the "final" set of force and interaction constants did not give as good an agreement with the few and poorly resolved natural isotopic bands as was the case for the homo-trinuclear compounds: instead of an agreement within ±0.3 cm^{-1} between calculated and observed isotopic bands for $M_3(CO)_{12}$ complexes, there was sometimes a discrepancy of as much as 2 cm^{-1} for the mixed compounds.

Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru_2Os(CO)_{12}$, 12389-47-8; $RuOs_2(CO)_{12}$, 12389-50-3; $Os_3(CO)_{12}$, 15696-40-9; $Ru_3(^{12}CO)_{11}(^{13}CO)$ (eq isomer), 73295-93-9; $Ru_3(^{12}CO)_{11}(^{13}CO)$ (ax isomer), 73346-53-9; $Os_3(^{12}CO)_{11}(^{13}CO)$ (eq isomer), 73295-94-0; $Os_3(^{12}CO)_{11}(^{13}CO)$ (ax isomer), 73346-54-0.

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Infrared Spectroscopic Studies on Metal Carbonyl Compounds. 23.[1a] A Simple Quantitative Treatment of the Infrared Band Intensity and the Induced Metal–Metal Dipole Contribution to It in Polynuclear Metal Carbonyls. An Application to the Spectrum of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in the Carbon–Oxygen Stretching Region

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The use of the spectra of ^{13}CO-enriched species to determine the extent of coupling between axial and equatorial C–O stretching symmetry coordinates for species E′ of the $M_3(CO)_{12}$ (M = Ru, Os) molecules with D_{3h} symmetry permits a quantitative study of the relative IR band intensities. A simple treatment is presented which considers not only the local oscillating CO dipoles but also the contribution of the dipole moment induced at the electronic centers on the metal atoms. It is assumed that the induced dipole moment is a linear function of the eigenvectors and that it can have the same *or opposite* direction with respect to the resultant of the local vibrating CO dipoles, giving rise to an increase or a decrease in the expected intensity. The observed intensity anomaly in the (C–O stretching region of the) IR spectrum of $Ru_3(CO)_{12}$, as compared with that of $Os_3(CO)_{12}$, which seems to contradict the analogous structures, can be explained by this simple treatment. The following numerical values, relative to the axial dipole moment gradient ($\mu_{ax}' = 1.0$), have been obtained: $\mu_{eq}' = 0.83$ (Ru) and 0.97 (Os); $\mu_M' = 0.83$ (Ru) and 0.68 (Os), where μ_M' is the gradient of the induced M–M dipole. The treatment is generally applicable for other types of di- and polynuclear metal carbonyls.

Introduction

The fundamentals of the interpretation and prediction of the infrared band intensities of simple mononuclear metal carbonyl derivatives have been given by Orgel[2] and by El-Sayed and Kaesz.[3] These treatments based on the local oscillating dipoles have been later enriched by contributions of Bigorgne et al.,[4] Lewis, Manning and Miller,[5] Abel and Butler,[6] Beck et al.,[7] Wing and Crocker,[8] Haas and Sheline,[9] and others.[10] The quantitative interpretation of the intensities is fundamentally related to the exact determination of the extent of coupling between the axial and radial types of CO sets.[11] In this direction a very important step was made by Kaesz et al.[12] and independently by Cotton et al.[13] in introducing the use of isotopically substituted molecules to make the force field more determinate. The most important further refinement, introduced by Braterman, Bau, and Kaesz[14] for $XM(CO)_5$ (M = Mn, Re), was then the recognition that the dipole moment gradients are generally not equal for different sets of C–O vibrators. Moreover, another additional term has been introduced by Darensbourg and Brown[15] to account for the intensity contribution arising from the vibration of a dipole induced by the in-phase vibration of all CO groups of a $LM(CO)_5$ derivative, where a charge is created on the central metal atom, which is then compensated by an electron flow along the L–M bond. This type of intensity enhancing effect was first predicted (as "electronic migration" along the M–L axis) by Orgel[2] and considered as "synergic motion of electrons on the axis" also by Braterman et al.;[14] it is called also "vibronic contribution"[15] or "orbital following effect".[10c] Also our own analysis[16] of the $Me_3EFe(CO)_4$ (E = N, P, As, Sb, Bi) series dealt with a possible increase of the intensity of the highest frequency band by the contribution of an induced dipole along the E–Fe axis. Darensbourg introduced subsequently the concept of the "vibronic contribution" also into the analysis of the intensities of the $X_3EM(CO)_4$ type with C_{3v} symmetry[17] and later presented an extensive compilation based upon an extended set of data.[18]

The hypothesis that an intensity contribution from an induced dipole moment in the metal–metal direction can be

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(1) (a) Previous paper of this series: ref 24. (b) Laboratory for the Chemistry and Technology of the Radioelements, CNR. (c) Department of Industrial and Engineering Chemistry of the Swiss Federal Institute of Technology.
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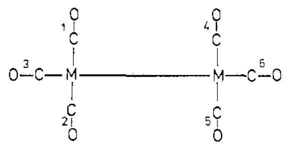

Figure 1. Structure and ligand numbering of the hypothetical model molecule $M_2(CO)_6$ referred to in the section "Examples".

responsible for anomalously high intensity in the higher B_2 mode, in the dinuclear $M_2(CO)_{10}$ (M = Mn, Re) compounds, was first put forward by Cotton and Wing.[19] Later, Parker and Stiddard,[20] expressed their doubts about this interpretation since they did not observe this anomalously high intensity for the corresponding B_2 band in the $Mn_2(CO)_8(PF_3)_2$ compound. However, some of us emphasized that, with good π-acceptor ligands, there is the possibility of the cancellation of the charge formed on the metal atoms during the vibrations through the hetroligands by a "vibronic contribution".[21] The phenomenon of highly increased intensity for one or more C–O stretching normal modes is present also for tetranuclear clusters, and we gave earlier a schematic picture of this mechanism for the (arene)$Co_4(CO)_9$[21] and $M_4(CO)_{12}$ (M_4 = Co_4, Rh_4, Co_3HFe)[22] compounds. The ideas of Cotton and Wing[19] have been further developed for the quantitative interpretation of the spectra of Mn_2- and $Re_2(CO)_{10}$.[23] A new feature of this theoretical approach was that not only an intensity increase but also an intensity decrease can arise from the induced dipole moment or "vibronic" mechanism. But all these treatments on the mono- and polynuclear carbonyls need a new critical control. We have found, during the vibrational analysis of the spectra of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$,[24] that these compounds give an excellent model for this topic, and we present this analysis in the present paper.

Results and Discussion

Conventions. When, in a normal mode, the CO groups bonded to a metal atom stretch in phase, while the CO groups bonded to another metal atom contract in phase, π-electronic charge flows on the electronic metal centers, inducing a dipole moment in the metal–metal direction and thus affecting the infrared band intensities. If we assume that this induced dipole moment is a linear function of the eigenvectors, it can have the same *or* opposite sense with respect to the resultant of the local oscillating CO dipoles, resulting in an increase or a decrease in the intensities expected on the basis of a local oscillating dipole model. Our simplified treatment of the IR band intensity and the induced dipole moment contribution requires the following conventions: (i) an expanding C–O bond creates a given amount of charge on the metal atom, and a contracting C–O bond creates, if the amplitude is the same, the same amount of opposite charge on the metal atom; (ii) equal amplitudes for C–O bond sets (i.e., axial or radial) result in equal electronic effect and the same extent of the induced dipole moment, irrespective of the normal mode symmetry.

Examples. A simple example to demonstrate that the resultant of the induced metal–metal dipole moment (IDM) can have an opposite sense too, cancelling or overcompensating the resultant of the local oscillating dipole moment (LODM), is provided by the hypothetical molecule $M_2(CO)_6$ of D_{2h} symmetry, shown in Figure 1. The CO stretching symmetry and normal coordinates are given in Tables I and II, respectively.

Table I. Terminal C–O Stretching Symmetry Coordinates for a Hypothetical $M_2(CO)_6$ Compound

$$\begin{aligned}
S_1(A_{1g}) &= (\Delta r_1 + \Delta r_2 + \Delta r_4 + \Delta r_5)/2\\
S_2(A_{1g}) &= (\Delta r_3 + \Delta r_6)/2^{1/2}\\
S_3(B_{1u})^a &= (\Delta r_1 + \Delta r_2 - \Delta r_4 - \Delta r_5)/2\\
S_4(B_{1u})^a &= (\Delta r_3 - \Delta r_6)/2^{1/2}\\
S_5(B_{2u})^a &= (\Delta r_1 - \Delta r_2 + \Delta r_4 - \Delta r_5)/2\\
S_6(B_{2g}) &= (\Delta r_1 - \Delta r_2 - \Delta r_4 + \Delta r_5)/2
\end{aligned}$$

[a] IR active.

Table II. Normal C–O Stretching Coordinates for a Hypothetical $M_2(CO)_6$ Compound[a]

$$\begin{aligned}
&\left.\begin{aligned} Q_1 &= N_{11}S_1 + N_{21}S_2\\ Q_2 &= -N_{12}S_1 + N_{22}S_2 \end{aligned}\right\} A_{1g}\\
&\left.\begin{aligned} Q_3 &= N_{33}S_3 + N_{43}S_4\\ Q_4 &= -N_{34}S_3 + N_{44}S_4 \end{aligned}\right\} B_{1u}{}^b\\
&Q_5 = S_5 \qquad B_{2u}{}^b\\
&Q_6 = S_6 \qquad B_{2g}
\end{aligned}$$

[a] Q_k is the kth normal mode and N_{ij} is an element of eigenvector matrix N, correlating the normal modes with the symmetry coordinates:

$$N_{ij} = \begin{pmatrix} \cos\phi_\kappa & -\sin\phi_\kappa \\ \sin\phi_\kappa & \cos\phi_\kappa \end{pmatrix}$$

$\kappa = 1$ for $i,j = 1$ or 2, $\kappa = 2$ for $i,j = 3$ or 4. [b] IR active.

In the normal mode Q_3 the direction of the two types of the oscillating dipoles is always the same, resulting in an increase of the total intensity as compared with that calculated from the LODM. However, in Q_4 there are the following possibilities (assuming 90° angles between axial and radial CO directions): (i) when $N_{44} = 1$, or as long as $N_{44} \gg |N_{34}|$, S_4 will dominate, the amplitudes of Δr_3 and Δr_6 will be greater than the sums ($|\Delta r_1| + |\Delta r_2|$) and ($|\Delta r_4| + |\Delta r_5|$), and there will be created an IDM, which adds to the sum of the LODM; (ii) as N_{44} decreases to a value corresponding to $S_3 = S_4/2^{1/2}$ (i.e., $|\Delta r_3| = |\Delta r_1| + |\Delta r_2|$ and $|\Delta r_6| = |\Delta r_4| + |\Delta r_5|$), no IDM is formed and the total intensity must correspond to the sum of the LODM only; (iii) as N_{44} continues to decrease so that $|\Delta r_3| < (|\Delta r_1| + |\Delta r_2|)$ and, of course, $|\Delta r_6| < (|\Delta r_4| + |\Delta r_5|)$, then an IDM will be formed which has the opposite polarity to that of the sum of the LODM; as a consequence, the total intensity will be smaller than the intensity arising from the vectorial sum of the LODM; (iv) by decreasing N_{44} further on, we can reach a point (which depends not only on N_{44} but also on the relative value of the axial and radial LODM and IDM derivatives) where the two types of dipoles cancel and no intensity at all can be observed; (v) with N_{44} even smaller than before, the IDM will have an absolute value greater than that of the sum of the LODM and there will be a resultant dipole (usually small) with a sense opposite to that of the sum of the LODM; (vi) finally, when $N_{44} = 0$ there will be no contribution to the intensity from the LODM and all of the observed intensity arises from the IDM change.

General Theory. For a given molecule, assuming mechanical and electrical harmonicity, the intensity of the kth normal mode is given by[25]

$$(I_k)_g = K(\partial\mu_g/\partial Q_k)^2 \qquad (1)$$

where $K = \pi N/3c$ and $(\partial\mu_g/\partial Q_k)$ is the change of molecular dipole moment, in the gth molecule-fixed axis with normal coordinate Q_k. Since the normal coordinates are related to internal ones by

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$$\mathbf{R} = \mathbf{lQ} \text{ or } (\partial R_j/\partial Q_k) = l_{jk}$$

assuming, in the C–O stretching factored force field, that the overall dipole moment change derives only from changes in CO bonds, we can obtain

$$(I_k)_g = K[\sum_j^n l_{jk}(\partial\mu_{\mathrm{CO}}/\partial R_j)_g]^2 \qquad (2)$$

The symmetry coordinates are related to normal and internal coordinates by **S** = **LQ** and by **S** = **UR** (**U** is orthogonal) respectively; in the Cotton–Kraihanzel method,[26] using our previous notation $\mathbf{N} = m^{1/2}\mathbf{L}$ (where m is the effective reduced mass of CO[27]), we can obtain

$$(I_k)_g \propto [\sum_j^n\sum_i^n N_{ik}U_{ij}(\partial\mu_{\mathrm{CO}}/\partial R_j)_g]^2 \qquad (3)$$

where $(\partial\mu_{\mathrm{CO}}/\partial R_j)_g$ is the projection of the local dipole moment derivative, on the gth axis, with the internal coordinate R_j, assuming that the dipole lies along the axis of the CO group; i.e., $(\partial\mu_{\mathrm{CO}}/\partial R_j)_g = (\mu'_{\mathrm{CO}})_g = \mu'_{\mathrm{CO}} \cos \alpha_j$ where α_j is the angle between the molecular axis g and the CO bond axis. The *local* dipole derivative $(\partial\mu_{\mathrm{CO}}/\partial R_j)$ is different for different CO sets.

Generally, some of the observed infrared intensities in the CO stretching region are noted to be considerably more intense than those predicted by coupling alone, as "electronic rearrangements may occur in bonds close to the vibrating one even though they are not coupled vibrationally".[28] It is therefore of the utmost importance to give detailed consideration to the IDM change.

If we make the simple approximation that the induced charge on a metal atom attached to a CO group (Δq) is identical for all terminal CO groups and use the arguments given above, we can obtain for the kth normal mode

$$(\sum_j^t\sum_i^n N_{ik}U_{ij})_{\mathrm{M}_r}(\partial q)_{\mathrm{M}_r}{}^t/\prod_l^t \partial R_l \propto (\Delta q)_{\mathrm{M}_r} \qquad (4)$$

where t is the number of the CO ligands bonded to metal M_r and all the $(\partial q)_{\mathrm{M}_r}/\partial R_l$ terms are equal.

If the sum of the induced charges over all metal atoms of the molecule, during a normal vibration, is zero, as will usually be true for high-symmetry compounds, then

$$\sum_r^m (\Delta q)_{\mathrm{M}_r} = 0 \qquad (5)$$

where m is the number of the metal atoms in the molecule, and there will be a unique resultant of the induced dipole changes $(\partial\vec{\mu}/\partial Q_k)$ over the metal atoms, during a given normal mode (which we shall take to be the kth).

We measure the induced dipole derivative from a suitable point P (usually a metal atom). Hence

$$\partial\vec{\mu}/\partial Q_k = \sum_r^m (\Delta q)_{\mathrm{M}_r}\vec{d}_r \qquad (6)$$

where d_r is the P–M_r distance. This expression may be rewritten, using (4), as

$$\partial\vec{\mu}/\partial Q_k \propto \sum_r^m [(\sum_j^t\sum_i^n N_{ik}U_{ij})\{(\partial q)_{\mathrm{M}_r}{}^t/\prod_l^t \partial R_l\}\vec{d}_r]_{\mathrm{M}_r} \qquad (7)$$

If t is the same for all the M_r in the molecule and the $\vec{d}_r$ have the same modulus, this becomes

$$\propto \sum_r^m (\sum_j^t\sum_i^n N_{ik}U_{ij})_{\mathrm{M}_r}\vec{\mu}'_{\mathrm{M}_r} \qquad (8)$$

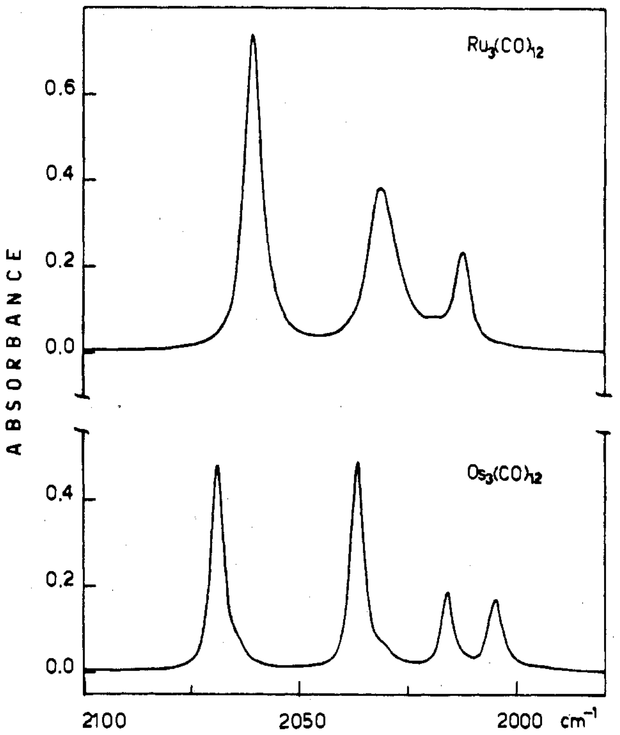

Figure 2. Spectra, in absorbance, in the C–O stretching region for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, in hexane.

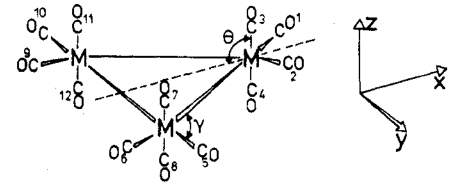

Figure 3. Structure, ligand numbering, and bond angle notation convention used for the $M_3(CO)_{12}$ (M = Ru, Os) complexes.

The overall intensity for the kth normal mode along the gth axis in the general form is then

$$I_k \propto [\sum_j^t\sum_i^n N_{ik}U_{ij}(\mu'_{\mathrm{CO}})_g + \sum_r^m(\sum_j^t\sum_i^n N_{ik}U_{ij})_{\mathrm{M}_r}(\mu'_{\mathrm{M}})_g]^2 \qquad (9)$$

where the induced dipole gradient $(\mu'_{\mathrm{M}})_g$ lies in the gth axis

$$(\mu'_{\mathrm{M}})_g = \mu'_{\mathrm{M}} \cos \omega \qquad (10)$$

and ω is the angle between the molecular axis and the direction of the induced dipole derivative. It is to be noted that relationship 9 calculates *nonzero* intensity only for an IR-active normal mode.

Application to $M_3(CO)_{12}$ Molecules. The differences in the relative intensities of the CO normal modes for the IR solution spectra of $M_3(CO)_{12}$ (M = Ru, Os) complexes, reported in Figure 2, seem to be in contradiction to their analogous structures.[29] Therefore, we have investigated the possibility that the treatment and relationships reported above provide an explanation for this behavior. (A detailed vibrational analysis on these D_{3h} metal carbonyls has been reported in ref 24.) The $M_3(CO)_{12}$ structure, the ligand numbering, and coordinate axes used in this work are given in Figure 3.

The sum of irreducible representation spanned by the ν(CO) vibrations is

$$\Gamma_{\mathrm{CO}} = 2\ \mathrm{A}_1' + \mathrm{A}_2' + \mathrm{A}_2'' + 3\ \mathrm{E}' + \mathrm{E}''$$

of which only the A_2'' and E′ modes are IR active. Equation 5 is fulfilled for all but the two A_1' normal modes; however, for the IR-inactive totally symmetric modes, A_1', there is no

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Table III. Calculated and Observed Relative Intensities and Relative Dipole Moment Gradients

	rel intens of IR-active normal modes (eq ax coupling considered)				rel dipole moment gradients		
compd	I_5	(I_4)	I_6	I_7	μ_{eq}'	μ_{ax}'	μ_M'
$Ru_3(CO)_{12}$	E′(2061)	A_2''(2031)	E′(2018)	E′(2012)	0.83	1.00	0.83
obsd	1.37	1.00	0.05	0.38			
calcd	1.37	1.00	0.05	0.38			
$Os_3(CO)_{12}$	E′(2069)	A_2''(2036)	E′(2015)	E′(2004)	0.97	1.00	0.68
obsd	1.08	1.00	0.35	0.37			
calcd	1.08	1.00	0.35	0.38			

contribution to the intensities through the IDM change.[30]

Since the change in the overall dipole moment arises from the components of the changes in the LODM (related to the dipole moment gradients μ_{eq}' and μ_{ax}'), lying along the relative axes, and in the IDM (related to the magnitude of the induced M–M dipole moment gradient, μ_M'), lying along the metal–metal axes, we can obtain from eq 9 the intensities for the *k*th normal mode along the *x*, *y*, and *z* axes using the appropriate values for μ_{eq}', μ_{ax}', and μ_M'.

In the case of the C–O stretching vibrations of the $M_3(CO)_{12}$ (D_{3h}) molecules only the intensities of the E′ modes are influenced by an induced metal–metal dipole contribution. In the A_2'' mode there can be no such contribution, and therefore, in the practical application of our approach, this band was used as intensity standard ($I(A_2'') = 1.0$). The general but explicit form of eq 9 applied for the actual geometry of $M_3(CO)_{12}$ and for the relative intensity along the *x* direction, for *k*th normal mode, is given in eq 11 where $n = m^{1/2}l$, and γ and θ are the

$$(I)_x = \{[(n_1 + n_2) \cos (150° - \gamma) + (n_5 + n_{10}) \cos (\gamma - 30°) - (n_6 + n_9) \sin \gamma]\mu_{eq}' - [n_3 + n_4 - (n_7 + n_8 + n_{11} + n_{12}) \sin 30°](\cos \theta)\mu_{ax}' + (\sum_{i=1}^{4} n_i - \sum_{i=5}^{12} n_i)(\cos 30°)\mu_M'/2\}^2 \quad (11)$$

bond angles shown in Figure 3 (their numerical values were taken as averages of those reported by Churchill[29]).

The calculated and measured integrated intensities (relative to the A_2'' intensity = 1.00) for the IR-active modes in the CO stretching region, with the equatorial LODM and the IDM gradients (relative to $\mu_{ax}' = 1.00$), are reported in Table III. The integrated relative band intensities of $Ru_3(CO)_{12}$ compared with those of $Os_3(CO)_{12}$ differ particularly for the first and second E′ modes. The intensity of the second E′ mode, in $Os_3(CO)_{12}$, is about one-third of the first one, while in $Ru_3(CO)_{12}$ it is nearly zero. In the present model this observation has two reasons: (a) different amount and sense of coupling between the three symmetry coordinates of species E′, as expressed in terms of the **N** matrices (cf. Table IX of ref 24), and (b) the contribution of the IDM.

The symmetry coordinate for $\nu_5^{E'}$ (S_5: axial only, see Tables VII and IX of ref 24) is strongly coupled in phase with $\nu_6^{E'}$ (S_6: equatorial only); therefore, in this normal mode, the resultants of the separate LODM and IDM changes have the same sense and so result in an increase of the total intensity. This high relative intensity is mainly due to the great contribution of the IDM change. According to our results only ~24% of the total intensity of the highest energy band (ν_5^E) of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ arises from the LODM and more than three-fourths of the intensity has its origin in the induced dipole mechanism. The higher value (1.37) for this $Ru_3(CO)_{12}$ band as compared to 1.08 (relative to $I(A_2'' = 1.0)$, found for $Os_3(CO)_{12}$, is due to differences in the extent of coupling (cf. N_{ij} values in Table IX of ref 24) between the three symmetry coordinates of species E′. The above quantitative results match well with our previous values found for the Mn_2- and $Re_2(CO)_{12}$ series of compounds, where ~72 and ~45% of the intensity of the higher (in that case species B_2) bands had its origin in an induced dipole moment mechanism.[23] Regarding $\nu_6^{E'}$ (equatorially dominated), the symmetry coordinates $S_5^{E'}$ and $S_6^{E'}$ (Table VII of ref 24) are coupled out of phase for both compounds, but the extent of this coupling is smaller for the $Os_3(CO)_{12}$ case (~95% LODM origin), whereas a slight positive IDM contribution to I_6 (2015 cm^{-1}) is obtained for $Os_3(CO)_{12}$ (total intensity − LODM ~ 22%). The main factor responsible for the great difference of the intensities of the 2018/2015-cm^{-1} band pair (Ru/Os) is the opposite phase of mixing with symmetry coordinate S_7 which nearly cancels, in the case of $Ru_3(CO)_{12}$, the resultant of the LODM. For the third E′ band (lowest IR-active fundamental) we have a strong (for Ru) and a medium-strong (for Os) IDM in opposite sense relative to the resultant of the LODM. Hence ~42 and ~22%, respectively, of the intensity calculated only on the basis of LODM is cancelled by the induced dipole moment mechanism.

A higher μ_M' value for $Ru_3(CO)_{12}$ than for $Os_3(CO)_{12}$ reproduces the same tendency previously found for Mn_2- and $Re_2(CO)_{10}$.[23] In both cases, the heavier the metal, the smaller the induced effect. However, it must be stressed that we have not made absolute intensity measurements and so we cannot compare in an absolute way the dipole moment gradients found for these compounds.

Experimental Part

Spectra of Ru_3- and $Os_3(CO)_{12}$, registered for this study with linear absorbance scale in the CO stretching region, are shown in Figure 2. Details of the scanning conditions were given in the ref 24.

Calculations were performed as follows: The C–O stretching (factored) force field was determined, as described in details in the "Appendix" of ref 24, by the use of the spectra of ^{13}CO-enriched samples. The diagonalization procedure of the 12th order force constant matrix **f** according to $\tilde{\mathbf{n}}\mathbf{fn} = \mathbf{Y}$ (cf. Appendix of ref 24) furnished the eigenvector matrices **n**; each column of this matrix refers to a C–O stretching normal mode, and the eigenvalues are directly the n_{ij} elements needed for eq 11. Since each column of the eigenvectors is normalized, the intensities calculated therefrom, according to the geometry of the molecule, are obtained relative to $\sum_{n=1}^{12} I_n = 12$ units. This step corresponds to the case when, in eq 9, $\mu_{eq}' = 1$ and $\mu_M = 0$, and hence only the intensity arising from the LODM is calculated. Then, by the use of our computer program CAR312, the input values for the relative dipole moment gradients of the equatorial ligands, μ_{eq}', and of the IDM, μ_M', were varied in cycles until a good agreement between experimental and calculated band intensities was reached.

Comment

The numerical value to be used for θ in eq 11 has an important effect on the results. Since the axial M–C–O groups were found[29] to deviate from linearity by about 7°, we made calculations with several θ values ranging from 90 to 97°

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(30) We have carried out the present intensity calculations also for the isotopically monosubstituted $M_3(^{12}CO)_{11}(^{13}CO)$ molecules, but in these cases the condition $\sum_r{}^m(\Delta q)_{M_r} = 0$ is not fulfilled. This difficulty can be overcome by assuming $(\Delta q)_{M_r}{}^{^{13}CO} = (\Delta q)_{M_r} - (\overline{\Delta q})_{av}$, where $(\overline{\Delta q})_{av} = [(\Delta q)_{M_1} + (\Delta q)_{M_2} + (\Delta q)_{M_3}]/3$. This assumption makes the calculated intensities, in this case, slightly less reliable than those in the $M_3(^{12}CO)_{12}$ case. For these calculations we use the **L** matrix values since the **N** matrices do not have, in these cases, a constant mass factor.

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(values for $Ru_3(CO)_{12}$). Only in the latter case was simultaneous agreement for all three E′ bands reached. Hence we have a very strong indication that in metal carbonyl intensity studies the angles formed with the CO vectors, rather than those with the MC ones, should be used in the geometrical terms of the equations.

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Synthesis and Spectroscopic Characterization of Ruthenium and Osmium Complexes with Sterically Hindering Ligands. 3.[1] Tris Complexes with Methyl- and Dimethyl-Substituted 2,2′-Bipyridine and 1,10-Phenanthroline

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Metal complexes of the type $[M(L)_3]Cl_2$, where M = Ru(II) and Os(II) and L = 6-methyl-2,2′-bipyridine, 6,6′-dimethyl-2,2′-bipyridine, 2-methyl-1,10-phenanthroline, and 2,9-dimethyl-1,10-phenanthroline, have been prepared and isolated. Absorption spectra, emission spectra, luminescence quantum yields, and lifetimes of these complexes have been measured, and values of the radiative and nonradiative rate constants have been calculated. Although the positions of absorption and emission bands are hardly affected by the methyl substituents, the molar extinction coefficients, emission quantum yields, and lifetimes are decreased in value compared to complexes of the parent 2,2′-bipyridine or 1,10-phenanthroline ligands. Quantum yield and lifetime changes are greater for the dimethyl-substituted complexes of ruthenium, while methyl and dimethyl substitution produces about the same change for osmium complexes. Possible causes of the decrease in quantum yield are discussed.

Introduction

The excited state properties of the tris(2,2′-bipyridine)ruthenium(II) ion have been the subject of a large number of experimental studies in recent years. In particular the luminescence,[2] photosensitization of energy- and electron-transfer processes of both organic and inorganic acceptors,[3] and photochemical[4] and photophysical[5] processes have been extensively studied. There has also been much interest in this ion and related complexes as catalysts in the photochemical decomposition of water.[6]

A few studies have delineated the effects of ligand substituents on the optical properties and excited states of tris(2,2′-bipyridine)ruthenium(II) and tris(1,10-phenanthroline)ruthenium(II) complexes,[7] but little work has been reported on complexes with substituents in sterically hindering positions or with analogous complexes of osmium(II). In a previous paper we reported significant red shifts in the absorption and luminescence spectra of ruthenium(II) and osmium(II) complexes with the sterically hindering benzo-substituted 2,2′-bipyridine ligands: 2-(2′-pyridyl)quinoline and 2,2′-biquinoline.[1a]

In the present work we report the synthesis of ruthenium(II) and osmium(II) complexes with sterically hindering methyl-substituted 2,2′-bipyridine and 1,10-phenanthroline ligands and the effect of these substituents on the luminescence quantum yields, lifetimes, and emission and absorption spectra of the complexes.

Experimental Section

General Information. All syntheses were carried out by using reagent grade materials. 2,9-Dimethyl-1,10-phenanthroline was used as obtained from Aldrich Chemical Co. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., and the results are listed in Table I. The abbreviations bpy = 2,2′-bipyridine, 6-Me(bpy) = 6-methyl-2,2′-bipyridine, 6,6′-Me_2bpy = 6,6′-dimethyl-2,2′-bipyridine, phen = 1,10-phenanthroline, 2-Me(phen) = 2-methyl-1,10-phenanthroline, and 2,9-Me_2phen = 2,9-dimethyl-1,10-phenanthroline are used in the text.

Preparation of 6-Me(bpy). A 25-g sample of 2,2′-bipyridine in 200 mL of diethyl ether was added under nitrogen to 300 mL of a 1.3 N solution of methyllithium prepared by the method of Gilman et al.[8] The orange mixture was refluxed with stirring until a deep red solution was obtained and then stirred at room temperature for 4 h. The mixture was added to a slush of 300 g of ice and 60 mL of 12 M HCl. After being warmed to room temperature, the solution

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