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Relative Labilities of Different Ligands L in Group VI Metal Carbonyl Derivatives of the Type $M(CO)_4L_2$

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The kinetics of the substitution with α,α'-bipyridyl (N–N) for the neutral ligands L in *cis*- and *trans*-disubstituted carbonyl derivatives of the group VI metals, $M(CO)_4L_2$, in toluene to form $M(CO)_4(N–N)$ have been studied over a range of temperature and entering group concentration. A first-order rate law is observed and the rate constants and activation parameters are reported and compared for compounds with different leaving groups. In accord with the generally positive values of activation entropy, a dissociative mechanism is proposed. For the *cis*-$Mo(CO)_4L_2$ derivatives, the group lability decreases with changes in L in the order: $PCl_3 \gg py \gg C_8H_{12} \backsim As(C_6H_5)_3 \geqslant P(C_6H_5)_3 > PCl_2C_6H_5 \geqslant Sb(C_6H_5)_3 \gg CO$. A comparison between the order of lability of the leaving groups and the CO stretching frequencies is presented. The reactivity order for analogous carbonyl derivatives involving the same ligands with different metals strongly depends on the nature of the central atom, the order being Mo > Cr > W. For the hexacarbonyl compounds this is related to the order of the strengths of the metal–carbon bonds as deduced from infrared studies. The results are discussed in terms of possible M–L π bonding.

Introduction

There is little work reported in the literature concerning the kinetic behavior of the coordinately bonded derivatives of the group VI metal carbonyls, whereas an increasingly large body of experimental data deals with the preparative and physicochemical properties.[1–7]

Mechanistic studies have been devoted to the labeled CO exchange reactions with $M(CO)_6$ (M = Cr, Mo, or W) in the gas phase. The processes were found[8,9] to be first order with respect to the complex, consistent with a mechanism involving the formation of a five-coordinated species, followed by rapid recombination

$$M(CO)_6 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M(CO)_5 + CO \qquad k_2 \gg k_1$$

An SN1-type mechanism was recently proposed for the reactions of $M(CO)_6$ with polydentate ligand entering groups having N and P as donor atoms and with monodentate ligands with N, P, As, and Sb as donors.[10,11] The CO substitution by di- or oligoolefins and aromatic hydrocarbons, L, is also first order in the substrate concentration.[12] Under the same experimental conditions, however, the values of the first-order rate constants were found to be somewhat different for the various entering groups, according to the different ability of L to compete with CO for the five-coordinated intermediate

$$M(CO)_6 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} M(CO)_5 \xrightarrow{+L_\pi} L_\pi M(CO)_5$$

The dissociative mechanism appears to be consistent with numerous observations concerning the chemical reactions of the hexacarbonyls induced by ultraviolet irradiation.[13–16] For the exchange reactions of the ligands of diolefin carbonyls, $(L–L)M(CO)_4$ (M = Cr or Mo), there is kinetic evidence for a mechanism involving a slow cleavage of the diolefin–metal bond, followed by the rapid attack of the entering groups on the coordinately unsaturated intermediate.[17]

Only recently has it been reported that $Mo(CO)_6$ undergoes CO replacement by phosphines and phosphites (at concentrations $>5 \times 10^{-2}$ *M*) following the two-term rate law

$$\text{rate} = (k_1 + k_2[\text{L}])[\text{complex}]$$

in which the k_1 path is believed to involve a dissociative process and the k_2 path is attributed to a bimolecular displacement.[18] Whereas the reaction of $Cr(CO)_4(N–N)$ (N–N = bipyridyl or substituted bipyridyl) with different phosphites (L) to form *cis*-$Cr(CO)_3(N–N)L$ follows a first-order rate law,[19] the analogous molybdenum and tungsten carbonyl derivatives undergo substitution reactions according to a two-term rate law.[20] Also, in this case, a seven-coordinated species is believed to be formed as an activated complex in the k_2 path. Some examples have been reported recently where different molybdenum arene (Ar) derivatives, $(Ar)Mo(CO)_3$, react with various neutral ligands to form *cis*-$Mo(CO)_3L_3$ and the rates of the re-

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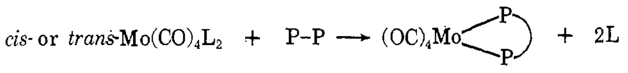
actions are first order in the concentration of both substrate and entering group. Occurrence of the displacement (SN2) mechanism is attributed to the nature of the Mo–Ar bond which can readily adjust to accommodate a pair of electrons from the entering group.[21] Similar behavior is shown by cyclopentadienyl- or nitrosylmetal carbonyls.[22,23]

For the reactions

$$Mo(CO)_4(C_8H_{12}) + 2L \longrightarrow cis\text{-}Mo(CO)_4L_2 + C_8H_{12}$$

the rates depend also on the concentration of both the complex and the entering groups.[24,25] On the other hand, a first-order rate law has been found for the reactions[24]



where P–P = $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$. The rates of reaction increase with changes in L in the order: $PCl_2(C_6H_5) \ll PCl_3$, for the *cis* isomers, and $P(OC_6H_5)_3 \ll P(C_6H_5)_3$, for the *trans* isomers.

To determine the relative labilities of different ligands L in group VI metal carbonyl derivatives, a kinetic investigation of the following reactions in toluene was undertaken

$$M(CO)_4L_2 + N\text{–}N \longrightarrow M(CO)_4(N\text{–}N) + 2L$$

where M = Mo or W and L = pyridine, phosphine, arsine, or stibine. For these reactions, which proceed by a dissociative mechanism, the dependence of the rate on the temperature has been recorded.

Experimental Section

Materials.—Reagent grade α,α'-bipyridyl (Fisher Scientific Co.) was used without further purification. Toluene was refluxed over sodium wire and then fractionally distilled. $Mo(CO)_4(C_8H_{12})$ was prepared following the method given in the literature.[26] The compounds $M(CO)_4(bipy)$ (M = Mo or W) were prepared following the method of Stiddard.[27] A previously reported method[28] was used to prepare the *cis*-$M(CO)_4(py)_2$ compounds. The *cis*-$Mo(CO)_4L_2$ compounds (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, or $Sb(C_6H_5)_3$) were prepared by adding, under nitrogen, a solution of the ligand in *n*-heptane to a solution of $Mo(CO)_4(C_8H_{12})$ in the same solvent. The method of Hieber and Peterhans[29] was used to prepare the *trans*-$M(CO)_4(P(C_6H_5)_3)_2$ derivatives.

The identity and purity of all of these compounds were confirmed by their elemental analyses and by their infrared spectra (Table I).

Kinetics.—The reactions were followed spectrophotometrically by measuring the changes of optical density in the range from 450 to 550 mμ of the spectrum over a period of time by means of an Optica CF-4 or a Beckman DK-2A double-beam recording apparatus. Freshly prepared solutions of the complex, stored under nitrogen in an aluminum foil wrapped flask, were used for each kinetic run. The reactions were started by mixing known volumes of standard solutions of the reagents in the thermostated (±0.1°) cell compartment of the spectrophotometer. In the case of slow reactions and at relatively high temperatures, the optical density was measured on samples of the thermostated reaction mixture removed at various times with an eyedropper. A solution containing the same concentration of ligand was used as a reference. Light and air were always excluded. To ascertain if the exposure of the reaction mixtures to the light in the spectrophotometer accelerated the reactions, duplicate runs were carried out in the case of *trans*-$Mo(CO)_4(P(C_6H_5)_3)_2$ by performing measurements of changes in infrared absorption intensities of the solutions. The rate data obtained by these two techniques show good agreement (see Table II), indicating that under these experimental conditions photochemical substitution does not occur. For the infrared measurements a Perkin-Elmer Model 621 spectrophotometer was used.

TABLE I

CO STRETCHING FREQUENCIES (CM^{-1}) OF THE PREPARED CARBONYL DERIVATIVES

Compounds	ν_{CO}		Solvent
cis-$Mo(CO)_4(P(C_6H_5)_3)_2$	2021 m	1927 s	*n*-Heptane
	1908 vs	1897 s	
cis-$Mo(CO)_4(As(C_6H_5)_3)_2$	2023 m	1926 s	*n*-Heptane
	1912 vs	1896 s	
cis-$Mo(CO)_4(Sb(C_6H_5)_3)_2$	2024 m	1934 s	*n*-Heptane
	1919 vs	1907 s	
cis-$Mo(CO)_4(py)_2$	2025 m	1907 s	CH_3CN
	1881 vs	1839 s	
cis-$Mo(CO)_4$bipy	2015 m	1907 vs	$CHCl_3$
	1878 s	1828 m	
trans-$Mo(CO)_4(P(C_6H_5)_3)_2$	1952 m	1903 vs	*n*-Heptane
cis-$W(CO)_4(py)_2$	2012 m	1888 vs	$CHCl_3$
	1869 vs	1828 s	
cis-$W(CO)_4$bipy	2010 m	1899 vs	$CHCl_3$
	1880 sh	1829 s	
trans-$W(CO)_4(P(C_6H_5)_3)_2$	1940 w	1887 vs	$CHCl_3$

The infrared analyses quite clearly show that only the disubstituted derivative is formed during the course of the reactions. The entering group was present in sufficient excess to provide pseudo-first-order rate constants, k_{obsd} (sec^{-1}), and to avoid complications from the reverse reactions. In these conditions all of the reactions proceed to completion and the "infinite" spectra were in good agreement with those of the products prepared and characterized independently. The values of k_{obsd} were obtained from the slope of the plot of ln $(A_\infty - A_t)$ *vs.* time, where A_t and A_∞ are the optical densities of the reaction mixture at time t and after 7–8 half-lives, respectively. The values of k_{obsd} were reproducible to better than 10%.

Results and Discussion

All of the reaction rates reported in this paper are concerned with the replacement of the first of the two ligands bonded to the metal in the complexes $M(CO)_4L_2$. There was no evidence, in fact, for a second step after the first stage of the reaction, and the final product was in every case the disubstituted derivative, $M(CO)_4(N\text{–}N)$. It is pertinent to note that in reactions involving polydentate entering groups the chelate ring generally closes very rapidly.[30,31] Consequently, the reactions can be described as

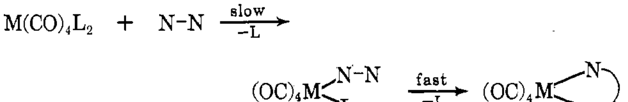


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TABLE II

RATES OF THE REACTION: $M(CO)_4L_2 + L\text{–}L$ (OR L') $\longrightarrow M(CO)_4(L\text{–}L)$ (OR $M(CO)_4L'_2$) + 2L IN TOLUENE SOLUTION AT DIFFERENT TEMPERATURES AND 0.005 *M* CARBONYL (RATE DATA FOR THE DISSOCIATIVE PATHWAY)

Carbonyl	L–L (or L′)	Solvent	Temp, °C	10^5k,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
$Cr(CO)_6$[b]	^{14}CO	Toluene	32	Very slow		
$Cr(CO)_4(bipy)$[c]	$P(OCH_2)_3CCH_3$	Chlorobenzene	37.8	4.9	28.6	+13.6
	$P(OCH_2)_3CCH_3$	1,2-Dichloroethane	37.8	13.7	23.4	−1.1
$Cr(CO)_6$[d]	^{14}CO	Gas phase	108.2	0.67	39	
trans-$Mo(CO)_4(P(C_6H_5)_3)_2$	bipy	Toluene	60	2.3	23.9	−8
	bipy	Toluene	70	6.8		
	diphos[j]	Benzene	60	2.9		
cis-$Mo(CO)_4(P(C_6H_5)_3)_2$	bipy	Toluene	40	7.2	26.2 ± 2.9	+6 ± 9.6
	bipy	Toluene	46.3	15		
	bipy	Toluene	50	28		
cis-$Mo(CO)_4(As(C_6H_5)_3)_2$	bipy	Toluene	40	18	26.8 ± 2.2	+9.8 ± 7.3
	bipy	Toluene	46.1	38		
	bipy	Toluene	50	71		
cis-$Mo(CO)_4(Sb(C_6H_5)_3)_2$	bipy	Toluene	50	2.5	22.8	−9
	bipy	Toluene	60	7.5		
cis-$Mo(CO)_4(py)_2$	bipy	Toluene	25	210	23.3 ± 0.2	+7.4 ± 0.7
	bipy	Toluene	30.8	450		
	bipy	Toluene	35	780		
cis-$Mo(CO)_4(PCl_3)_2$[e]	diphos	Benzene	25	Very fast		
cis-$Mo(CO)_4(PCl_2C_6H_5)_2$[e]	diphos	Benzene	60	21		
trans-$Mo(CO)_4(P(OC_6H_5)_3)_2$[e]	diphos	Benzene	60	Very slow		
$Mo(CO)_4(C_8H_{12})$[f]	bipy	Benzene	30.5	8	25	+5
	bipy	1,2-Dichloroethane	30.5	10	25	+5
	py[e]	Chloroform	25	7	24	+3
$Mo(CO)_4(bipy)$[g]	$P(OCH_2)_3CCH_3$	1,2-Dichloroethane	37.8	4.43	23.7	−2.3
	$P(OCH_2)_3CCH_3$	Chlorobenzene	37.8	1.74	28.9	+12.5
$Mo(CO)_6$[h]	$P(OC_2H_5)_3$	Decalin	97.8	6.22	31.7	+6.7
$Mo(CO)_6$[i]	^{14}CO	Gas phase	116	7.5	30.8	
trans-$W(CO)_4(P(C_6H_5)_3)_2$	bipy	Toluene	80	1.1	28.8	0
	bipy	Toluene	90	3.5		
cis-$W(CO)_4(py)_2$	bipy	Toluene	51	110		
	bipy	Toluene	60	300	23.2	−0.5
$W(CO)_4(bipy)$[g]	$PO_3C_6H_9$	Chlorobenzene	100	9.8	24.6	−12.5
$W(CO)_6$[i]	^{14}CO	Gas phase	142	0.257	40.4	

[a] As an average of a set of three or four values of k_{obsd} (sec^{-1}) obtained by changing the entering-group concentration in around a tenfold range. [b] See F. Basolo, *Chim. Ind.* (Milan), **43**, 403 (1961). [c] See ref 19. [d] See ref 8. [e] See ref 21. [f] See ref 25. [g] See ref 20. [h] See ref 18. [i] See ref 9. [j] diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

The pseudo-first-order rate constants, k_{obsd} (sec^{-1}), for the first stage of the reactions are independent of the concentration of the bipyridyl, so that a first-order rate law is obeyed: rate = k[complex]. The values of the rate constants, k (sec^{-1}), given in Table II, are averages of several runs over a tenfold range of concentration of the entering group. Also given in the table are the derived activation parameters. For comparison purposes we have reported the rate constants of dissociative processes (k, sec^{-1}) found by other authors for similar group VI metal carbonyl derivatives, including the ^{14}CO-exchange reactions of the hexacarbonyls in the gas phase.

The first-order rate law suggests a dissociative (SN1) mechanism, in accord with the generally positive activation entropies[32] and with the observed small solvent effect. This is expected, in fact, for a process involving the dissociation of a neutral ligand L in the rate-determining step.[33]

Although these reactions refer to dissociative processes which occur on substrates with different ligands L in the *cis* position to the leaving groups, the rate data can nevertheless be considered as a reliable index of the relative labilities of these groups. It certainly would be desirable to study the lability of the group L in the simplest of possible systems, $M(CO)_5L$. However, our attempts to use these complexes were frustrated by the fact that the substitution of L was never observed by treating $M(CO)_5L$ with neutral ligands L′. The *cis*-disubstituted product was, in fact, generally obtained. Thus, our attention was focused on a somewhat less desirable but nevertheless amenable series of complexes, *cis*-$M(CO)_4L_2$. The kinetic *cis* effect in these should be relatively small when L is a π-acceptor ligand. The groups in the *cis* position, in fact, are unable to compete on favorable terms with the leaving group for d electrons of the metal. This is found, for instance, for the reaction of *cis*-$Mn(CO)_4BrAs(C_6H_5)_3$ with $As(C_6H_5)_3$ to give *cis*-$Mn(CO)_3Br(As(C_6H_5)_3)_2$; the value of the first-order rate constant is $k_1 = 4 \times 10^{-5}$ sec^{-1}, which is practically the same as for the CO exchange of $Mn(CO)_5Br$ ($k_1 = 3.9 \times 10^{-5}$ sec^{-1}).[34] Apparently, a relatively larger *cis*

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effect is shown for the reactions of $Mn(CO)_4BrL$ with L′ to form the *cis*-$Mn(CO)_3BrLL'$ in tetrachloroethane, largely because of the steric properties of L. The k_1 values range from 77×10^{-5} sec^{-1} for L = $P(C_6H_5)_3$ to 3.1×10^{-5} sec^{-1} for L = $P(OC_4H_9)_3$. Similar results have been obtained for the analogous rhenium carbonyl derivatives. The change in only one ligand (from $P(C_6H_5)_3$ to $P(n\text{-}C_4H_9)_3$) in the octahedral *cis*-$Re(CO)_4BrL$ reacting with L′ to yield *cis*-$Re(CO)_3BrLL'$ gives values of k_1 which vary from 14×10^{-5} sec^{-1} to 3×10^{-5} sec^{-1}.[35]

On comparing the rate constants listed in Table II, there are two points to take into account in the discussion, namely, (i) the relative lability order of the different groups coordinately bonded to the same metal carbonyl and (ii) the role of the central atom in determining the reactivity of the carbonyl derivatives and the discriminatory power of different leaving groups.

Group Lability.—Looking at the data of Table II, it clearly appears that the solvent has practically no effect on the reaction rates and that the changes in the entropies of activation which accompany the reactions are roughly the same. Thus, any conclusion that can be drawn is independent of these two factors.

The greater reactivity of the *cis*-$Mo(CO)_4(P(C_6H_5)_3)_2$ isomer, relative to the *trans* isomer, may be due, in part, to the relief of the greater steric crowding in the former in going to the five-coordinate intermediate. It is of interest to recall that Wojcicki and Farona[36] were unable to prepare *cis*-$Mn(CO)_3L_2(SCN)$ for L = $P(C_6H_5)_3$ but were able to do so for L = $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$, where the larger size of the donor atoms places the phenyl rings further away from the metal. The smaller reactivity of *trans*-$Mo(CO)_4(P(C_6H_5)_3)_2$ may be due in part to the fact that in this compound the Mo–P bond strength is reinforced by increased d_π–d_π back-donation. On the other hand, in the *cis* isomer the phosphorus atom is unable to compete to the same extent with the *trans*-CO group for the d electrons of the metal and the rupture of the metal–ligand bond becomes easier. In attempting to rationalize the order of lability of the leaving groups in *cis*-$Mo(CO)_4L_2$ (for which the larger number of data are presently available), the comparison in Table III seems significant.

TABLE III

Complex	10^5k, sec^{-1}, toluene, 50°	CO stretching freq, cm^{-1}			
cis-$Mo(CO)_4(Sb(C_6H_5)_3)_2$	2.5	2024	1934	1919	1907
cis-$Mo(CO)_4(P(C_6H_5)_3)_2$	28	2021	1927	1908	1897
cis-$Mo(CO)_4(As(C_6H_5)_3)_2$	71	2023	1926	1912	1896
cis-$Mo(CO)_4(py)_2$	780 (35°)	2025	1907	1881	1839

Except for the first band, which remains essentially constant, the CO stretching frequencies decrease, indicating increasing π bonding to the CO groups, as the lability of the leaving group increases (an allowance has to be made for the solvent effect; see Table I). Listed in the same manner as the above, comparisons involving the same ligands with different metals, *e.g.*, the *trans*-triphenylphosphine and *cis*-pyridine complexes, do not show the same trends, but this is not surprising. Thus, although the energy of the activated complex has a great deal to do with the labilities of the L groups, we are inclined to believe that, apart from steric effects, the cleavage of the M–L bond should be the driving force of the reaction and that the group lability partly reflects the M–L bond strength. Rate data for the *cis*-$Mo(CO)_4L_2$ derivatives show that the labilities of the leaving groups decrease with changes in L in the order: $PCl_3 \gg py \gg C_8H_{12} \backsim As(C_6H_5)_3 \geqslant P(C_6H_5)_3 > PCl_2C_6H_5 \geqslant Sb(C_6H_5)_3 \gg CO$. The rate of replacement of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ was too small to measure. Incidentally, there is no relationship between this order and that found for some of these groups when they are incoming ligands in bimolecular displacements on molybdenum carbonyl systems.[24,25] As far as the group lability reflects the Mo–L bond strength, an explanation for the observed sequence may be offered in terms of the extent to which both σ and π bonding contribute to the Mo–L bond strength. This accounts for the relatively pronounced reluctance to dissociate of a strong π-bonding acceptor such as CO which, conversely, has a very poor σ-donating ability. Such a conclusion is somewhat different from that previously reached for some $Mo(CO)_4L_2$ phosphorus derivatives (based on the limited number of kinetic data obtained by using the infrared technique[24]) in which the σ-bonding Mo–P appeared to play a predominant role. The relatively low values of $\Delta S^{\ddagger}$ observed (<16 eu; see Table II) suggest that the bond breaking in the transition state should not be extensively developed. It should be noted that in the case of the olefin dissociation from $(C_5H_5)Mn(CO)_2(olefin)$ complexes, the activation entropies range from +12 to +35 eu.

For the replacement of L in $Ni(CO)_2L_2$, the process is also dissociative, but the case of Ni–L bond cleavage increases with decreasing basicity of L, suggesting that the Ni–L bond strengths are due primarily to σ bonding.[37] A behavior similar to the group VI metal carbonyl is exhibited by some olefin derivatives of manganese carbonyl. Thus, the relative lability of the olefin in complexes of the type $(C_5H_5)Mn(CO)_2(olefin)$ drastically decreases on going from propylene to the ethylene derivative. This has been interpreted as being due to the electron-releasing nature of the methyl group which, by overwhelming the steric acceleration, would decrease the amount of π bonding from the manganese to the olefin, resulting in a weaker manganese–olefin bond in the case of the propylene derivative.[32,38]

The Role of the Metal.—Data in Table II show that, for a given leaving group (*i.e.*, CO or py) the reactivity order is: Mo > Cr > W. It is of interest that the

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infrared absorption spectra of M(CO)$_6$ (M = Cr, Mo, or W) in the gaseous phase also indicate that the strengths of the metal–carbon bonds apparently do not follow the order of the periodic table.[39] In fact, in agreement with the observed bond distances,[40–42] the order of the force constants is: $F_{WC} > F_{CrC} > F_{MoC}$. From a recent study of the solvent effect upon the infrared spectra of these hexacarbonyls, it has been established that one should expect the same order of force constants in solution as in the gaseous phase, owing to the fact that the solvent shift of the fundamental vibration ν_{M-C} (ν_8) is very small. Moreover, there is clear evidence that the interaction between the hexacarbonyls and the solvent, polar or apolar, is practically the same.[43] Therefore, the observed differences in the reactivities should not be due to a different solvation of the substrates. At present, no satisfactory theory accounts for this behavior and further studies should be carried out, including group VII carbonyl derivatives.

It is of interest that the relative lability of a given leaving group L increases with increasing π-bonding capacity of L upon changing the metal. Thus, for py (which is a poor π-bonding ligand in these systems[4]) as the leaving group, the estimated relative labilities are $(k_{Mo}/k_W)_{py} = 35$, whereas for CO (which is a very strong π-acceptor and a poor σ-donor ligand) the calculated ratio is: $k_{Mo}: k_{Cr}: k_W = 500:200:1$. It seems that a delicate balance between the σ and π character of the M–L bond determines the observed kinetic sequence, unless the energy of the activated complex markedly depends upon the nature of the leaving group.

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Notes

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Infrared Spectra of Several Hydroxy-Bridged Complexes of Chromium(III) and Iron(III) from 650 to 80 Cm^{-1}[1a]

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Very little infrared data have appeared in the literature concerning the hydroxy-bridged complexes of the transition metals. The most extensive studies have been the work recently reported for the Cu(II) complexes.[2,3] This paper reports on an extension of this work to include the analogous complexes of Cr(III), Fe(III), and Co(III).

Single crystals of these materials cannot be readily grown, and this precludes making any X-ray structural studies. The infrared method can prove helpful, in such cases, to provide inferences as to the nature of the metal–ligand bonding. In particular, the infrared region from 650 to 80 cm^{-1} provides information concerning the metal–ligand vibrations. Other physical properties for these compounds, including magnetic susceptibilities, will be presented in a separate publication.[4]

Experimental Section

The hydroxy-bridged iron(III) complexes were prepared as previously described.[5–6] The hydroxy-bridged chromium(III) complex, $[(phen)_2Cr(OH)_2Cr(phen)_2](NO_3)_4 \cdot 5H_2O$, was prepared by the method of Inskeep and Benson.[7] The bipyridyl analogy was prepared by a similar method and the corresponding bromides were made from the nitrates by double decomposition. $K_4[(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2] \cdot 3H_2O$ was prepared by the method of Grant and Hamm[8] and $K_4[(C_2O_4)_2Co(OH)_2Co(C_2O_4)_2] \cdot 3H_2O$ according to the method Palmer.[9] The elemental analyses of all of these compounds follow. *Anal.* Calcd for $[(phen)_2FeOH]_2Cl_4 \cdot 4H_2O$ (I): Fe, 10.3; Cl, 13.1. Found: Fe, 10.4; Cl, 13.5. Calcd for $[(phen)_2FeOH]_2Br_4 \cdot 2H_2O$[10] (II): C, 47.1; H, 3.1; N, 9.2; Fe, 9.1, Br, 26.2. Found: C, 48.5 H, 3.3; N, 9.1; Fe, 9.1; Br, 24.7. Calcd for $[(phen)_2FeOH]_2(ClO_4)_4$[11] (III): C, 45.5; H, 2.7; N, 8.9; Fe, 8.8. Found: C, 45.8; H, 3.2; N, 8.9; Fe, 8.8. Calcd for $[(phen)_2FeOH]_2(ClO_4)_4 \cdot 6H_2O$: C, 42.0 H, 3.2; Fe, 8.2. Found: C, 42.7; H, 3.3; Fe, 7.8. Calcd for $[(phen)_2FeOH]_2(SO_4)_2 \cdot 9H_2O$[10] (IV): C, 47.2; H, 4.3; N, 9.2; Fe, 9.2. Found: C, 47.3; H, 4.2; N, 8.8; Fe, 9.2. Calcd for $[(phen)_2CrOH]_2(NO_3)_4 \cdot 5H_2O$ (V): C, 48.2; H, 3.7; Cr, 8.7. Found: C, 47.9; H, 3.4; Cr, 8.0. Calcd for $[(phen)_2CrOH]_2Br_4 \cdot 6H_2O$[10] (VI): C, 44.8; H, 3.6; N, 8.7. Found: C, 44.9; H, 3.7; N, 8.9. Calcd for $[(bipy)_2FeOH]_2(SO_4)_2 \cdot 7H_2O$[10] (VII): C, 44.1; H, 4.4; N, 10.3; Fe, 10.3. Found: C, 43.7;

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(1) (a) Based on work performed under the auspices of the U. S. Atomic Energy Commission; (b) Argonne National Laboratory, Argonne, Ill.; Mr. Wozniak was a summer student (1966) from St. Procopius College, Lisle, Ill.; (c) University of Newcastle, New South Wales, Australia.

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