be taken by the species existing in solution.

Now the visible absorption spectra are considered. The spectrum of copper(II) solution in 14 M aqueous ammonia shows an absorption maximum at a lower wavenumber with a higher intensity than that in the spectrum of the tetraammine complex (Figure 4). The orbital energies for tetraammine-, hexaammine-, and pentaamminecopper(II) complexes of tetragonal symmetries (Figure 5) are calculated according to the scheme of the angular-overlap model (Table II).[17,18] The e_σ parameter is a measure of σ-antibonding energy. The order of orbital energies for both square and elongated-octahedral forms is $d_{xy}, d_{yx}, d_{zx} < d_{z^2} < d_{x^2-y^2}$, if π interactions are disregarded. A smaller Cu–N$_{eq}$ distance, as reported by Yamaguchi et al., would give a higher value of e_σ and result in a shift of the bands to higher energies. This is not consistent with the experimental findings. We obtained a bond length close to that of the tetraammine complex. Then, no appreciable shift of the main band would be observed, if the complex retained the D_{4h} symmetry (or a quasi-D_{4h} symmetry with a NH_3 and a H_2O ligand at the axial site). However, if the species existing in solution has a square-pyramidal (C_{4v}) symmetry as shown in Figure 5 ($\theta > 90°$), the energy of the $d_{x^2-y^2}$ orbital decreases. (In Table II, θ denotes the angle between axial and equatorial bonds). For $\theta = 103°$, the calculated transition energy of the d_{xy}–$d_{x^2-y^2}$ transition will be 10% less the energy for $\theta = 90°$. This agrees well with the experimental finding (the decrease in the energy is about 10%).

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Registry No. $[Cu(en)_2]Cl_2$, 15243-01-3; $[Cu(NH_3)_5]^{2+}$, 44237-19-6; $CuSO_4$, 7758-98-7; NH_3, 7664-41-7.

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Contribution from the School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K., and Istituto di Chimica Generale e Inorganica, Universita di Torino, 10125 Torino, Italy

Two-Mode ν(CO) Vibrational Frequency Changes as Indicators of Geometry Changes in Mixed Crystals of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$

SIDNEY F. A. KETTLE*[†] and PIER-LUIGI STANGHELLINI[‡]

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Small changes in the frequency of the two-mode ν(CO) A_1' vibrations of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in mixed crystals are interpreted as indicating the molecular geometry changes by which each species adapts to sites in the mixed crystal.

Introduction

One of the consequences of the impact of NMR spectroscopy on inorganic chemistry in recent years has been the recognition that molecules may be nonrigid.[1] Other evidence on this point is available from X-ray studies where, for instance, it has been found that two rather different geometries for the $[Ni(CN)_5]^{3-}$ ion may occur in the same crystal lattice.[2] Such observations raise the question of the extent to which a given molecular structure is determined by the environment of the molecule. With the accuracy now available from X-ray structure determinations, this question seems particularly relevant in interpreting bond length and angle data.

Until recently there seemed to be no direct experimental probe of the sensitivity of a molecule to its environment, apart from that provided by multiple structure determinations. We have found, however, that a detailed comparison of two-mode frequencies[3] seen in the Raman spectra of mixtures of pure crystals of isomorphous metal carbonyls with those of mixed crystals (i.e. cocrystallized) of the same species reveals small frequency shifts.[4] To date, all such shifts have been found on totally symmetric (and, thus, volume-changing) modes. The only consistent interpretation of these observations is that they reflect small bond length differences between a molecule in pure and mixed crystals. In general, the larger molecule appears to decrease in size (associated with frequency increases) whereas the smaller seems to increase in size. That is, in a mixed crystal, each molecule acts in a manner consistent with a distortion toward an "average" geometry.

In this context it was of interest to carry out similar studies on species that are closely similar in size. The molecules $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ immediately suggested themselves for this investigation and are the subject of the present report. Not only are they isostructural and their structures known with very high precision but they have unit cell parameters in the same space group ($P2_1/n$) that are all identical to better than 1% (the osmium unit cell being the smaller).[5,6]

We have therefore made detailed studies of the Raman spectra of mixed crystals and mixtures of pure crystals of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in the 2000-cm^{-1} region, which established that only the highest frequency feature—a volume-changing mode of molecular A_1' symmetry—is two mode in character and so the only feature of interest in the present work.[3] Most of our data were obtained by using conventional single-beam spectroscopy since the frequency differences between the two A_1' modes were readily measured. However, two difference Raman spectra (a mixed-crystal sample against

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[†] University of East Anglia.
[‡] Universita di Torino.

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(3) Two-mode features are those that are vibrationally uncoupled and so appear as distinct peaks in the spectra of crystals containing both components. Such modes display an insensitivity to environment in other ways. Thus, in the present work, the peak half-widths of the A_1' features are, within error limits, independent of the composition of the mixed crystal.
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Table I[a]

R	ν(CO) A_1', cm^{-1} Os	ν(CO) A_1', cm^{-1} Ru	$\Delta\nu(A_1')$, cm^{-1}
25	2128.5	2119.1	9.4
13	2128.3	2119.0	9.3
7	2128.2	2119.3	8.9
3	2128.4	2119.6	8.8
1.8	2128.4	2120.1	8.3
1.1	2127.4	2119.6	7.8
1.0	2128.0	2120.1	7.9
0.6	2127.8	2120.2	7.6
0.5	2126.8	2119.4	7.4
0.4	2127.4	2120.0	7.4
0.25	2127.4	2120.5	6.9
0.2	2126.6	2119.8	6.8

[a] R is the $[Ru_3(CO)_{12}]/[Os_3(CO)_{12}]$ ratio (see text). The ν(CO) values for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are 2118.9 and 2127.1 cm^{-1}, respectively.

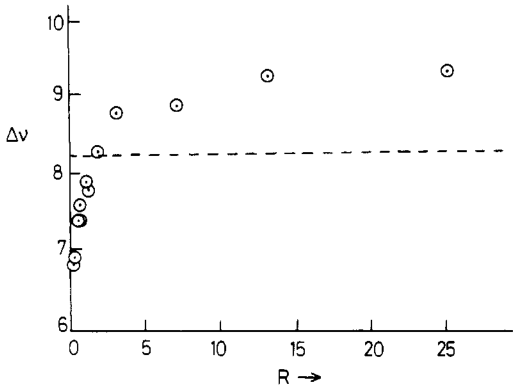

Figure 1. Difference in frequencies between A_1' ν(CO) modes of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ as a function of the ratio R (=$[Ru_3(CO)_{12}]/[Os_3(CO)_{12}]$) in mixed crystals. The frequency difference between the pure species is shown as a dashed line.

crystals of either pure component) were also recorded.

Results

Because the ruthenium and osmium species have very different solubilities in common organic solvents (ruthenium high, osmium low), it was not a trivial matter to prepare mixed crystals of uniform composition. The samples used in this study were taken from midcut crystallizations. No significant intensity changes occurred on rerunning the spectra several times with fresh samples from the same crystallization so we believe that inhomogeneities may be ignored. Because the composition of the solution may differ from that of the crystals, the ruthenium:osmium ratio in the latter was determined from the relative intensities of the A_1' ν(CO) peaks for the two species and checked by similarly comparing the intensities of the A_1' ν(M–M).

In Table I we detail the frequencies observed for the A_1' ν(CO) modes of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in 12 cocrystallized mixed crystals over an approximate Ru:Os range from 25:1 to 1:5, together with the corresponding frequencies for the pure components.

The observed frequencies show a somewhat erratic behavior (by ca. ±0.5 cm^{-1}). Most of the frequency noise arises from instrumental effects, as is evident when the frequency *difference* between the ruthenium and osmium A_1' ν(CO) features is considered. As shown in Figure 1, this difference varies smoothly with crystal composition. The frequency difference is 8.2 cm^{-1} for the two pure compounds, a difference that is also found for mixed crystals with an approximate 1:1 composition ratio. That this coincidence in frequency separation is misleading is evident from the data on mixed crystals containing one component in low concentration. Here, a difference of differences of 2.6 cm^{-1} between ruthenium-rich and osmium-rich samples was observed (Table I).

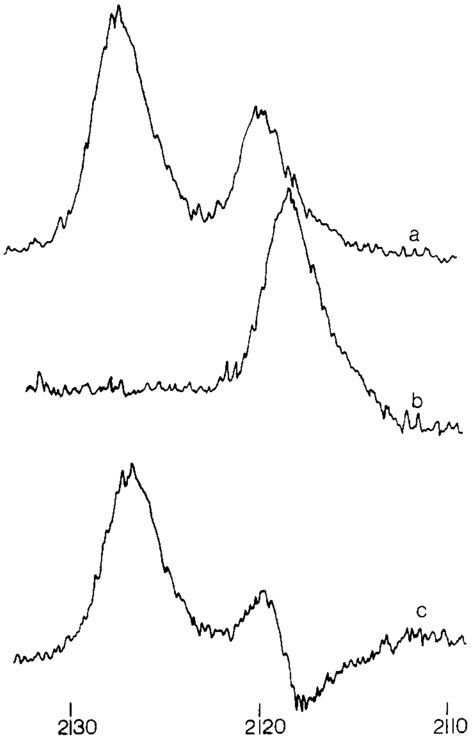

Figure 2. Spectra of an $Os_3(CO)_{12}/Ru_3(CO)_{12}$ mixed-crystal sample (a) and a sample of pure $Ru_3(CO)_{12}$ (b) and the difference spectrum (c) (spectrum a − spectrum b). The spectra shown in this figure are of the sample with R = 0.5 (Table I).

It is clear that inherent instrumental errors can mask the frequency shifts that are the object of the present study. Although the study of a series of samples can reveal some aspects of the real variations, it is desirable to be able to completely circumvent the problem of instrumental errors. Difference Raman spectroscopy is the simplest method of achieving this end. Two samples are alternately presented to the laser beam and data on each separately recorded. The frequency interval at which samples are changed is small compared to the instrumental resolution. Backlash and other mechanical errors are thus, essentially, identical for the two samples. In our work, a two-compartment spinning cell containing semicircular capillaries was used. One capillary was filled with a mixed crystal (i.e. cocrystallized) and the other with a sample of one of the pure metal carbonyls. By the similar use of separate recording electronics for each channel, two conventional Raman spectra were obtained. From these data difference spectra in which the two conventional spectra were subtracted (with weighting, if appropriate) were also obtained. An example of a set of spectra obtained in this way is shown in Figure 2.

Unfortunately, the spinning-cell arrangement requires rather large quantities of sample (at least $^1/_4$ g in each capillary), and in order to ensure that the cocrystallized sample is of uniform composition, it is necessary to crystallize several grams of mixture. On the grounds of both the cost and the technical feasibility of preparing uniform crystals, we have therefore only carried out two double-beam measurements. They gave frequency results in close accord with those of Table I. The data of Table I were obtained under conditions in which frequency errors were minimized. We therefore have confidence in the trends shown in the absolute frequency data of Table I.

Discussion

Table I shows that when $Os_3(CO)_{12}$ is a low-concentration impurity in an $Ru_3(CO)_{12}$ host (R large), its ν(CO) A_1' fre-

Table II

	$Ru_3(CO)_{12}$	$Os_3(CO)_{12}$
M-M, Å	2.8542 (22)	2.8771 (27)
M-C_{ax}, Å	1.942 (2)	1.946 (6)
M-C_{eq}, Å	1.921 (5)	1.912 (7)
C-O_{ax}, Å	1.133 (2)	1.134 (8)
C-O_{eq}, Å	1.127 (2)	1.145 (5)
av M-C_{ax}-O, deg	173.0 (2)	175.3 (4)
av M-C_{eq}-O, deg	178.9 (7)	178.4 (4)
a, Å	8.1172 (8)	8.0817 (6)
b, Å	14.8627 (15)	14.7683 (11)
c, Å	14.6140 (20)	14.5773 (11)
β, deg	100.667 (10)	100.56 (1)
V, Å^3	1732.6 (4)	1710.41 (23)
ref	6	5
$i_{ax,ax}$	0.399	0.481
$i_{eq,eq}$	0.339	0.376
ref	8	8

quency rises; conversely, when $Ru_3(CO)_{12}$ is the guest in an $Os_3(CO)_{12}$ host, its ν(CO) A_1' frequency also rises. Two data points at the low-ruthenium-concentration limit show the ν(CO) A_1'(osmium) frequency dropping below its pure-compound value. The corresponding ν(CO) A_1'(ruthenium) values also appear low; the two difference spectra confirmed that these frequencies are low. Thus, a difference spectrum of the $R = 0.5$ sample (Figure 2) shows that at this ratio the ν(CO) A_1'(ruthenium) has risen by 1.2 cm^{-1} relative to the pure-compound value.

The close similarity of the unit cell dimensions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ conceals small differences between the two species. Pertinent average bond length data are collected in Table II. Within error limits, the axial M–C and C–O bonds are of equal length in the two compounds as too are the M–C_{eq} bonds. However, significant differences exist between the M–M and C–O_{eq} bonds. It seems from Table II that, in terms of bond lengths, $Os_3(CO)_{12}$ is a slightly larger molecule than $Ru_3(CO)_{12}$. That the osmium species occupies a slightly smaller unit cell volume must, then, be because of a more efficient packing in $Os_3(CO)_{12}$, attributable to small bond angle differences between the two species. If this analysis of the crystal structure data is correct, at the ruthenium-rich limit of the mixed-crystal series the larger osmium impurity molecules are constrained to (effectively smaller) ruthenium sites. It is therefore understandable that, under compression, their ν(CO) A_1' frequency should rise, thus paralleling the behavior of the metal hexacarbonyls.[4] Put another way, in a ruthenium lattice, the osmium species is constrained to a slightly less efficient packing, and although the site that it occupies is almost of the same volume as in its own lattice, it is also of a slightly different, more extended, shape; the distortion resulting from this situation is accommodated by a slight compression of the C–O bonds on the "outside" of the molecule (our difference Raman studies indicate no detectable frequency shift on modes internal to the molecule). However, on this basis we might well expect that the ν(CO) A_1' feature of a ruthenium impurity in an $Os_3(CO)_{12}$ host would be lower in frequency than that in pure crystalline $Ru_3(CO)_{12}$, contrary to what is observed. Clearly, more is involved than bond extension as a mechanism of site adaption. The most reasonable additional feature is bond angle changes—it is in a situation such as the present one, when molecules occupy almost identical volumes, that shape changes are likely to be most evident. The fact that the $M_3(CO)_{12}$ molecules occupy positions of no crystallographic symmetry (i.e. general positions) means that molecular shape adaption to the crystal environment is already apparent in the crystallographic data. If it is assumed that the most probable angle adaption occurs in those angles showing the greatest deviation between the two molecules, the conclusion is clear. The differences between the average bond angles reported for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ are all less than 0.7° with the exception of the average M–C_{ax}–O angles, where the difference is 2.3° (Table II), the angle in the osmium compound being greater than that in the ruthenium compound. Interestingly, the greatest difference between the vibrational interaction constants reported for the two species is in the axial–axial constants[8] (Table II). Insofar as the coupling between axial vibrators is angle dependent, a distortion of the ruthenium molecules to an osmium site is likely to increase the axial–axial interaction term and, with it, the frequency of the ruthenium ν(CO) A_1'.[9] While this argument explains the frequency shifts seen when ruthenium is doped into an osmium lattice, its converse would lead to an expectation of a frequency drop when osmium is doped into a ruthenium lattice. We should then, be selective in our explanations in order to give an account of our results: when osmium is the dopant, bond length changes are more important than angle changes; when ruthenium is the dopant, angle changes represent the more important adaption.

Conclusion

It is commonplace to comment that "site effects" are involved in the spectroscopic properties of crystalline species.[7] Apart from the consequences of site symmetry, these site effects have been little investigated. In the present paper we have argued that some of the frequency changes seen between isolated and crystalline species (ignoring factor group effects) originate in the shape and size of the molecule undergoing minor changes to adapt to its site. Further, these geometrical changes may be revealed in the frequency changes themselves. We cannot claim that the interpretation of our data that we present is unique, only that no other consistent interpretation is evident to us. Clearly, an independent check on our interpretation is desirable, and here EXAFS, possibly at the limits of its resolution, suggests itself as one possibility for species rather simpler than those that have been the subject of the present study.

Experimental Section

Spectra were recorded on a Spex 1401 spectrometer using an Ar/Kr mixed-gas laser with ca. 25 mW at the sample. Resolution was ca. 1 cm^{-1}. Difference spectra were obtained as described in the text.

Acknowledgment. We are indebted to Dr. S. Rakshit for some preliminary measurements on this system and to the British Council for support.

Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9.

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(9) Although such an angle dependence is predicted by a multipolar expansion of the interaction term, it is to be noted that the angle dependence of the dipole–dipole term alone in no way accounts for the magnitude of the difference of $i_{ax,ax}$ between the two pure compounds. However, this dependence may be sufficient to make a significant contribution to the small frequency changes under discussion here.