In subsequent cycles the input configuration(s) are altered until a self-consistent result is obtained. The result is considered self-consistent if the input and output configuration(s) for the cycle are practically the same. For example, in the final cycle of the MnO_4^- calculation using H_2O I.P., Mn input charge was +0.53, $d^{5.87}s^{0.23}p^{0.37}$, and output charge +0.60, $d^{5.81}s^{0.22}p^{0.37}$.

CONTRIBUTION NO. 1616 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Infrared Spectra of $(CO)_5Mn{-}Re(CO)_5$ and the Carbonyls of Manganese, Technetium, and Rhenium; Assignment of C≡O and M=C Stretching Absorptions[1]

BY N. FLITCROFT, D. K. HUGGINS, AND H. D. KAESZ

Received March 23, 1964

The infrared spectrum of $(CO)_5Mn{-}Re(CO)_5$ in the region 3000 to 290 cm.$^{-1}$ is reported and compared to the spectra of the parent carbonyls, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. An assignment of the carbonyl and metal–carbon stretching bands for these compounds is proposed. The spectrum of $Tc_2(CO)_{10}$ in the region 800–290 cm.$^{-1}$ is reported for the first time.

Introduction

Recent determination under high resolution of the infrared spectra in the carbonyl stretching region of the carbonyls of Mn, Tc, and Re[2] has shown that their band patterns were similar but not superimposable. We were interested, therefore, to compare the absorptions in the new mixed metal carbonyl $(CO)_5Mn{-}Re(CO)_5$[3] to those in the parent carbonyls and if possible to assign these to the expected carbonyl stretching modes. Also, we have extended the comparisons between the mixed metal carbonyl and the parent carbonyls to the low energy region, 800–290 cm.$^{-1}$, and were able to scan this for $Tc_2(CO)_{10}$ for the first time.

Experimental

Preparation of Carbonyls.—$Mn_2(CO)_{10}$ was obtained from the Ethyl Corporation and resublimed before use. $Re_2(CO)_{10}$ was prepared as described earlier.[2] The new mixed metal carbonyl was prepared according to the Russian work,[3] from the treatment of $NaMn(CO)_5$ (from $Mn_2(CO)_{10}$ and Na–Hg)[4] in tetrahydrofuran with $Re(CO)_5Cl$ (from $Re_2(CO)_{10}$ and Cl_2).[2] After 24 hr. of stirring, the ether was removed under reduced pressure and cyclohexane brought in. The resulting solution gave a number of new bands in addition to a set of bands which were identically superimposable with those of $Mn_2(CO)_{10}$. Air oxidation of the solid product for about 4 days removed the $Mn_2(CO)_{10}$ (as observed through infrared spectra in cyclohexane solution). The product thus obtained was purified by sublimation at 0.5 mm. and 50°. The new derivative is resistant to air oxidation over short periods, in which it resembles $Re_2(CO)_{10}$. A purified sample was analyzed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Anal. Calcd. for $MnRe(CO)_{10}$: C, 23.04; Re, 35.73; Mn, 10.54; mol. wt., 521. Found: C, 23.26; Re, 35.00; Mn, 10.31; mol. wt., 538 (determined with a Mechrolab vapor pressure osmometer for a solution containing 59.3 mg. of compound in 6.42 g. of cyclohexane; molality interpolated from a log ΔR *vs.* log m plot using benzil as standard; we are indebted to Mr. J. M. Smith of this Department for assistance).

$Tc_2(CO)_{10}$ was prepared as described previously.[2]

Infrared Absorptions.—Using a combination of instruments, we were able to scan the region 3000–290 cm.$^{-1}$ in the infrared; the maxima observed are listed in Table I. The bands in the carbonyl stretching region, 2200–1900 cm.$^{-1}$, were much stronger than the other bands in the spectrum and also were greatly distorted by the pellet technique described below so they were observed separately in dilute cyclohexane solution. Samples of about 4×10^{-5} mole/ml. were taken to read the maxima of the weak carbonyl bands (and of about a tenfold dilution for the strong peaks) in cells of 0.081-mm. sample thickness. A Beckman I.R.-4 equipped with a LiF prism was used under the same instrumental conditions and calibration of spectra as described previously.[2] The absorptions for the mixed metal carbonyl in this region are shown in Fig. 1 along with those of the parent carbonyls for comparison at two concentrations. Spectra for the parent carbonyls have been reported before, but at lower resolution,[5] and for the parent carbonyls and technetium carbonyl at higher resolution but lower intensity[2] such that the weaker bands were not observed.

For all but the carbonyl stretching region, it was convenient to scan the samples in a KBr pellet; solubility problems were avoided for observations on the weaker bands, and KBr is essentially transparent in the entire region 3000–290 cm.$^{-1}$ for disks of approximately 0.2 to 0.3 mm. thickness. Most of the bands in this region other than the carbonyl stretching frequencies suffered little or no distortion with this sampling technique, and the few that looked suspicious could often be checked in cyclohexane solution. The suspicious features of the spectra are appropriately marked in Table I. The pellets contained carbonyl in about 1% concentration by weight to read the maxima of the strong bands, and 4% by weight for the weaker ones. The region 3000–580 cm.$^{-1}$ was scanned with a Perkin-Elmer 421, equipped with a ruled grating. The spectra in the region 900–290 cm.$^{-1}$ were scanned with a Beckman IR-5A, equipped with a CsBr prism, and are shown in Fig. 2. The natural broadness of the absorptions limited the reproducibility in reading the maxima to within 3 cm.$^{-1}$ in this region, which we have found to be the reproducibility of the instrument in this range without further calibration of each individual spectrum.

In the other parts of the region scanned here, *i.e.*, 3000–2200

---

(1) This work has been supported in part by Grant No. GP 1696 from the National Science Foundation.

(2) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).

(3) A. N. Nesmeyanov, K. N. Anisimov, H. Ye. Kolobova, and I. S. Kolomnikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 194 (1963).

(4) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 198 (1963).

(5) F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 141 (1956).

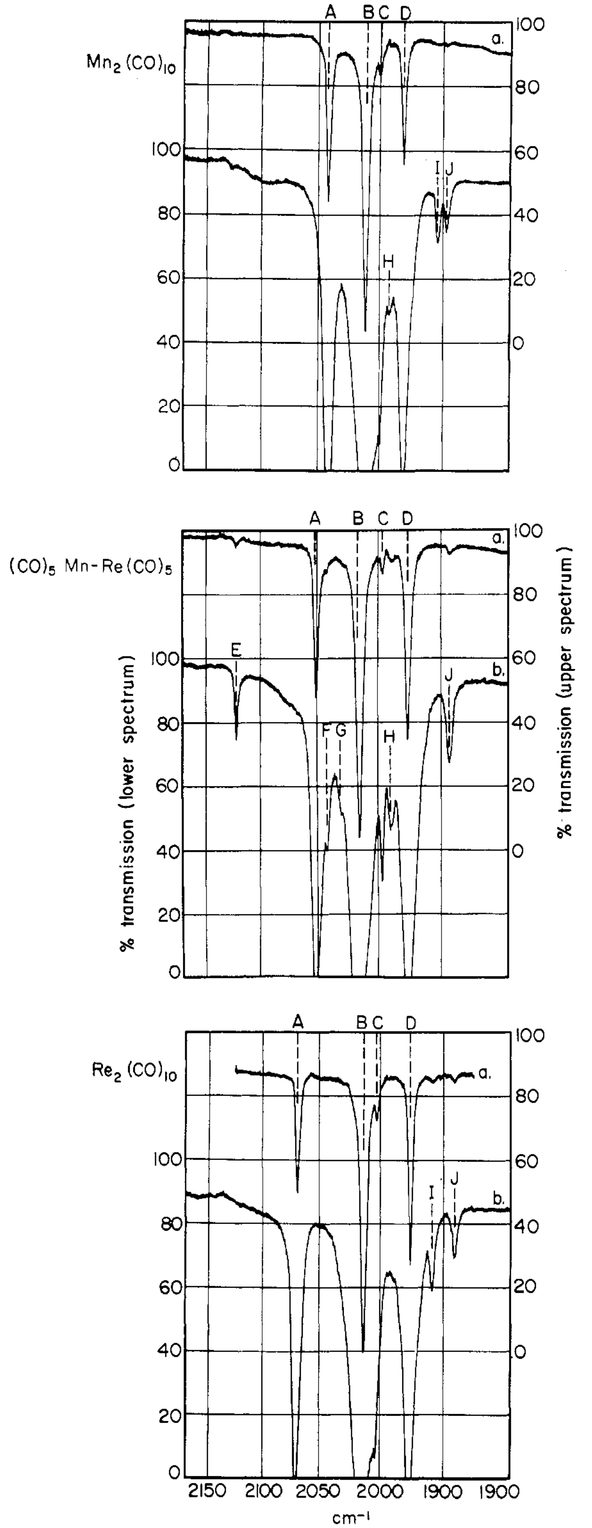


Fig. 1.—High resolution infrared spectra in the carbonyl stretching region for dimetal decacarbonyls, LiF prism, cyclohexane solution, 0.08-mm. path length: a, 3 μmoles/ml.; b, $Mn_2(CO)_{10}$, 54 μmoles/ml.; $(CO)_5Mn–Re(CO)_5$, 40 μmoles/ml.; $Re_2(CO)_{10}$, 32 μmoles/ml.

and 1900–900 cm.$^{-1}$, only weak bands occurred; these are listed in Table I but are not reproduced.

Table I

Infrared Absorptions for Carbonyls in the Region 3000–290 cm.$^{-1}$

$Mn_2(CO)_{10}$	$(CO)_5Mn-Re(CO)_5$	$Tc_2(CO)_{10}$	$Re_2(CO)_{10}$
KBr pellet, Perkin-Elmer 421[a]			
2585 vw	2600 vw	2620 vw	2590 vw
	2515 vw	2510 vw	2510 vw
2450 vw	2440 vw	2410 vw	2415 vw
2390 vw	2380 vw		
Cyclohexane soln., Beckman I.R.-4, LiF prism[b]			
J 1949 vw	J 1945 vw	J 1950 vw	J 1942 vw
I 1956 vw		I 1964 vw	I 1959 vw
D 1983 m	D 1978 m	D 1984 m	D 1976 m
H 1993 vw	H 1992 vw	H 1997 vw	
C 2001 w	C 1998 w	C 2006 w	C 2003 w
B 2013 vs	B 2017 vs	B 2017 vs	B 2014 vs
	G 2031 vw		
	F 2044 w		
A 2044 m	A 2054 m	A 2065 m	A 2070 m
	E 2124 w		
KBr pellet, Perkin-Elmer 421[a]			
1232 vw			
1195 vw	1206 vw		
1176 vw			
1103 vw	1086 vw	1081 vw	1086 vw
1023 vw	1033 vw	1037 vw	1044 vw
	964 vw	947 vw	964 vw
909 vw	937 vw		
888 vw	904 vw	887 vw	933 vw
	851 vw		
Cyclohexane soln., Perkin-Elmer 421[c]			
649 s	665 s	595 s	590 s
643 s	653 s		
	598 s		
	590 sh		
KBr pellet[c] and cyclohexane soln.,[d] Beckman I.R.-5A, CsBr prism			
705 vw			
655 sh	662 s		
637 s	652 s	(606 sh)[d]	
	592 s	589 s	586 s
557 vw	559 vw	527 w	538 w
470 m	540 vw	500 vw	473 w
429 vw	477 w	485 vw	436 w
401 w	411 w	445 vw	(404 sh)[d]
	388 m	427 sh	398 m
	348 w	416 w	(388 sh)[d]
		392 m	

[a] Absorptions not reproduced here; relative intensities correspond to per cent transmission as follows: w, 5–10%; vw, <5%. [b] See Fig. 1 for spectra and band designations; relative intensities do not necessarily correlate with the rest of the table, as the absorptions in this region were of the order of about five to ten times as strong as the next most intense absorptions. [c] See Fig. 2 for reproduction of spectra; in the region 700–580 cm.$^{-1}$ in which the Beckman I.R.-5A overlapped with the Perkin-Elmer 421, the latter gave slightly better resolution; for instance, note band near 640 cm.$^{-1}$ for $Mn_2(CO)_{10}$ taken in cyclohexane solution on both instruments (Fig. 2, traces a and b). Most bands labeled w or vw in this region could be seen only in KBr pellets of about 4% concentration of sample by weight, which are not reproduced here. [d] Shoulder in KBr pellet, not observed in cyclohexane solution; some slight shifts in maxima of the order of 2 to 6 cm.$^{-1}$ were observed for some bands in going from KBr pellet to cyclohexane solution.

Discussion

We will consider two prominent features of the spectra: (i) in the carbonyl stretching region, 2200–1900 cm.$^{-1}$, the mixed derivative gives a pattern basically no different from that of the parent carbonyls, but (ii) in

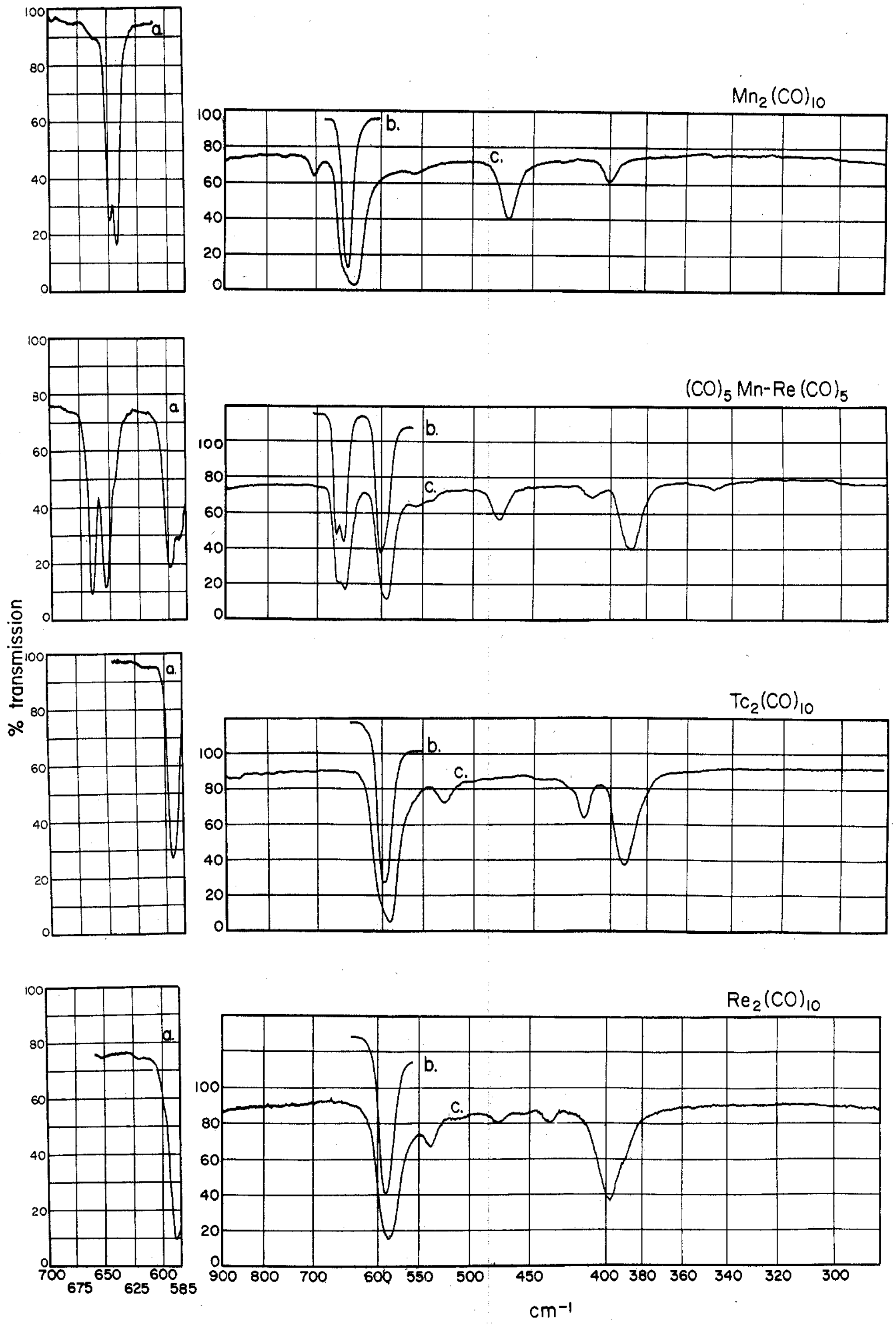


Fig. 2.—Infrared spectra in the low energy region for dimetal decacarbonyls: a, Perkin-Elmer 421, ruled grating, cyclohexane solution, 0.4-mm. path length, 4 mmoles/ml.; b, Beckman IR-5A, CsBr prism, cyclohexane solution, 0.4-mm. path length, 4 mmoles/ml.; c, Beckman IR-5A, CsBr prism, KBr pellet, 0.03 mmole/g.

the lower energy region, 700–320 cm.$^{-1}$, the mixed carbonyl shows two sets of absorptions where only one of each was present in the parent carbonyls. These lead to some useful generalizations concerning the interpretation of spectra of polynuclear carbonyls.

Vibrational Analysis of Metal Carbonyls.—The structure of the parent carbonyls has been determined by single-crystal X-ray diffraction.[6] This may be approximated for the purposes of vibrational analysis to the one shown in Fig. 3, in which the internal coordinates for the carbonyl bond stretching motions are also shown. In the refined structure for $Mn_2(CO)_{10}$,[6a] it is seen that the radial carbonyl groups on each metal (in staggered conformation) are bent out of the plane to-

---

[6] (a) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963); (b) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

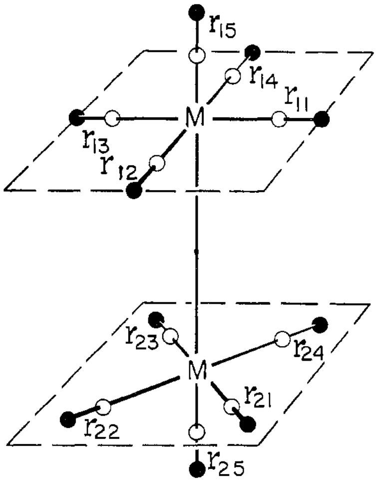


Fig. 3.—Structure and internal coordinates of carbonyl groups for $M_2(CO)_{10}$, M = Mn, Tc, or Re: M, metal atoms; O, carbon atoms; ●, oxygen atoms.

ward each other, but this has no effect in assigning the structure to a point group, which is D_{4d} for the one shown in Fig. 3.

A simplified vibrational analysis has been carried out from symmetry properties and group theory, and the results are summarized in Table II. First, the total number of modes in each representation is calculated. Then, considering the carbonyl groups as point masses, the number of skeletal modes is obtained, which, when subtracted from the total, gives the number of modes characteristic of the motions of the carbonyl groups. The carbonyl stretching modes are constructed from the internal coordinates,[7] as shown in Table III and illustrated in Fig. 4. These have recently appeared elsewhere[8] and have also been mentioned before.[6b] In an even earlier analysis,[5] only two infrared active carbonyl stretching modes were put forward for a structure of D_{4d} point group for dimetal decacarbonyls. As a consequence of this and other factors, the correct structure was passed by in that earlier work which predated the first X-ray structure determination.[6b]

Table II

Number and Representation of the Expected Infrared Active Vibrations of Dimetal Decacarbonyls

Species	Number of modes: Total	Skeletal	C≡O stretch	C≡O deformation
	$M_2(CO)_{10}$, D_{4d} point group			
b_2	6	3	2	1
e_1	8	4	1	3
	$(CO)_5Mn\text{-}Re(CO)_5$, C_{4v} point group			
a_1	13	7	4	2
e	16	8	2	6

For the derivative $(CO)_5MnRe(CO)_5$, a structure like that shown in Fig. 3 may reasonably be anticipated, but this would belong to the C_{4v} point group. Due to the properties of this group, the internal coordinates of the carbonyl groups on one metal are not transformed into those on the other and the calculations lead to internal symmetry coordinates for the carbonyl stretching modes for *each* $M(CO)_5$ group which are of the same number (3) and type (a_1 and e) previously shown for $LM(CO)_5$ derivatives.[9] We therefore expect six infrared active normal carbonyl stretching modes as listed in Table II. In these we would have the same motions as for an $LM(CO)_5$ derivative, but repeated for each of the two different $M(CO)_5$ groups, and they need not be shown here.

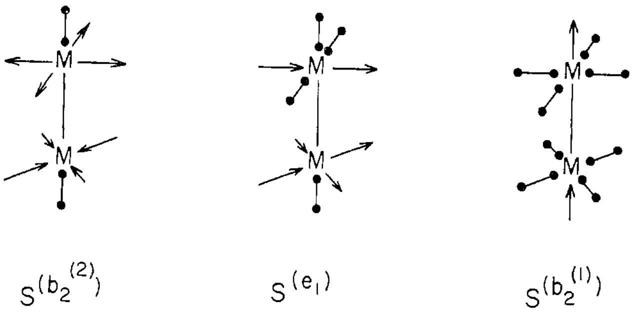


Fig. 4.—Relative orientation of internal coordinates for carbonyl bond stretching modes in the infrared active species of the D_{4d} point group for $M_2(CO)_{10}$, M = Mn, Tc, or Re.

Table III

Internal Symmetry Coordinates for C≡O Stretching Modes for $M_2(CO)_{10}$, D_{4d} Point Group[a]

$$S^{(b_2^{(2)})}{}_{\text{radial}} = \frac{1}{2\sqrt{2}}(r_{11} + r_{12} + r_{13} + r_{14} - r_{21} - r_{22} - r_{23} - r_{24})$$

$$S^{(b_2^{(1)})}{}_{\text{axial}} = \frac{1}{\sqrt{2}}(r_{15} - r_{25})$$

$$S^{(e_1)}{}_{\text{radial}} = \frac{1}{2\sqrt{2}}(\sqrt{2}r_{11} - \sqrt{2}r_{13} + r_{21} + r_{24} - r_{22} - r_{23})$$

[a] See ref. 7.

Assignment of the Bands in the CO Stretching Region for $M_2(CO)_{10}$.—For derivatives $M_2(CO)_{10}$ we observed, as expected, three principal carbonyl stretching absorptions, bands A, B, and D, upper traces, Fig. 1. We also obtained spectra at higher concentrations (lower traces, Fig. 1) in anticipation of comparisons we would make with the spectrum of $(CO)_5MnRe(CO)_5$, discussed below. We assign band B to the e_1 mode and bands A and D to the b_2 modes, though we defer for the moment to make any distinction between axial and radial carbonyl motions in the modes of the b_2 species. This assignment is based on the relative band intensities and also is arrived at by an analogy to previous assignments for $LM(CO)_5$ derivatives[9] whose spectra in this region bear some similarity to the present spectra (and whose symmetry species, e and a_1 of C_{4v} point group, are related, respectively, to those of the D_{4d} point group).

This assignment may be verified through a calculation of approximate force constants after the method of

---

(7) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 117–125.

(8) A. G. Osborne and M. B. H. Stiddard, *J. Chem. Soc.*, 634 (1964).

(9) (a) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962); (b) R. Poilblanc and M. Bigorgne, *Bull. soc. chim. France*, 1301 (1962); (c) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962); (d) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

Cotton and Kraihanzel.[10] For $M_2(CO)_{10}$, the $|\mathbf{F} - (\mathbf{G}^{-1})\lambda|$ matrix factored into the carbonyl vibrations will contain additional terms not found for mononuclear $LM(CO)_5$ derivatives, *i.e.*, the interaction constants of carbonyl groups across the metal–metal bond, k_9, k_{10}, and k_{11} in the potential energy terms in Table IV. We must assume that these will be negligible. If these are dropped, then a simplified secular equation for $M_2(CO)_{10}$ derivatives of D_{4d} symmetry is obtained which is the same as that for $LM(CO)_5$ derivatives of C_{4v} symmetry, given by Cotton and Kraihanzel.[10] In solving the second-order secular equation for the force constants using the b_2 modes, we choose a root such that k_i (the interaction constant of carbonyls on the same metal atom, *cf.* Cotton and Kraihanzel for its definition and justification) turns out to be positive, by requirements of simple valence bond theory. The other force constants are then calculated to be positive, larger, and of relative magnitude $k_2 > k_1$, in agreement with the other valence bond requirements,[10] and serve to verify our assignments. The force constants are listed in Table V, which also contains those for $(CO)_5ReMn(CO)_5$, $Re(CO)_5Cl$, $Mn(CO)_5I$, and $HMn(CO)_5$[11] for comparison.

TABLE IV

FACTORED $|\mathbf{F} - (\mathbf{G}^{-1})\lambda|$ MATRIX FOR ν_{CO} VIBRATIONS FOR $M_2(CO)_{10}$[a]

	$b_2^{(2)}$	$b_2^{(1)}$	e_1
$b_2^{(2)}$	$k_2 + 2k_5 + k_6 - 2(k_9 + k_{10}) - \frac{\lambda}{\mu}$	$2k_4$	
$b_2^{(1)}$		$(k_1 - k_{11}) - \frac{\lambda}{\mu}$	
e_1			$k_2 - k_6 + \sqrt{2}(k_9 - k_{10}) - \frac{\lambda}{\mu}$

[a] μ = (reduced mass of CO group)$^{-1}$ = 0.14583; $\lambda = (5.8890 \times 10^{-2})\nu^2$, where ν = frequency in cm.$^{-1}$ Force constants in dynes/cm. are defined in terms of the internal CO bond coordinates, r_{ij}, shown in Fig. 3: k_1 = axial CO bond (r_{15} or r_{25}) force constant; k_2 = radial CO bond (r_{11}, r_{12}, etc., or r_{21}, r_{22}, etc.) force constant; k_4 = out-of-plane *cis* interaction force constant ($r_{15,11}$ or $r_{25,21}$); k_5 = in-plane *cis* interaction force constant ($r_{11,14}$, etc., or $r_{21,24}$, etc.); k_6 = in-plane *trans* interaction force constant ($r_{11,13}$, etc., or $r_{21,23}$, etc.); k_9 = interaction force constant across M–M bond, *cis* ($r_{11,24}$, etc.); k_{10} = interaction force constant across M–M bond, *trans* ($r_{11,23}$, etc.); k_{11} = interaction force constant across M–M bond, *trans* ($r_{15,25}$).

In addition to the principal bands, at least four minor absorptions were observed for $M_2(CO)_{10}$, the bands labeled C, H, I, and J in Fig. 1 and Table I. Band J seems to appear at a constant distance, 34 cm.$^{-1}$ to lower energy, from the more intense absorption D in all the carbonyls studied here and, in keeping with such bands in other derivatives,[12] is assigned as the ^{13}CO satellite of band D. Similar satellites for the other intense absorptions would be hidden by the principal bands observed here. Bands C, H, and I are not recognizable as satellites of any of the presently assigned fundamentals; they are of sufficiently low intensity that they could belong to modes which are not infrared active in the parent carbonyl but are rendered infrared active in an isotopically substituted molecule of lower symmetry.[12c,d]

TABLE V

COMPARISON OF APPROXIMATE FORCE CONSTANTS[a] CALCULATED FOR THE PRINCIPAL C≡O STRETCHING ABSORPTIONS IN SOME METAL CARBONYLS

	k_1, mdynes/Å.	k_2, mdynes/Å.	k_i, mdynes/Å.
$Mn_2(CO)_{10}$	15.91	16.52	0.08
$(CO)_5MnRe(CO)_5$	15.83	16.62	0.10
$Tc_2(CO)_{10}$	15.94	16.68	0.12
$Re_2(CO)_{10}$	15.82	16.67	0.14
$Mn(CO)_5I$[b]	16.29	17.30	0.22
$Re(CO)_5Cl$[b]	15.98	17.47	0.29
$HMn(CO)_5$[c]	16.42	16.93	0.26

[a] Calculated from secular equations in Table IV simplified as mentioned in the text; these data are comparable only with other force constants obtained by similar approximate methods, such as contained in references listed in ref. 10. [b] From spectral data and assignments mentioned in ref. 2, 9a, and 9c. [c] From spectral data and assignments mentioned in ref. 11.

We now come to the problem of assigning radial and axial modes for the bands A and D, the b_2 species. In the case of $LM(CO)_5$ derivatives, and more specifically the pentacarbonyl halides, both the behavior on substituting halogen and the relatively weaker intensity of the highest energy band (A) were taken as clues that this might be due principally to the radial carbonyl groups.[9a,c] By analogy, we might assume this is also true for the bands of the corresponding species in the dimetal decacarbonyls. In the present case, however, the relative intensity of the two bands in question (A and D) is not quite comparable to that in the pentacarbonyl halides or in $HMn(CO)_5$.[11] In the spectra of $Re(CO)_5Cl$ or $HMn(CO)_5$, for example, the higher energy band appears vanishingly weak. But in the dimetal decacarbonyls the high energy mode (A) has gained a great deal of relative intensity compared to the lower mode (B). It is difficult to believe, under these circumstances, that the motions of the two types of carbonyl groups are discretely separated in these two bands in the dimetal decacarbonyls.

Three-dimensional refined structural data are now available for only two of the entire series of $LM(CO)_5$ and $M_2(CO)_{10}$ derivatives, namely, $Mn_2(CO)_{10}$[6] and $HMn(CO)_5$.[13] In both of these derivatives, the radial carbonyl groups are bent 6° out of the plane normal to

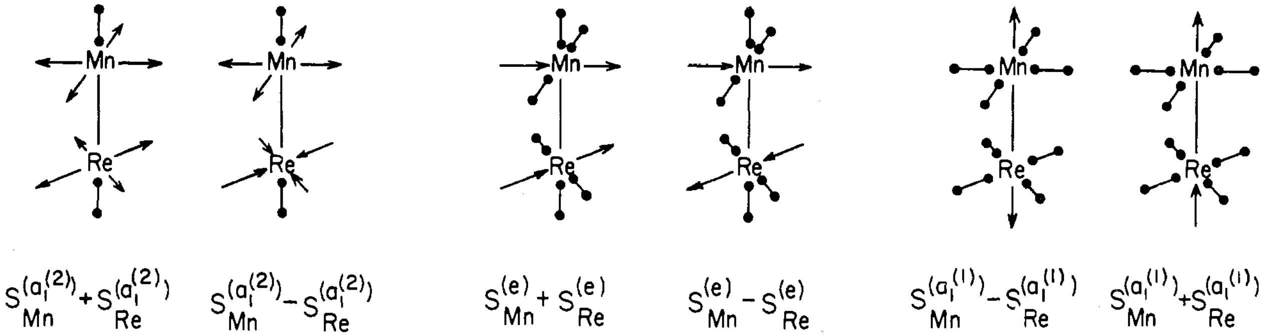
---

(10) (a) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); (b) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963); (c) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(11) D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964).

(12) Similar assignments have been made following more extensive vibrational analyses, *cf.*: (a) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963); (b) R. S. McDowell, W. D. Horrocks, Jr., and J. T. Yates, *J. Chem. Phys.*, **34**, 530 (1961); (c) L. H. Jones, *ibid.*, **36**, 2375 (1962); (d) see also the section on infrared spectra of carbonyls in the recent review by E. Abel, *Quart. Rev.* (London), **17**, 133 (1963).

(13) S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2288 (1964), as also reported by J. A. Ibers at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964 (Paper No. 50, Symposium on Metal Carbonyls and Related Complexes).



$S^{(a_1^{(2)})}_{Mn} + S^{(a_1^{(2)})}_{Re}$ $S^{(a_1^{(2)})}_{Mn} - S^{(a_1^{(2)})}_{Re}$ $S^{(e)}_{Mn} + S^{(e)}_{Re}$ $S^{(e)}_{Mn} - S^{(e)}_{Re}$ $S^{(a_1^{(1)})}_{Mn} - S^{(a_1^{(1)})}_{Re}$ $S^{(a_1^{(1)})}_{Mn} + S^{(a_1^{(1)})}_{Re}$

Fig. 5.—Relative orientation of internal symmetry coordinates for carbonyl bond stretching modes in the infrared active species of the C_{4v} point group for $(CO)_5Mn-Re(CO)_5$, assuming coupling of modes across M–M bond.

the M–M bond axis, *away* from the axial CO group. Despite this similarity in the geometrical array of radial carbonyl groups (in the crystal) these two derivatives represent near extremes in the relative intensities (in solution) of the two bands attributed to radial carbonyl groups, as discussed above. This is a problem which will require further attention and is under study in these laboratories.

Assignment of Bands in the CO Stretching Region for $(CO)_5MnRe(CO)_5$.—In the mixed metal derivative, only three principal absorptions were observed instead of the six which might have been expected from symmetry considerations alone (see above). In addition, the total intensity of the principal carbonyl bands is not significantly greater than in the parent carbonyls. There are two possible explanations for these observations.

If we assume that the carbonyl groups are not coupled across the metal–metal bond,[14] then the appearance of only three bands for the mixed metal derivative implies that some equalizing effect of the force constants within each $M(CO)_5$ group has occurred. The force constants are sensitive to the metal and the nature of the substituent as is reflected in the difference of force constants in the parent carbonyls, *cf.* Table V. However, in the mixed derivative, it is possible that any difference in electronegativity (to choose a property that encompasses many things about the atom in its compounds) which might have existed between the two metals could be averaged out through inductive effects[15] in the metal–metal bond. Thus the force constants calculated in Table V would be an average of those of the two types of CO groups in the derivative (radial or axial) regardless of the metal to which they were attached.

On the other hand, it is possible that the carbonyl vibrations are coupled across the metal–metal bond in each of the vibrations within a symmetry species. In that case, we expect our normal modes to have the appearance as shown in Fig. 5. However, far from expecting modes of equal intensity within each symmetry species, we now expect that the modes labeled $S^{(a_1^{(2)})}_{Mn} + S^{(a_1^{(2)})}_{Re}$, $S^{(e)}_{Mn} - S^{(e)}_{Re}$, and $S^{(a_1^{(1)})}_{Mn} - S^{(a_1^{(1)})}_{Re}$ in Fig. 5 will be very weak. These would correspond to Raman active modes in $M_2(CO)_{10}$ of D_{4d} point group and would explain why in this case we still do not expect the intensity of the principal infrared bands in the mixed metal derivative to be greatly enhanced over those in the parent carbonyls. After identifying the three most intense bands (A, B, and D) in the mixed metal derivative as those belonging to the other three combination modes shown in Fig. 5, we are left with the problem of locating the weak bands singled out above. An extension of the simple valence bond considerations[10] leads us to expect that the sign of the coupling constant of carbonyls across the metal–metal bond will be negative (opposite to that for the interaction of carbonyl groups on the same metal) owing to the intervention of an additional atom (the second metal atom) in the linking of the groups. Therefore, if present, any weak bands due to the combination modes singled out above would be expected on the low energy side, high energy side, and low energy side, respectively, of the combination modes presently identified as bands A, B, and D.

In the mixed metal derivative, the minor bands resolved by us are labeled C, F, E, G, H, and J, Fig. 1 and Table I. It is likely that bands C, H, and J correspond to bands we have already observed and discussed in the parent carbonyls. As before, we assign band J as the ^{13}CO satellite of band D. The relative position of the minor band labeled C is somewhat different here from that in the parent carbonyls; it is found about 19 cm.$^{-1}$ to low energy from band B in the mixed metal derivative while in the latter, for all three cases, it was found at only 11 or 12 cm.$^{-1}$ to lower energy from the more intense band, B. Perhaps the two minor bands do not correspond to one another in the two sets of compounds. Curiously enough, we do not see a band in this derivative which would correspond to band I in the parent carbonyls. In addition to these, we find bands E, F, and G in the mixed derivative which have no apparent counterparts in the parent carbonyls. Band E is 70 or 107 cm.$^{-1}$ to higher energy from the nearest intense peaks, bands A and B. It could not be one of the weak carbonyl combination modes which we might expect as mentioned above be-

---

[14] This could occur, among other reasons, if there were free rotation around the metal–metal bond, as pointed out by one of the referees. Of course, this is possible only if the position of the radial carbonyl groups were materially altered in solution from what they are observed to be in the crystal.

[15] For instance, an electronegative substituent draws less s-character into the orbital of the atom bonded to it, which leaves more s-character for the other orbitals of that atom and in effect enables it to appear more electronegative to its other substituents than it otherwise would have, *cf.* H. A. Bent, *Chem. Rev.*, **60**, 275 (1960), and *Can. J. Chem.*, **38**, 1235 (1960).

cause of its position to *higher* energy from band A and because of the relatively large separation from band B. It is tempting to assume that band E is due to a combination of a band of 70 cm.$^{-1}$ (of a_1 species) with band A, because there is also a minor peak, band F, of about the same energy separation to the high frequency side of band D (also assigned to the a_1 species). This would then constitute an assignment for both minor bands, E and F. (It is further tempting to believe that the hypothetical band at 70 cm.$^{-1}$ could be the M–M′ stretching frequency; it would be of the required symmetry and also this is approximately where one would expect such an absorption.) In all, this leaves only one weak band, G, to the high energy side of band B, which could qualify as one of the three low intensity combination modes we are seeking. It is entirely possible, however, that if the coupling is weak, as it might very well be over such long distances, the low intensity modes would be separated from the corresponding intense bands by only a very small amount and would be buried under the band envelopes of the latter. Hence, from the appearance of the spectra, either of the two possible explanations advanced above would seem to fit.

Comparison of Principal Carbonyl Stretching Absorptions.—In the present spectra, the pattern as a whole is shifted to lower energy than that of other $LM(CO)_5$ derivatives of this subgroup, such as the pentacarbonyl halides[9a,c] or the pentacarbonyls containing an organic group.[9d] This suggests that in the decacarbonyls, greater negative charge is present on the metal which must be dissipated into the carbonyl groups, generally lowering the bond order between carbon and oxygen.

Metal–Carbon Stretching Modes.—Based on previous vibrational analyses,[12] we may expect two types of fundamental modes in the low energy region, namely the carbonyl deformations, δ_{CO}, in the environment of 600 cm.$^{-1}$ and the metal–carbon stretching modes, ν_{MC}, near 400 cm.$^{-1}$. Let us first consider the latter; we may expect the same number and species of fundamental modes for ν_{MC} as for ν_{CO}, since the internal coordinates for both are transformed identically under the operations of the symmetry properties of the group. The vibrations in the lower energy region will not be nearly so pure as the higher energy CO stretching modes. (For instance, in $Co(CO)_3NO$,[12b] the absorption assigned as the carbonyl stretching mode is composed 95% of ν_{CO} with only 5% of ν_{MC} admixed, whereas the absorption assigned to the metal–carbon stretching mode at lower energy contains only 87% of ν_{MC} with other various modes of the proper symmetry mixed in.) Nonetheless we believe they are sufficiently characteristic that it is possible to make some plausible assignments. Of the expected ν_{MC} bands, we anticipate that the most intense will be due principally to the radial metal–carbon mode of e_1 (or e) symmetry species. Therefore, we assign the most intense band that can be observed in the vicinity of 400 cm.$^{-1}$ to this mode. Additional support of this assignment is available from the spectra of the pentacarbonyl halides in this region.[16] A band is observed for $Mn(CO)_5I$ and $Re(CO)_5Cl$ at 429 and 348 cm.$^{-1}$, respectively, which is shifted to lower energy from the analogous bands in the corresponding dimetal decacarbonyls, the bands at 470 and 398 cm.$^{-1}$, respectively. The general trend of band positions is exactly the opposite for the carbonyl modes of the same species, *cf.* comparison of principal carbonyl stretching frequencies, above. By contrast, the bands in the low energy region near 600 cm.$^{-1}$ are not observed to shift at all in going from $M(CO)_5X$ to $M_2(CO)_{10}$. The inverse relationship of the effect of substituents on the ν_{CO} and ν_{MC} modes is understood on the basis of the electronic interactions in the π-systems. A factor which causes an increase of CO bond order will cause a decrease in the MC bond order, as has been pointed out by Jones[12a,c] and by Bigorgne and Zelwer.[17]

On the basis of those arguments and on the relative intensities of the bands, we can pick the following assignments: for the e_1 mode for $M_2(CO)_{10}$, M = Mn, 470; M = Tc, 392; M = Re, 398 cm.$^{-1}$, respectively; and for the e modes for $MM'(CO)_{10}$, M = Mn, 477; M′ = Re, 388 cm.$^{-1}$, respectively. These are in the order Mn > Re > Tc which indicates the same probable order for the M–C force constants. In addition to the e_1 (or e) mode we expect two weaker bands which would be the b_2 (or a_1) modes, which should be located near the more intense band. To arrive at a plausible assignment for these a calculation of approximate force constants will be needed as was done for the carbonyl modes above. However, this is complicated in this region by many factors and will be the subject of a separate study.[16a]

Carbonyl Deformation Modes.—In the region near 600 cm.$^{-1}$ we observe some strong bands which we assign to the carbonyl deformation modes.[12] One interesting feature of these is that they behave as if they might be characteristic of the central metal atom, and less so or even not at all of the substituent. The effect of the central metal atom is clearly seen from the trend of the bands near 600 cm.$^{-1}$, in Fig. 2. The strong doublet for $Mn_2(CO)_{10}$ is centered around 646 cm.$^{-1}$ and this shifts to lower energy as the metal is changed; it seems to have some relationship to the weight of the metal, but not a linear one. We note the same behavior for bands in this region for carbonyl halides.[16a] It is interesting to note that in the mixed metal carbonyl two strong bands in this region are observed, one characteristic for each of the two metals contained in the molecule. In the case of the bands characteristic of manganese, these may be resolved in solution spectra into a doublet, as is shown in Fig. 2, traces a and b. The Perkin-Elmer 421, a grating instrument, gave slightly better resolution than the Beckman IR-5A equipped with a CsBr prism. This is seen, for example, for the band centered around 646 cm.$^{-1}$ for $Mn_2(CO)_{10}$. For the same sampling conditions, the band was split

---

(16) (a) N. Flitcroft and H. D. Kaesz, manuscript in preparation, *cf.* also (b) M. A. Bennett and R. J. H. Clark, *Chem. Ind.* (London), 861 (1963), who report the spectra of $Mn(CO)_5X$ (X = Cl, Br, and $Mn(CO)_5$) in the region 200–450 cm.$^{-1}$, but consider only metal–halogen modes (in the region 200–300 cm.$^{-1}$).

(17) M. Bigorgne and A. Zelwer, *Bull. soc. chim. France*, 1986 (1960).

into a doublet separated by 6 cm.$^{-1}$ by the former instrument, trace a, which could not be resolved by the latter, trace b, Fig. 2. Also, in contrast to the ν_{CO} region, here we found unmistakeable indication of increased infrared activity for the mixed metal derivative. The molar absorptivities obtained from integrating a plot of log % transmission against cm.$^{-1}$ for the bands near 600 cm.$^{-1}$ gave the following results (for equimolar concentrations): the relative areas for the bands in this region were $Mn_2(CO)_{10}$:$Re_2(CO)_{10}$:$(CO)_5MnRe(CO)_5$, 1:1:1.5.

Acknowledgment.—We are indebted to Professor M. A. El-Sayed of this department for helpful discussions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, OHIO

Spectra of Manganese(III) Complexes. I. Aquomanganese(III) Ion and Hydroxide, Fluoride, and Chloride Complexes

BY J. P. FACKLER, JR., AND I. D. CHAWLA

Received March 16, 1964

The absorption spectrum of aqueous manganese(III) is described in the presence and absence of added halide ions. Addition of fluoride to solutions containing aqueous manganese(III) causes a distinct splitting of the $^5T_{2g} \leftarrow {}^5E_g$ (in O_h) to occur. This is shown to be consistent with the formation of MnF^{2+}, $Mn^{3+} + F^- = MnF^{2+}$ with $K \cong 10^6$ at ~23°. Jahn–Teller effects are thought to influence the observed spectra.

Introduction

Attempts to correlate spectral properties of tris(β-ketoenolato)manganese(III) complexes[1] with known spectra of manganese(III) species in an environment of ligands bonding through oxygen[1-7] caused us to reëxamine the spectrum of aqueous manganese(III). Hexaaquomanganese(III) ion has been observed spectrally[2-4] in the species $CsMn(SO_4)_2 \cdot 12H_2O$. In these studies only one band in the 6000–30,000 cm.$^{-1}$ region of the spectrum was observed. It occurs at 21,000 cm.$^{-1}$ with a molar extinction of ~5 l. mole^{-1} cm.$^{-1}$. This band has been attributed[4] to the $^5T_{2g} \leftarrow {}^5E_g$ absorption expected in an octahedral symmetry.

Aqueous solutions thought to contain Mn^{3+} have been observed spectrally by Piper and Carlin[5] and Furlani and Ciana.[6] Ibers and Davidson[7] earlier reported the absorption spectrum of manganese(III) in 10 *N* hydrochloric acid. In each case two bands were observed, one near 20,000 cm.$^{-1}$, the other near 12,000 cm.$^{-1}$. The latter authors report molar extinctions of ~70 and ~340, respectively, for the low and high energy bands. Hatfield, *et al.*,[8] observed $MnCl_6^{3-}$ in a pressed salt pellet, finding no band at 12,000 cm.$^{-1}$ but observing bands at 17,540 and 22,400 cm.$^{-1}$. The latter band was thought to arise from "charge transfer." Runciman and Syme[9] recently reported the spectrum of $CrCl_2 \cdot 4H_2O$. This d^4 ion complex[10] shows three "crystal-field" bands at 77°K.

Recently Diebler and Sutin[11] published the solution spectrum of manganese(III) in perchloric acid. This spectrum, as well as the spectra of solutions containing added fluoride and chloride, suggests previous spectral assignments[5,6,8] for aqueous manganese(III) are incorrect.

Experimental

Preparation of Solutions.—Manganese(III) solutions were prepared by dissolving a weighed quantity of $Mn(ClO_4)_2 \cdot 6H_2O$ in water containing $HClO_4$ and adding a measured quantity of aqueous $KMnO_4$. In a typical experiment, 15.0 g. of $Mn(ClO_4)_2 \cdot 6H_2O$ (G. Frederick Smith) is dissolved in 25 ml. of water and 5.0 ml. of $HClO_4$ (60%) is added. To this solution 2.0 ml. of a water solution of $KMnO_4$ containing 1.0 mg./ml. is added. The resulting solution, which is ~1.44 *M* in $HClO_4$, remains stable for periods up to 1 week. Solutions containing added NaCl and NaF were prepared by adding the reagent grade salt directly to the solution.

Quantitative measurements of the observed molar extinction as a function of added fluoride were obtained for two concentrations of acid and manganese(II). These data are summarized in Table I.

Spectral Studies.—Spectra were observed on a Cary Model 14 spectrophotometer at room temperature, ~23°. After ascertaining that the spectrum of manganese(II) in this perchloric acid medium was identical with the spectrum presented in the

---

[1] J. P. Fackler, Jr., and I. D. Chawla, to be published.

[2] H. Hartmann and H. L. Schläfer, *Z. Naturforsch.*, **6a**, 754 (1951).

[3] O. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

[4] See also D. S. McClure, "Solid State Physics," Vol. 9, F. Seitz and D. Turnbull, Ed., Academic Press, Inc., New York, N. Y., 1959.

[5] (a) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1961); (b) *Inorg. Chem.*, **2**, 260 (1963).

[6] C. Furlani and A. Ciana, *Ann. Chim.* (Rome), **48**, 286 (1958).

[7] J. A. Ibers and N. Davidson, *J. Am. Chem. Soc.*, **72**, 4744 (1950).

[8] W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *ibid.*, **85**, 265 (1963).

[9] W. A. Runciman and R. W. G. Syme, *Philosophical Mag.*, **8**, 605 (1963).

[10] The Cr^{2+} in $CrCl_2 \cdot 4H_2O$ is surrounded[9] by six ligands with point group symmetry C_{2h}. There are two long and two short Cr–O bonds.

[11] (a) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964). This paper appeared during the preparation of the original manuscript. (b) D. R. Rossiensky, *J. Chem. Soc.*, 1181 (1963), reported the stability of aqueous manganese(III) solutions.