succession as the proton is added to one nitrogen. Hence, the kinetics are not characteristic of a stepwise mechanism.

The restricted rotation of CyDTA results in a rather small coordination cage for metal ions. Large metal ions should have greater steric hindrance in moving in and out of the cage and be less likely to proceed in a stepwise mechanism. The ionic radii (A) calculated from Goldschmidt values for crystal radii according to the method of Couture and Laidler[34] are Cu^{2+} (0.87), Ni^{2+} (0.97), Mg^{2+} (0.98), Co^{2+} (1.03), Zn^{2+} (1.04), Mn^{2+} (1.14), Ca^{2+} (1.33), Hg^{2+} (1.40), and Pb^{2+} (1.65). Although calcium and manganese are larger than the metal ions in group 1, magnesium is not and the mechanism for mercury and lead is uncertain. Ionic size alone cannot explain the difference in behavior.

Recent measurements[35] report primary hydration numbers for some of these metal ions: Mg^{2+} (3.8), Ca^{2+} (4.3), Zn^{2+} (3.9), Hg^{2+} (4.7), and Pb^{2+} (5.7). The anomalous behavior of Mg^{2+} and Ca^{2+} cannot be correlated directly to their low coordination number because Zn^{2+} also has a low hydration number.

A simple correlation which does appear to be valid is based on the relative stabilities of the metal glycinate or metal iminodiacetate complexes. The metals in group 1 form more stable complexes with these segments of CyDTA than those in group 2. If the stability is greater than the electrostatic repulsion between the metal and the protonated nitrogen, then structure III is a reaction intermediate and a stepwise path is observed. If the stability is less than the electrostatic repulsion, both metal–nitrogen bonds break when the one nitrogen is protonated and the simultaneous bond dissociation mechanism is observed. Accordingly, the steric requirements of CyDTA, the size of the metal ion, and its coordination number may all affect the degree to which the proton–metal repulsion is shielded. Recent nmr studies[36] of the ligand-exchange kinetics of calcium-EDTA indicate that the HEDTA^{3-} reaction with Ca^{2+} is much slower than with EDTA^{4-}. The HEDTA^{3-} reaction is more sluggish than the $k_{\mathrm{Ca}}{}^{-\mathrm{H_2O}}$ value would predict. Hence, protonation of the ligand may be an important effect as well as the size of the coordination cage.

The fact that one metal ion cannot kinetically participate in the replacement of another metal in the CyDTA complexes but that a proton can take part in the reaction is a direct result of steric hindrance. It is known that rigid chelates such as the porphyrins are very sluggish in their reactions. Thus, the formation reactions of Mn, Co, Ni, Cu, and Zn with a porphyrin-type chelating agent[37] are much slower than individual water substitution reactions. In the CyDTA reactions some metals show such an effect. As the coordination cage of a ligand becomes more confined and rigid, more metal ions would be expected to deviate from their characteristic water substitution rates. However, with CyDTA the shift in mechanism appears to be due to changes in the relative stabilities of protonated intermediates rather than a direct function of size or coordination numbers of the cation.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF
THE UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

Absolute Infrared Intensities and Bonding in Metal Carbonyls. I. Decacarbonyl Manganese—Its Isoelectronic Analogs and Derivatives[1]

BY R. M. WING AND D. C. CROCKER

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Absolute infrared intensity data are given for several metal carbonyls of the type $M_2(CO)_{10}$ in the carbonyl stretching region. These data as well as cross metal–metal bond C–O stretch–stretch interaction constants are explained using a model based on electrostatic interaction between dπ orbitals on opposite metal atoms. The effect of replacing the apical carbonyl groups by nonback-bonding ligands is discussed. Some comment is made concerning the value of infrared intensity data as a structural tool.

Introduction

There has been considerable discussion recently concerning the infrared spectra of binuclear metal carbonyls of the dimanganese decacarbonyl type.[2-6] While endeavoring to learn more about the interactions between the metal carbonyl moieties and, in particular,

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(1) Supported by an intramural grant of the University of California.

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to use the presence or absence of such interactions as a structural tool, we found it difficult in many instances to obtain the Raman data necessary to make meaningful force constant calculations. Hence we have begun to evaluate the absolute intensities of infrared-active carbonyl stretching modes.

It is well known that the intensity of an infrared band is proportional to the square of the change in the prerequisite component of the molecular dipole moment,[7] certain components vanishing because of symmetry restrictions. The intensity is thereby related in a fairly straightforward manner to the structure and structural changes of a molecule. In numerous instances[8,9] intensity variations, within a series of compounds, for a particular band are more evident than are the frequency shifts for the same band. Band intensities should therefore prove to be a sensitive structural tool.

Generally speaking, the difficulty in interpreting intensity data arises from a lack of knowledge (or a complexity) of the normal coordinate for the vibration in question. The fact that, for extremely rigid oscillators, symmetry coordinates very closely approximate normal coordinates allows us to interpret intensities in the carbonyl stretching region with comparative ease.

Experimental Section

The infrared spectra were obtained on a Perkin-Elmer 621 grating infrared spectrometer which as operated had an average spectral slit width of 3.0 cm^{-1}. The samples were run in a "matched pair" of nominal 0.05-mm path length NaCl solution cells (sample 0.0463, reference 0.0454 mm) calibrated using the interference spectra of the empty cells. Solutions of the metal carbonyls were prepared by carefully weighing (± 0.1 mg) about 20 mg of solid and making up to volume in a 5-ml volumetric flask.

The integrated absorbances were determined by applying Simpson's rule to a greatly expanded (4.16 cm^{-1}/cm of chart) spectrum on absorbance paper. The bands were sketched in by hand where necessitated by the overlap of neighboring bands. Attention was given, in this process, both to symmetry of the components about the band center and to the preservation of the total area under the spectral curve. The raw summed area was diminished by a trapezoidal base line area which approached, as an upper limit, the area under a superimposed spectrum taken with pure solvent in both cells. This area amounted to 5–50% of the total area and contributed an uncertainty of *ca.* 1% typically (10% for diminuative bands) to the final result. Wing corrections ranging from 5 to 20% depending on band widths and maxima were applied using Table VII of Ramsay's paper.[10] These wing corrections account for residual area, based on ideal Lorentzian curves, which accumulates as the bands tail off past the limits of practical graphical integration. The corrected areas were then reduced to apparent integrated intensities B by the defining equation $B = (1/cl) \ln (I_0/I)_\nu \, d\nu$, where c = concentration in moles $liter^{-1}$, l = path length and centimeters, and $\ln (I_0/I)_\nu = 2.303 \times$ absorbance at frequency ν. Under the conditions of the experiments, B should be less than A (the absolute integrated absorption intensity) by no more than 5%, so we represent these values as being equal to A.[11]

We checked our technique by measuring the absolute intensity of the C≡N stretch of benzonitrile. Our result, 3810 M^{-1} cm^{-2}, compares well with the literature value of 3740 M^{-1} cm^{-2}.[12]

Spectroscopic grade cyclohexane and chloroform were used as received. The tetrahydrofuran was refluxed over and distilled from $LiAlH_4$ just prior to use.

$Mn_2(CO)_{10}$ purchased from Alpha Inorganics was recrystallized from acetone–water[13] and sublimed at 45° (0.1 mm).

$Re_2(CO)_{10}$ from Alpha Inorganics was used as received.

$BrMn(CO)_5$ and $BrRe(CO)_5$ were kindly provided by Professor M. F. Hawthorne of this department.

The hydrides $[HM_2(CO)_{10}]^-$ were given to us by Dr. R. G. Hayter of Shell Development, Emeryville, Calif.

Choice of the Structure-Sensitive Band

There are many instances, for metal carbonyl oligomers, in which the intensity of a particular infrared-active vibration can be shown *a priori* to be small, lacking some cross fragment interaction. Vibrational bands of this variety, for a series of compounds, are likely to show strong intensity changes depending on structural variations within the series and their influence on the intensity-producing interaction.

For the particular case of D_{4h} or D_{4d} $L_2M_2(CO)_8$ molecules, the infrared vibration which satisfies the above-mentioned criterion is shown as S_3 in Figure 1.

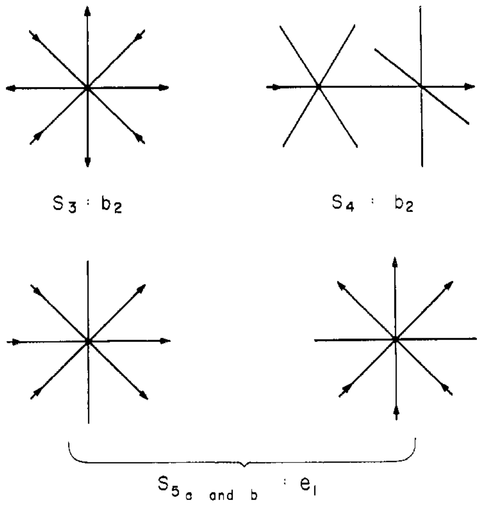

Figure 1.—Forms of the infrared-active C–O stretching fundamentals; following the convention of Lewis, *et al.*[3b]

This corresponds to the highest frequency infrared band, which has been assigned as ν_3 in ref 3 and 4. This vibration which is predicted by group theory to be infrared active requires (in the harmonic oscillator approximation) a dipole change parallel to the molecular axis of the dimer. Unless the radial CO groups are bent out of the plane perpendicular to this axis or, in the case where L = CO, the CO axial vibrations mix with the radial vibrations to form the normal coordinate corresponding to ν_3, this is clearly impossible.

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TABLE I

SUMMARY OF INTENSITY DATA FOR CO STRETCHES

Compound	Solvent	Integrated intensities,[a] M^{-1} cm^{-2} × 10^5		
		ν_3: b_2	ν_4: b_2	$\nu_{5,8}$: e_1
$Mn_2(CO)_{10}$	Cyclohexane	1.42 (2044)	0.935 (1978)	4.26 (2012)
$Mn_2(CO)_{10}$	*n*-Hexane[b]	1.48 (2045)	0.99 (1981)	3.80 (2013)
$Mn_2(CO)_{10}$	Tetrahydrofuran	1.52 (2044)	1.32 (1977)	6.02 (2008)
$Mn_2(CO)_{10}$	Chloroform	1.49 (2045)	1.23 (1979)	5.41 (2012)
$Re_2(CO)_{10}$	Cyclohexane	1.05 (2064)	1.77 (1979)	5.41 (2008)
$HCr_2(CO)_{10}^-$	Tetrahydrofuran	0.216 (2033)	2.98 (1878)	8.21 (1940)
$HW_2(CO)_{10}^-$	Tetrahydrofuran	0.357 (2040)	3.81 (1874)	10.4 (1934)
$BrMn(CO)_5$	Chloroform	0.0538 (2144)	1.23 (2004)	2.53 (2056)
$BrRe(CO)_5$	Chloroform	0.0346 (2152)	1.42 (1985)	3.32 (2046)

[a] Vibrational frequencies (cm^{-1}) given in parentheses. [b] From ref 5, normalized to our data.

Treatment of the Intensity Data

The observed intensities are given in Table I, along with vibrational assignments which correspond to those given in Figure 1.

In this section we wish to show how one can factor out the contributions of the two mechanisms *besides cross metal–metal bond interaction* which serve to supplement the intensity of ν_3, the structure-sensitive band. These two factors are: (1) increased mixing of the b_2 vibrations (the high- and low-frequency bands) resulting from the depression of the high-frequency band toward the low-frequency band (a consequence of dimer formation), and (2) the out-of-planeness of the radial CO groups. We will discuss these mechanisms in the order given for reasons which will be apparent shortly.

The increase of intensity *via* mixing of modes can be calculated in a straightforward way as long as we have the data to do a normal coordinate analysis. That is, we need to know how each symmetry (or internal) coordinate distributes itself over the various normal modes of vibration. In a localized oscillator approximation this means only that we need know the inverse eigenvectors for the 2 × 2 b_2 factored block of the secular determinant (Table II).

TABLE II

SPLITTING OF THE HIGH- AND LOW-FREQUENCY SYMMETRIC STRETCHING MODES AND NORMALIZED INVERSE EIGENVECTORS FOR THOSE MODES[a]

Compound	Δ, cm^{-1} [b]	$L_{3,3}^{-1}$	$L_{3,4}^{-1}$
$Mn_2(CO)_{10}$	61	0.8324	−0.5498
$Re_2(CO)_{10}$	94	0.9355	−0.3551
$H\ Mn(CO)_5$	111	0.9584	−0.2902
$MeMn(CO)_5$	117	0.9698	−0.2482
$BrMn(CO)_5$	140	0.9775	−0.2062
$HW_2(CO)_{10}^-$ [c]	165	0.9622	−0.2635
$BrRe(CO)_5$	166	0.9775	−0.2062

[a] The secular determinant used in this calculation is given in ref 4. [b] For other compounds the inverse eigenvectors can be estimated by interpolation. [c] Based on Raman and infrared data which were obtained by the authors and are to be published.

Factorization of the intensity between the two symmetry modes is then reduced to solving two equations for two unknowns. Thus the intensity attributable to S_3 of a decacarbonyl dimer is given by the expression[7,14]

$$\sqrt{I_{S_3}} = L_{3,3}^{-1}\sqrt{I_{Q_3}} + L_{4,3}^{-1}\sqrt{I_{Q_4}}; \quad I_{Q_j} \propto \left(\frac{\partial \bar{p}}{\partial Q_j}\right)^2$$

Intensities for the monomers and dimers studied in this work, corrected by the coordinate mixing term are given in Table III along with intensities (taken from the literature) of various axially substituted dimers for which this correction is not required.

TABLE III

SYMMETRY-FACTORED INTENSITIES FOR SELECTED $XM(CO)_5$ AND $L_2M_2(CO)_8$ SPECIES

Compound	Intensities, M^{-2} cm^{-2} × 10^5		
	S_3	S_4	S_5
$BrMn(CO)_5$[a]	0.000	1.27	2.53
$BrRe(CO)_5$[a]	0.004	1.45	3.32
$Mn_2(CO)_{10}$	0.210	2.13	4.26
$Mn_2(CO)_8[As(C_6H_5)_3]_2$[b]	0.323	...	4.00
$Mn_2(CO)_8[P(OC_6H_5)_3]_2$[b]	0.342	...	2.47
$Mn_2(CO)_8(PF_3)_2$[b]	0.304	...	3.23
$Re_2(CO)_{10}$	0.237	2.71	5.41
$HCr_2(CO)_{10}^-$	0.007	3.18	8.21
$HW_2(CO)_{10}^-$	0.004	4.14	10.4

[a] S_1, S_2, and S_4, respectively. [b] From ref 5.

On the basis of the crystal structures of dimanganese decacarbonyl[15] and manganese pentacarbonyl hydride,[16] we would estimate the distortion of the radial CO groups from planarity to be about equal to or perhaps slightly larger than that for monomers. Because the hydride is probably poorly representative of half a dimer, it is of some interest that the intensity data themselves can give us information regarding this distortion[17] in the case of monomers. The basis for this type of structure determination is as follows. Given, for example, a set of equivalent oscillators in a symmetric top molecule, there will be two modes of vibration which will, by virtue of the fact that they exhibit dipole fluctuations in different directions, have different intensities. Now since the oscillators are isolated and equivalent, their bond dipole derivatives are expected to be the same. Hence any discrepancy in intensity between these two vibrations has to do with

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(14) In actuality the summation should be over all terms of like symmetry and would also include contributions from CO wags, etc., but this is impossible at present owing to the lack of a complete vibrational assignment.

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the directional deviation of the oscillators from that required by the selection rule. Thus, in a symmetric top molecule, the ratio of symmetric to antisymmetric infrared intensities gives the orientation of the equivalent set of oscillators with respect to the principal molecular axis

$$\frac{I_{\text{sym}}}{I_{\text{antisym}}} = \frac{\cos^2 \alpha}{\sin^2 \alpha}$$

where α is angle between the principal axis and any one of the oscillators.

Of course, if there are, as in metal pentacarbonyl derivatives, additional sets of oscillators which (by mixing of vibrational coordinates) can contribute to the intensity of either of the two mentioned infrared bands, this must be corrected for. This type of calculation has been presented previously for pentacarbonyl derivatives by Beck,[18] *et al.*, but apparently no correction was made for the mixing of the two a_1 symmetry coordinates to form ν_1.

Our calculations using symmetry-factored intensities are given in Table IV and seem to substantiate the view that the out-of-plane distortion of radial carbonyl groups is about the same for monomers and dimers.

TABLE IV

RADIAL DISTORTION OF SOME $XM(CO)_5$ SPECIES

	α, deg	
	Infrared	X-Ray
$BrMn(CO)_5$	90	. . .
$BrRe(CO)_5$	88	. . .
$HMn(CO)_5$[a]	85	83
$CF_3Mn(CO)_5$[b]	84	. . .

[a] Based on $\epsilon_{\max}$ values derived from H. D. Kaesz, *et al.*, *J. Am. Chem. Soc.*, **86**, 2734 (1964). [b] Gas-phase spectrum from unpublished work of one of the authors (R. M. W.).

Reference to Table III shows that the "symmetry factored" b_2 radial stretch intensity (S_3) for the dimers has been increased many times over the corresponding a_1 radial mode intensity S_1 of the monomers. Mixing of the two b_2 modes causes a further gain of intensity of about a factor of 4. (Compare I_{S_3} in Table III to I_{ν_3} in Table I.)

This result confirms the experimental results of Lewis, Manning, and Miller[3b] and Parker and Stiddard[5] for various axially substituted dimers. On the basis of these data we would say that about 20% of the intensity of ν_3 is due directly to cross dimer interactions and that the other 80% is attributable to mixing in of some axial stretch character, much of this in turn resulting directly from cross dimer interactions (see Table II).

The Molecular Model and Intensity Structure Correlation

The model used here will be that proposed by Cotton and Wing.[4] In essence it was postulated that the CO oscillators on opposite $M(CO)_5$ moieties interact *via* an electrostatic repulsive force between the $d\pi$ metal orbitals on the opposite halves. This model qualitatively explains both the depression in frequency and gain in intensity of the high-frequency infrared band (ν_3).

If indeed the electrostatic model for interaction is correct, we would expect a linear dependence of $A^{1/2}$ on $1/r^2$, the square root function of intensity being used to bring it onto a scale proportional to dipole moment change (*vide supra*). The total intensity gain (above that for monomers) is used in the correlation, since even the gain due to decreased mixing in of S_4 is directly related to dimer formation. The intensity correlation and an equivalent correlation using the cross metal–metal bond stretch–stretch interaction constant K as the dependent variable are in essential agreement. The r values were taken as the experimental metal–metal distances.[19,20] This is not likely to be an exact representation of the distances between centers of electronic charge; however, any adjustment here both is difficult to justify and defeats the one advantage of the electrostatic approach, simplicity!

It is encouraging to note that these correlations (from the intercept with the abscissa) predict the reasonable value of 4.0 ± 0.15 A as the distance for zero interaction.

There is a dilemma concerning the results for the $L_2Mn_2(CO)_8$ species, since the intensities are larger than those for $Mn_2(CO)_{10}$ when the latter is corrected for coordinate mixing, whereas the cross dimer interaction constant (ref 3b) has decreased. Since a force balance based on the electrostatic repulsion resulting from placing half an electronic charge on each metal atom, reasonable from the observed decrease of vibrational frequencies,[21] predicts a bond length expansion of the same size (0.1 A) predicted by the force constant correlation, we feel this result is the more reliable. Thus, while the phosphine and arsine ligands must have some effect on the measured intensities, perhaps owing to their great size and dissymmetry, their intensities serve to confirm that our intensity factorization is essentially correct.

Other Comparisons

As a result of a great amount of work on organic ketones, etc., the stretching of a carbonyl group has been described as an electron-demanding process.[8,22] On this basis it is not surprising that carbonyl band intensities (on a per carbonyl basis) for metal carbonyls are significantly greater than those for CO and for organic ketones, aldehydes, amides, etc. (Table V). The trends for the intensities given are as expected, although the data, collated as they are from several sources, are not sensitive enough to show small differences in substituent character.[23] Note, however, such

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(23) A much more complete study of these effects in compounds of the type $XMn(CO)_5$ is being made by T L. Brown of the University of Illinois.

TABLE V

SOME CARBONYL BAND INTENSITIES ON AN ORIENTATED PER OSCILLATOR CARBONYL BASIS

Compound	A, M^{-1} cm^{-2} × 10^5	
	Axial (*trans*)	Radial (*cis*)
$BrMn(CO)_5$	1.27	0.63
$IMn(CO)_5$[a]	1.01	...
$CH_3Mn(CO)_5$[a]	1.08	...
$CF_3Mn\ (CO)_5$[a]	1.15	...
$Mn_2(CO)_{10}$	1.06	0.53
$BrRe(CO)_5$	1.45	0.83
$Re(CO)_{10}$	1.36	0.53
$HCr_2(CO)_{10}^-$	1.49	1.03
$HW_2(CO)_{10}^-$	1.90	1.30
Dimethylacetonide[b]	0.57	
Acetyl chloride[b]	0.31	
Benzophenone[b]	0.24	
Acetone[b]	0.19	
CO gas[c]	0.058	

[a] From ref 18, in which we feel (although vibrational frequencies are unlisted) the band assigned as ν_4 must certainly be ν_2. [b] From ref 22. [c] J. Fahrenfort in "Infra-Red Spectroscopy and Molecular Structure," M. Davies, Ed., Elsevier Publishing Co., New York, N. Y., 1963, p 397.

changes as increased metal size and increased negative charge on the metal enhance intensities.

The relative variations in axial and radial carbonyl intensities imply that the *trans* or axial carbonyl is essentially "electron saturated" and that any additional electrons are preferentially donated to the *cis* (radial) carbonyls.

Summary and Conclusions

The intensity of one infrared-active carbonyl stretching vibration (ν_3) is very sensitive to structural changes in the binuclear system studied in this work. Indeed, the great sensitivity makes it imperative that structural modifications be made with care if any interpretation is to be attempted. The use of intensity data has several advantages over the frequencies themselves. First, in many instances it is difficult to get the required Raman data. Second, small errors in the frequencies as obtained from the several necessary experiments are unavoidable and make significant contributions to errors in the force constants. Third, the intensities are more directly related to structural changes. For instance, the force constants derived from the frequencies are based on potential fields which are in turn based on preconceived "or biased" molecular models. Of course the "truth" of the force field is reflected in the symmetry-factored intensities so one cannot completely avoid this pitfall.

In most instances those vibrational band intensities which will be influenced by structural variations can be selected *a priori* from simple group theoretical considerations.

Encouraging results are now being obtained on other metal carbonyl systems, particularly where bridging groups are present, and we feel that information of this type will prove to be a useful complement to the usual frequency data.

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