrared spectra of which also displayed a lowering of $\nu(C\equiv N)$, as a result of coordination. This unusual behaviour of the $\nu(C\equiv N)$ has been interpreted as resulting from the bonding of the cyano group through its π electrons. King and Bisnette[14] also obtained the unusual trinuclear complex $(C_5H_5)_3Fe_3(CO)_4(CH_3NCO)$, the $\nu(C\equiv N)$ of which shifted to lower frequencies by about 150 cm^{-1} as a result of π bonding of the isocyanate to the iron atom. All these observations strongly support our interpretation that the cyano groups in our compounds reported with diethylaminoacetonitrile in this publications are π bonded to the metal atoms.

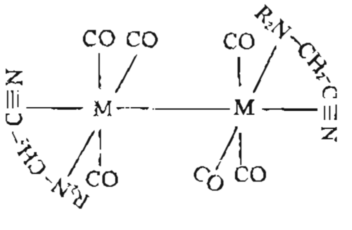
There is one more feature of the infrared data (Table II) which merits comments. It will be noted that for the compounds of the types A, B or C absorption bands in the bridging carbonyl region are absent. This leads to the conclusion that either the two metal atoms are held together by metal-metal bond or by a bridging ligand or by both. To investigate the above mentioned possibilities we prepared a sodium derivative $[Cr(CO)_3 . (C_2H_5)_2NCH_2CN]Na$ and an iodine derivative $[W(CO)_3 . (C_2H_5)_2NCH_2CN]I$ by cleaving the metal-metal bond of the compounds $[Cr(CO)_3 . (C_2H_5)_2NCH_2CN]_2$ and $[W(CO)_3 . (C_2H_5)_2NCH_2CN]_2$ respectively by the methods used by Abel *et al.*[10] Since the infrared spectrum of the sodium derivative $[Cr(CO)_3 . (C_2H_5)_2NCH_2CN]Na$ stays very similar to its parent compound in the $\nu(C\equiv N)$ and $\nu(C\equiv O)$ regions as well as in the CsI region it seems reasonable to believe that the ligand molecules do not bridge but only chelate on the metal atoms. In fact such binuclear compounds with metal-metal bonds have been reported by earlier workers.[10-11].

In order to check the validity of our hypothesis and propose structures we calculated the expected number of infrared active bands in molecules with different possible symmetries and the results of our calculations are found in Table IV. From the actual spectra observed it is difficult to differentiate pure $C\equiv O$ stretching bands from the combination bands.[15] The possibility of observing combination bands in the lower region is lesser than in the upper region. In the lower region we observed a number of bands which is in qualitative agreement with the proposed structures. Moreover, one band which really permits us to discriminate reasonably between possible structures is the $C\equiv N$ stretching frequency band. For the dinuclear structure, one should observe for all possibilities, except one, two $\nu(C\equiv N)$ bands but we observed only one and therefore propose C_{2h} symmetry and a symmetrical *trans*-structure of the dinuclear molecules. For the mononuclear sodium derivative we observe the same number of bands as for the C_{2h} symmetry which also corresponds to our previous observation on the parent compound. For the trinuclear structure we observed, as expected, two $\nu(C\equiv N)$ bands which indicates that all three ligands are symmetrically attached.

On the basis of the foregoing discussion of the results it seems reasonable to propose for these new compounds, the following structures.



Compound B



Compound A

Due to poor solubility of the C compound its molecular weight could not be determined and, therefore, its structure cannot be proposed.

Acknowledgment. The authors gratefully acnowledge the continued financial assistance from the National Research Council of Canada. The authors are also thankful to Dr. Surjit Singh for his helpful discussion of the IR spectra.

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