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

CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY,
ARGONNE, ILLINOIS, AND THE UNIVERSITY OF NEWCASTLE,
NEW SOUTH WALES, AUSTRALIA

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

BY J. R. FERRARO,[1b] R. DRIVER,[1c]
W. R. WALKER,[1c] AND W. WOZNIAK[1b]

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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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H, 4.5; N, 9.9; Fe, 10.2. Calcd for $[(bipy)_2CrOH]_2(NO_3)_4 \cdot 3H_2O$[10] (VIII): C, 45.1; H, 3.8; N, 15.8; Cr, 9.8. Found: C, 45.0; H, 3.8; N, 15.0; Cr, 9.3. Calcd for $[(bipy)_2CrOH]_2Br_4 \cdot 5H_2O$[10] (IX): C, 41.0; H, 3.8; N, 9.6. Found: C, 41.0; H, 3.5; N, 9.6. Calcd for $K_4[(C_2O_4)_2CrOH]_2$[12] (XI): C_2O_4, 54.6. Found: C_2O_4, 55.3. Calcd for $K_4[(C_2O_4)_2CoOH]_2 \cdot 3H_2O$ (XII): C, 13.4; H, 1.1. Found: C, 13.4; H, 1.2.

The analyses for C, H, and N were made by standard microanalytical techniques.[13] Iron was determined gravimetrically as "oxinate" after fuming with an H_2SO_4–$HClO_4$ mixture. Chromium was determined volumetrically as dichromate.

The infrared spectra from 4000 to 650 cm^{-1} were obtained with a Beckman IR-12 spectrophotometer, using Nujol mulls and AgCl windows. A Perkin-Elmer Model 301 spectrometer was used for the region from 650 to 80 cm^{-1}, using Nujol mulls and high-density polyethylene windows.

Results and Discussion

The infrared results from 4000 to 650 cm^{-1} are very similar to those obtained for the related Cu(II) compounds[2] and other 2,2′-bipyridyl and 1,10-phenanthroline compounds.[14] The anion absorptions for the nitrate, perchlorate, and sulfate appear in the usual regions for ionic anions. Some splitting of ν_3 does occur in the sulfate and the perchlorate, but no forbidden frequencies are observed. The OH vibration is usually observed as a shoulder to the strong water band in the hydrates in the 3-μ region. This shoulder appears anywhere from 3400 to 3600 cm^{-1}, depending on the complexes. Characteristic changes in the ring C–C and C–N absorptions of the ligands[15] occur upon complexation.[2,3,14,16,17]

TABLE I

ASSIGNMENTS FOR HYDROXY-BRIDGED Fe(III), Cr(III), AND Co(III) COMPOUNDS

L_1 = 1,10-phenanthroline								L_2 = 2,2′-bipyridyl					Oxalato			
L_1	Fe(III)				Cr(III)		Assignments	Fe(III)		Cr(III)		Assignments	Cr(III) X(21)	Cr(III) XI	Co(III) XII	Assignments
	I	II	III	IV	V	VI		L_2	VII	VIII	IX					
620(W)	647(W)	645(VW)	649(Sh)	647(W)	656(W)	661(M)	LIGAND BANDS	657(M) 622(M)	647(M)	649(W)	652(M)	LIGAND BANDS			645(W)	H_2O BAND
			622(VS)				ν_4 of ClO_4^-									
	595(W,Br)	595(W,Br)		601(VW)			ν_4 of $SO_4^=$ + H_2O bands		595(M)			ν_4 of $SO_4^=$	595	599(M)		H_2O BANDS
					563(Sh) 556(M)	567(Sh) 554(S)	ν_{CrO}		559(VW) 542(VW)	559(M)	547(S)	ν_{FeO} in VII, ν_{CrO} in VIII, IX	543	547(S,Br)	577(Sh) 554(S)	ν_4 (M-O to oxalate) + ν_{MO} to OH bridge
	542(W,V Br)	542(W,Br)	542(VW) 506(VW)	559(VW) 542(VS,Br) 506(VW)			ν_{FeO}									
													485	484(S)	475(M)	Ring deformation + δ (OC = O)
404(M)	424(M)	424(M)	437(Sh) 422(M)	438(M) 424(M)	433(W)	435(M)	LIGAND BANDS + ν_2 of $SO_4^=$ in IV, and ν_2 of ClO_4^- in III	404(S)	437(M) 415(M)	420(W)	442(W) 417(W)	LIGAND BANDS + ν_2 of $SO_4^=$ in VII	415	411(S)	447(M)	ν_{M-O} to oxalate + ring deformation
					343(W)	350(M)	ν_{Cr-N}			378(W) 352(W)	378(W) 354(W)	ν_{CrN}	358		382(W) 346(W)	δ (OC = O)
													313	311(W)	324(W) 308(W)	Out-of-plane bending
	294(S) 279(M) 262(W) 254(M)	293(S) 281(W) 272(W) 262(S)	290(S) 272(Sh) 265(M)	293(S) 266(S)	278(VW) 265(VW)	276(VW) 264(W)	ν_{FeN} in I → IV δ_{NCrN}, δ_{CrOCr} in V, VI		294(W) 277(Sh) 261(VW)	290(W)	286(W)	ν_{FeN} in VII, δ_{NCrN}, δ_{CrOCr} in VIII and IX				
257(W) 240(M)		239(S) 217(W)	235(W)	235(VW) 221(VW)	240(VW)	238(VW)	LIGAND BANDS		241(W)					224(S)	252(VW)	δ_{MOM} to OH and to the oxalate lattice vibration
	199(VW)	203(S) 192(W)	203(S) 189(W)	210(M) 189(VVW)			δ_{NFeN}, δ_{FeOFe} in I → IV		210(VW) 191(M)			δ_{NFeN}, δ_{FeOFe} in VII			214(VW)	
146(M) 116(S) 89(W)						92(W,Br)	LIGAND BANDS	168(S) 98(M)			96(W,Br)	LIGAND BANDS			148(W,Br) 118(VW)	

Abbreviations: S = strong, V = very, Br = broad, M = medium, W = weak, Sh = shoulder.
Compound Legend: Legend according to that used in presenting analytical results.

Chromium Complexes.—For both the 2,2′-bipyridyl and 1,10-phenanthroline complexes the ligand bands in the 400- and 600-cm^{-1} regions are shifted to higher frequency. The results are similar to those observed for the related copper(II) complexes[2] and are probably caused by ring vibrations. The high-frequency shifts reflect the change in the electronic environment of the ring upon complexation.

A fairly strong absorption is observed in the 500-cm^{-1} region where the ligands are free of absorption. Inskeep and Benson[7] reported an absorption in this region for the compound $[(phen)_2CrOH]_2(NO_3)_4 \cdot H_2O$. Related chromium compounds, free of hydroxy bridging, lack this absorption.[7] It is therefore suggested that this absorption is caused by the ν_{CrO} vibration in the hydroxy-bridged ring. If D_{2h} symmetry is assumed for the compounds, two infrared-active modes are expected for the Cr–O stretching vibration. In some of the compounds a shoulder is observed on the main band.

Weak-to-medium bands are found in the 350–380-cm^{-1} region. These are suggested as the ν_{MN} vibrations. Several bands are observed in this region in agreement with expectations for D_{2h} symmetry. Assignments for ν_{CrN} in complexes with stronger basic ligands have been made at 470 cm^{-1} (*e.g.*, ammine

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(12) Dried at 110°; takes up 3 moles of water in air.

(13) Microanalyses were made by the Australian Microanalytical Services.

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complexes)[18] and at 364 cm^{-1} for the complex $[(C_2H_5)_4N]_3Cr(NCS)_6$.[19] As has been pointed out,[20] the frequency of a metal–ligand vibration will be highest for the most basic ligand. The ligands used in this study are weakly basic compared to ammonia, and thus the ν_{MN} vibration would be expected at a lower frequency.

Weak bands are found in the ~280-cm^{-1} region. The δ_{NMN} and the δ_{MOM} vibration would be expected to occur at lower frequency than the ν_{MO} or ν_{MN} stretching vibrations. Assignments for these compounds are presented in Table I.

The assignment for ν_{CrO} in the compound $K_4[(C_2O_4)_2CrOH]_2 \cdot 3H_2O$ and for the ν_{CoO} vibration in $K_4[(C_2O_4)_2CoOH]_2 \cdot 3H_2O$ is made with less assurance, for other vibrations occur in the same general region (Table I).

Iron Complexes.—Assignments for the hydroxy-bridged iron complexes are made in Table I. The ν_{FeO} vibration in the hydroxy-bridged ring is assigned at 500–550 cm^{-1}. The ν_{FeN} vibration is suggested at 270–290 cm^{-1}. For both vibrations several bands are observed. The ligands are free of absorption in these regions. Similar behavior of the ligand bands to that observed for the chromium compounds is noted as complexation occurs.

It should be indicated that the complexity of these compounds prevents any possible normal coordinate treatment from being made to make more quantitative assignments of the frequencies. Similarly, O^{18} or N^{15} analogs are difficult to prepare, and it is questionable as to how valuable the infrared results of these substances would be. Our assignments, therefore, must be considered to be tentative.

A comparison of the ν_{MO} and ν_{MN} data for the Cr(III), Fe(III), and Cu(II)[2,3] compounds is made in Table II.

TABLE II

COMPARISON OF ν_{MO} AND ν_{MN} VIBRATIONS FOR Cr(III), Fe(III), AND Cu(II)

	ν_{MO}, cm^{-1}	ν_{MN}, cm^{-1}
Cr(III)	547–567	343–378 (A and B ligands)[a]
Fe(III)	506–550	260–294 (A and B ligands)
Cu(II)	480–490[2]	270[2] (A ligand)
	500–515[3]	300[2] (B ligand)

[a] A = 2,2′-bipyridyl; B = 1,10-phenanthroline.

The decrease in frequency for ν_{MO} as one goes from Cr(III) to Fe(III) to Cu(II) is the expected behavior for these transition metals and has been observed for other complexes.[21,22] A comparison of the hydroxy-bridged oxalato complexes of Cr(III) and Co(III) shows that the suggested assignment for the ν_{MO} vibration (stretching modes to oxalate plus hydroxyl) is at 565 cm^{-1} for Co(III) and at 547 cm^{-1} for Cr(III). The predominantly M–O stretching mode[21] is found at 447 cm^{-1} for Co(III) and at 411 cm^{-1} for Cr(III). This is similar to the trends observed for the oxalato complexes of the trivalent transition metals.[21]

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CONTRIBUTION FROM THE GOVERNMENT RESEARCH LABORATORY,
ESSO RESEARCH AND ENGINEERING COMPANY,
LINDEN, NEW JERSEY 07036

Lanthanum and Yttrium Tungsten Bronzes

BY BARRET BROYDE[1]

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Two new tungsten bronzes, one containing lanthanum and the other yttrium, have been prepared and characterized in this laboratory. These materials have a cubic perovskite-type structure, are acid resistant, and are electrically conductive.

Experimental Section

The tungsten bronzes were prepared by thoroughly mixing the required proportions of the transition metal oxide powder with tungsten metal powder and tungsten trioxide powder to give the desired stoichiometry. The mix was pelletized and sealed into a quartz tube under 5 × 10^{-4} torr. The tubes were heated in either a Leco or a Lindberg tube furnace at 1100° for 72 hr. They were cooled under ambient conditions to room temperature. This took about 20 min. In some cases the pellets were ground and pressed again every 24 hr but it was found that this did not change the results. The pellets remained intact during the heating. Less than 25 mg was lost from the pellets during the preparation, indicating that the resulting stoichiometry was quite close to that of the mix. Preparations normally were made in 9–10-g batches.

Reagents.—The yttrium and lanthanum oxides were obtained from the Rare Earth Division of the American Potash and Chemical Corp. and were at least 99.999% pure. Tungsten metal (0.70 μ) and tungsten trioxide (Grade TO-1) were obtained from the Chemical and Metallurgical Division of Sylvania Electric Products, Inc. Scandium oxide was 99.95% pure and was purchased from Leico Industries, Inc.

The scandium group oxides were ignited for 4 hr at 1000° prior to use.

X-Ray Investigation.—The products of the above preparations were examined for homogeneity both by microscopy and by X-ray powder methods. No materials were obtained that showed inhomogeneity in one method of examination but not the other. X-Ray studies were made with a Norelco X-ray diffractometer, Type 12045-6, modified for use with an Advanced Metals Research Corp. curved crystal focusing monochromator, Model 3-202. The copper Kα lines were detected with a Norelco scintillation counter attachment, Type 52245.

Results and Discussion

A homogeneous cubic perovskite-type structure is found for La_xWO_3 when x is between 0.08 and 0.19. Powder X-ray diffraction data show that the cubic lattice parameter increases in a nonlinear manner with x from 3.829 to 3.845 A in this region. Below x = 0.08 a tetragonal structure also appears, and at x = 0.02 it occurs as a pure form with lattice parameters of a = 7.52 and c = 3.89 A. Above x = 0.19 two additional phases are present. One has the same X-ray pattern as $La_2W_3O_{12}$,[2a] while the other gives an X-ray diffraction pattern similar to WO_2.[2b]

Y_xWO_3 also exists in tetragonal and cubic forms. The range of x yielding homogeneous cubic structures

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[1] Western Electric Engineering Research Center, Princeton, N. J. 08540.

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