Molybdenum(V).—Since molybdenum(V) absorbs at 425 and 350 mμ, the formation constant for the 1:1 molybdenum(V)–cysteine complex was calculated in the following manner: At the maximum point on the Job's method plot the total absorbance (A_T) is due to the complex [C] and the free molybdenum(V) species (M)

$$A_T = \epsilon_C[C]b + \epsilon_M[M]b \qquad (5)$$

where ϵ_C is the molar absorptivity for the complex. This was obtained from the Job's method plot at low mole fractions of Mo(V) where essentially all the metal ion is in the form of the complex. ϵ_M is the molar absorptivity for Mo(V). This was obtained from the plot of [Mo(V)] *vs.* absorbance. b is the path length.

Equations can be written for the total concentration M_T of molybdenum(V) and the total concentration L_T of cysteine at this point.

$$M_T = [M] + [C] \qquad (6)$$

$$L_T = [L] + [C] \qquad (7)$$

where [L] = total uncombined ligand concentration. Combining eq. 5, 6, and 7 and solving for [C] gives

$$[C] = \frac{A_T - \epsilon_M M_T b}{b(\epsilon_C - \epsilon_M)} \qquad (8)$$

Using the values of [C], [M], and [L] thus obtained, and the dissociation constants for cysteine, the formation constant was calculated with eq. 9.

$$K = \frac{[MoL]}{[Mo][L_1^-]} \qquad (9)$$

The value for log $K_{Mo(V)}$ was found to be 6.0 ± 0.1.

In conclusion, the 3:1 complex with molybdenum(VI) involves the ionized mercapto group and most likely the carboxyl group. In addition, complexes of similar stability are formed with related compounds involving the mercapto and amino groups. Thus, it would appear that molybdenum(VI) could complex with cysteine-containing enzymes, perhaps binding between the mercapto group and a free carboxyl or amino group. Further work involving small peptides to determine this is planned.

In view of the weakness of the molybdenum(V)–cysteine complex and its ease of oxidation it is unlikely that interaction of molybdenum(V) and sulfhydryl enzymes in this manner is of any biological significance.

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Infrared Spectra and Structures of Some Metal Hexacarbonyl Derivatives[1]

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The carbonyl stretching frequencies for a variety of substituted metal hexacarbonyls are reported, and the type of bonding to be expected in such complexes is discussed briefly. Arguments are given to show that $W(CO)_4(CH_3CN)_2$ and $W(CO)_3(CH_3CN)_3$ exist as the *cis* and symmetrical isomers, respectively, and that the acetonitrile ligands are attached to the metal by coördinate bonding through the nitrogen rather than by π-bonding through the CN group.

Introduction

When solutions of metal hexacarbonyls (M = Cr, Mo, W) in non-aromatic solvents are exposed to ultraviolet radiation, color changes, usually to yellow, are observed. In most cases these changes have been found to be caused by the formation of new complexes in which one or more solvent molecules have replaced carbonyl groups. Several such complexes have been isolated, characterized, and their infrared spectra recorded.[2–5] The formation of such complexes is believed to proceed through the stepwise replacement of carbonyl groups after the initial photolytic formation of $M(CO)_5$.[2,6–8] Little has been done, however, with respect to the determination of the structures of complexes of this nature, although both the stereochemistry and the nature of the bonding between the solvent molecules and the metal atom where either coördinate covalent or π-bonding is possible, *e.g.*, with acetonitrile, would be of considerable interest. This paper will explore some of these problems using infrared spectroscopy as the principal tool.

In general it has been found that solvent molecule-substituted metal hexacarbonyls are somewhat unstable and that irradiated solutions containing the complexes exhibit a marked tendency to shift back to the original reactants after the irradiation is stopped.[2] Such properties render isolation of many complexes imprac-

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[1] This work supported by the United States Atomic Energy Commission under contract No. AT-(40-1)-2434.

[2] G. R. Dobson, I. W. Stolz, M. F. Amr El Sayed, and R. K. Sheline, *Inorg. Chem.*, **1**, 526 (1962).

[3] W. Strohmeier and K. Gerlach, *Z. Naturforsch.*, **15b**, 622 (1960).

[4] W. Strohmeier and G. Schönauer, *Chem. Ber.*, **94**, 1346 (1961).

[5] D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, **1**, 433 (1962).

[6] W. Strohmeier, *Chem. Ber.*, **94**, 398 (1961).

[7] A. G. Massey and L. E. Orgel, *Nature*, **191**, 1387 (1961).

[8] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Am. Chem. Soc.*, **84**, 3589 (1962).

TABLE I

CARBONYL STRETCHING FREQUENCIES FOR METAL HEXACARBONYL COMPLEXES

Complex	Medium	Carbonyl stretching frequencies[a]
$W(CO)_5(CH_3CN)$	*n*-Hexane	2083 (w), 1948 (s), 1931 (ms)
$W(CO)_4(CH_3CN)_2$	KBr	2021 (m), 1913 (s), 1874 (s), 1825 (s)
$W(CO)_3(CH_3CN)_3$	Nujol	1892 (s), 1776 (s)
$W(CO)_5$(dimethylformamide)	Dimethylformamide	2067 (w), 1917 (s), 1847 (ms)
$W(CO)_4$(dimethylformamide)$_2$	Dimethylformamide	1997 (m), 1858 (s), 1832 (sh), 1791 (s)
$W(CO)_5$(acetone)	Acetone	2067 (w), 1920 (s), 1847 (ms)
$W(CO)_5$(ethyl ether)	Methylcyclohexane	2074 (w), 1931 (s), 1908 (ms)
$W(CO)_5$(ethanol)	Ethanol	2078 (w), 1929 (s), 1885 (ms)
$Mo(CO)_5$(methylformamide)	Methylformamide	2072 (w), 1932 (s), 1862 (ms)
$Mo(CO)_5$(isopropyl ether)	Isopropyl ether	2079 (w), 1940 (s), 1893 (ms)
$Mo(CO)_5$(*n*-hexanol)	*n*-Hexanol	2080 (w), 1940 (s), 1895 (ms)
$Mo(CO)_5$(dimethylformamide)	Dimethylformamide	2068 (w), 1924 (s), 1847 (ms)

[a] Band intensities: s, strong; m, medium; w, weak; sh, shoulder.

tical and the experimental work therefore was limited mainly to the determination of the spectra in solution of the carbonyl stretching region of the infrared.

Experimental

Spectra were recorded on a Perkin–Elmer Model 221 prism-grating interchange infrared spectrophotometer and were standardized against the known peaks of polystyrene. A 0.38 mmole sample of the appropriate metal hexacarbonyl was dissolved in 40 ml. of solvent, this concentration giving a carbonyl stretching peak of about 100% absorption in the hexacarbonyl for a cell of 0.15 mm. thickness. The solution was placed in a bubbling apparatus which then was flushed with pure nitrogen for about 15 min. before the irradiation was started. Nitrogen also was bubbled into the solution for the duration of the irradiation. After irradiation with a water-cooled G.E. AH-6 mercury arc lamp for a suitable length of time, a solution sample was withdrawn from the bubbler with a syringe, placed in a fixed infrared cell with NaCl windows, and the spectrum immediately recorded. When spectra of solutions exposed for different lengths of time were desired, a fresh solution was prepared for each exposure. It was assumed that the complexes were formed through the stepwise replacement of the carbonyl groups as described in the Introduction, and the assignment of peaks to a particular species was made on this basis. Fresh samples of $W(CO)_5(CH_3CN)$, $W(CO_4)(CH_3CN)_2$, and $W(CO)_3(CH_3CN)_3$ also were prepared using methods described by Strohmeier[3] and Tate,[5] and the infrared spectra were recorded over the CN stretching region of the infrared (2400–2100 cm.$^{-1}$). The carbonyl stretching frequencies for $W(CO)_5(CH_3CN)$ reported in our previous work[2] were used; the spectra of $W(CO)_4(CH_3CN)_2$ and $W(CO)_3(CH_3CN)_3$ were retaken in KBr or in Nujol.

Discussion

The zero-valent oxidation state for the transition metals is believed to be stabilized by ligands which can accept back into vacant π or δ orbitals some of the charge ordinarily expected to accumulate on the central metal atom as the result of the formation of coördinate covalent bonds.[9] The acetonitrile ligand, compared to the carbonyl group, is both a better electron donor and a poorer charge acceptor, so that one should expect to find an increasing reluctance to further substitution after the first few acetonitrile groups are attached, as well as an increased polarity of the complexes as the number of substituted acetonitrile groups increases. Both these expectations are realized; even under drastic conditions no more than three CH_3CN groups replace carbonyls while acetylene ligands, which more nearly approach the carbonyl group in their coördinating properties, probably can replace all six carbonyls in $W(CO_6)$.[10] Moreover, *n*-hexanol, a ligand which can accept back no charge, forms only the monosubstituted complex. The solubilities of the acetonitrile complexes themselves show that polarity increases with more extensive substitution, due probably both to the inability of CH_3CN to effectively accept the charge built up on the metal atom, and to the polarity of the acetonitrile ligands themselves. Further support for this explanation of the bonding lies in the observed decrease of the carbonyl stretching frequencies as the extent of substitution increases (see Table I), indicating that the remaining carbonyls are forced to accept a greater portion of the charge on the metal (into antibonding π orbitals) to compensate for the better electron-donating and poorer accepting ability of the CN. The carbon–oxygen bond order is thus lowered and with it the CO stretching frequencies.

Such a simple picture of the nature of bonding also may be used to predict the stereochemistry in this series of complexes. Starting with an octahedral arrangement of carbonyl groups about the metal, replacement of any one by an entering CH_3CN group will undoubtedly leave a square pyramid of CO groups, and will give C_{4v} symmetry to the molecule. A consideration of the electronic nature of the acetonitrile group as compared to that of the carbonyls will show that the second acetonitrile group enters *cis* to the first. Charge donated by the first acetonitrile ligand (to a directionally oriented bonding orbital) results in the accumulation of more of this charge on the carbonyl group *trans* to the ligand than on the other four. In such a case, there is additional mixing between the bonding and antibonding π-orbitals of CO, especially at the *trans* position, which results in both a reduction of metal–CO antibonding character and an increase of antibonding π CO character.[11] Both effects render *trans*-substitution more difficult. The former strengthens the metal–*trans*-CO bond, and the latter, by placing greater charge on the *trans*-CO group, increases the electrostatic repulsion between the

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[9] L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 132–143.

[10] W. Hubel, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 208 (1959).

[11] W. F. Edgell, *et al.*, *J. Am. Chem. Soc.*, **82**, 1254 (1960).

CO and a potential incoming ligand. Alternately, one may arrive at the same conclusion by noting that the charge donated by the incoming ligand results in a greater contribution of the mesomeric form $M^{+}{=}C{=}O^{-}$ at the *trans*-position. *trans*-Substitution would be expected with ligands whose bonding properties stabilize the zero oxidation state approximately as well or better than do those of the carbonyl group, in accordance with the well known *trans* effect. A simple extension of these ideas leads to the prediction that the trisubstituted complex will be the symmetrical isomer.

A normal coördinate analysis has shown that one may expect to find three bands (two A_1 and an E) in the carbonyl stretching region of the infrared for a monosubstituted carbonyl of C_{4v} symmetry.[12] Of these three bands which are active in the infrared, the weaker of the two A_1 vibrations will be of highest frequency and will be separated from the strongest band, E, by 100–120 cm.$^{-1}$ for molybdenum complexes[13]; one is unable to predict the position of the stronger A_1 band.

These expectations are realized to a remarkable degree in the spectra of the several diverse monosubstituted hexacarbonyls reported in this paper. The separation between the weak A_1 and the E bands varies by only about 13 cm.$^{-1}$ among the complexes reported, although it is somewhat greater (137–150 cm.$^{-1}$) than the predicted 100–120 cm.$^{-1}$. The position of the stronger A_1 band, however, requires some comment. This band is produced by the vibration of the unique carbonyl group *trans* to the substituent and its position therefore should be affected by the electronic nature of a coördinately bonded ligand to a greater extent than are the positions of the other two bands. A poorer acceptor of metallic charge should cause a greater amount of the charge to be displaced into the vacant antibonding π-orbital of the *trans*-carbonyl, decreasing the stretching frequency. The stronger A_1 band for $[P(C_2H_5)_3Mo(CO)_5]$ is found at approximately the same frequency as is the E band,[14] but for ligands for which the charge-accepting ability is at best doubtful, we find that the frequency of this A_1 band is considerably lowered (see Table I).

The ligands acetone, dimethylformamide, and methylformamide do not appear to function as charge acceptors to an appreciable extent; the values observed for the strong A_1 bands with these ligands seem to be a function of their relative electron-donating power alone. The alcohols and ethers are structurally unable to act as charge acceptors.

The four bands observed in the spectrum of $W(CO)_4(CH_3CN)_2$ (Fig. 1) correspond to those predicted for the *cis*-isomer.[13] The spectrum itself is quite similar to those reported for (*o*-phenanthroline)$Mo(CO)_4$ and (α,α'-dipyridyl)$Mo(CO)_4$,[15] which probably are stabilized through charge acceptance by p_π delocalized orbitals. For these three complexes, the two vibrations attributable to the carbonyl groups *cis* to one another are at lower frequencies than are the corresponding bands for $[P(C_2H_5)_3]_2Mo(CO)_4$.[14] This shift appears to be due to the seemingly poorer charge accepting and/or electron-donating ability of the *o*-phenanthroline, acetonitrile, and α,α'-dipyridyl ligands compared to these properties for the triethylphosphine ligand; frequencies for CO vibrations *trans* to a substituted ligand (involving carbonyl groups *cis* to one another) are affected to a greater extent than are the others in a manner similar to that described for the monosubstituted complexes. The spectrum for the complex $W(CO)_4$(dimethylformamide)$_2$ shows the bands attributable to carbonyls *cis* to one another at still lower frequencies than are the corresponding bands for complexes with the acetonitrile, α,α'-dipyridyl, and *o*-phenanthroline ligands, implying that this ligand has an electronic nature even more unlike CO than do the three ligands cited.

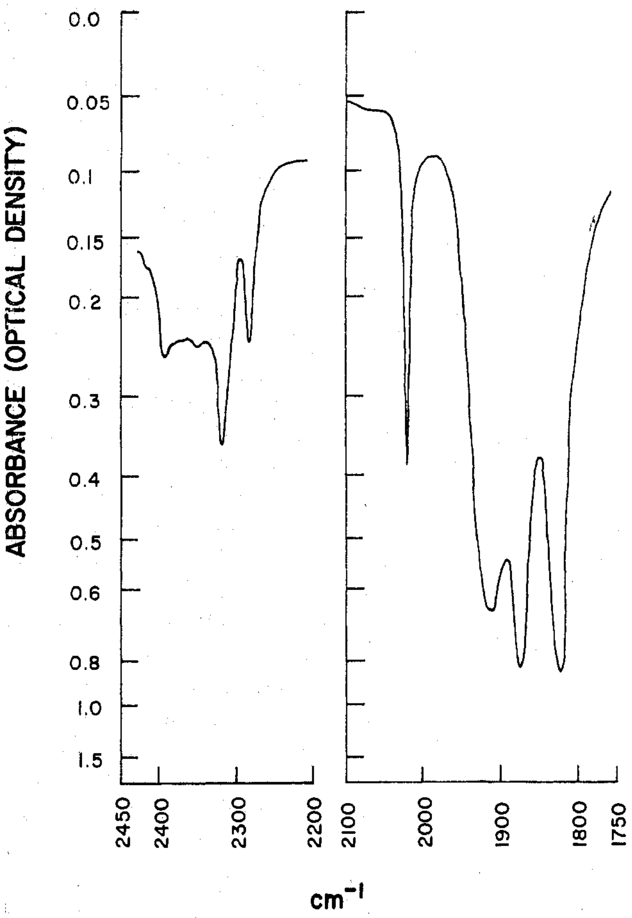

Fig. 1.—The C≡N and C≡O stretching regions of the infrared for $W(CO)_4(CH_3CN)_2$. The spectra were taken using KBr disks.

It seems quite likely that $W(CO)_3(CH_3CN)_3$ exists as the symmetrical isomer. For such a C_{3v} molecule, two bands, of A_1 and E symmetry, are predicted in the carbonyl stretching region of the infrared.[16] The observed spectrum (see Table I) is consistent with this

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(12) M. F. O'Dwyer, Doctoral Dissertation, Florida State University, 1959.

(13) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(14) R. Poilblanc and M. Bigorgne, *Compt. rend.*, **250**, 1064 (1960).

(15) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

(16) F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 175 (1955).

prediction. Furthermore, there is a marked similarity between the spectrum of $W(CO)_3(CH_3CN)_3$ and the spectra of many substituted hexacarbonyls of the type $(Ar)M(CO)_3$, where (Ar) is an aromatic group and M is Cr, Mo, or W.[17] Such π-bonded complexes must almost certainly contain symmetrically arranged carbonyl groups. Finally, one would expect symmetrical trisubstitution as the natural consequence of *cis*-disubstitution, as has been shown.

The last question involves the nature of the bonding between CH_3CN and the central metal atom. Orgel[18] mentions that alkyl cyanides can form complexes involving the donation of π-electrons to form T-shaped bonds. The other alternative would involve the donation of the lone pair from the nitrogen to the metal to form a linear coördinate covalent bond. The first mechanism could be expected to drastically lower the CN stretching frequency. Coördinate bonding, on the other hand, should raise the CN stretching frequency somewhat from the 2254[19] cm.$^{-1}$ found in the free acetonitrile molecule. Gerrard[20] has explained this effect in terms of mesomeric forms possible in a free nitrile which can lower the CN bond order from that of a pure CN triple bond; differences in hybridization make such mesomerism impossible in bonded RCN. Coerver and Curran[21] have reported the C≡N stretching frequency for the addition complex $CH_3CN:BF_3$, which undoubtedly contains a nitrogen-to-boron coordinate bond, to be 2359 cm.$^{-1}$. If bonding is through the lone pair, we should expect that increased orbital mixing due to the influence of the negative charge on the metal to result in the successive lowering of the CN stretching frequencies from this value for the mono-, di-, and trisubstituted complexes. These frequencies are given in Table II, and exhibit such a trend.

TABLE II

THE CYANIDE STRETCHING REGION OF THE INFRARED FOR ACETONITRILE-SUBSTITUTED TUNGSTEN HEXACARBONYLS

Complex	Medium	Obsd. CN stretching freq.,[a] cm.$^{-1}$	Predicted CN stretching bands for linear W–$NCCH_3$ bonds
$W(CO)_5(CH_3CN)$	KBr	2347	1, (A_1)
$W(CO)_4(CH_3CN)_2$	KBr	2311 (s), 2282 (m)	2, (A_1, B_1)
$W(CO)_3(CH_3CN)_3$	Nujol	[2276 (sh)], 2255 (m), 2215 (s)	2, (A_1, E)

[a] Band intensities: s, strong; m, medium; sh, shoulder.

Evidence for the linearity of the metal–$NCCH_3$ bond, to be expected for bonding through the lone pair of the nitrogen, comes from a comparison of the number of CN stretching vibrations predicted for linear bonding and the number found experimentally in the three acetonitrile derivatives. Table II gives these data; the experimentally determined numbers of bands can be seen to correspond to the numbers predicted by theory (with the possible exception of a weak shoulder in $W(CO)_3(CH_3CN)_3$). Although evidence of this nature often is inconclusive because close-lying infrared bands often remain unresolved, agreement between the predicted and observed spectra in three cases constitutes a strong argument for metal–CN bond linearity, especially when considered in conjunction with the other evidence cited to support coördinate bonding.

[17] R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960).

[18] L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 135.

[19] M. F. Amr El Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).

[20] W. Gerrard, *et al.*, *J. Chem. Soc.*, 2182 (1960).

[21] H. J. Coerver and A. C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958)

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Organosulfur Derivatives of Metal Carbonyls. II.[1] The Reaction between Triiron Dodecacarbonyl and Certain Episulfide Derivatives

BY R. B. KING

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Triiron dodecacarbonyl reacts with cyclohexene sulfide in refluxing benzene to produce cyclohexene and purple-red diamagnetic volatile $Fe_3(CO)_9S_2$ (II). This carbonyl sulfide of iron is different from the $Fe_3(CO)_9S_2$ (I) obtained from $HFe(CO)_4^-$ and sulfite ion.[2] The new $Fe_3(CO)_9S_2$ (II) may also be synthesized from 3-chloropropylene sulfide and $Fe_3(CO)_{12}$ in about 50% yield.

Triiron dodecacarbonyl has been found to react with dialkyl sulfides, dialkyl disulfides, and mercaptans to give compounds of general formula $[Fe(CO)_3SR]_2$ (III),[2-4] with alkyl vinyl sulfides to give compounds of general formula $RSCH{=}CH_2 \cdot Fe_2(CO)_6$ (IV),[5] and with thiophene to give the sulfur-free material $C_4H_4Fe_2(CO)_6$ (V).[6]

In a further study of reactions between triiron dodecacarbonyl and organic sulfur compounds it has been found that triiron dodecacarbonyl reacts with certain episulfide derivatives to give the purple-red diamag-

[1] For part I of this series see R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

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