Inorg. Chem. **1984**, *23*, 4466–4469

for an assessment of the respective merits of various spectroscopic techniques. The conclusions drawn during the course of the present investigation amply demonstrate the utility of combining luminescence work with NMR studies for the determination of the structure and solution behavior of lanthanide complexes.

The luminescence studies permit one to deduce results that would not have been easily obtained through NMR methods. For instance, it was shown that the lanthanide DOTMA compounds exhibit no tendency to self-associate and that these compounds contain a single water molecule bound at the inner sphere of the metal ion. Furthermore, the luminescence studies clearly indicate that a single, well-defined EuDOTMA species exists in the crystalline solid but that two nonequivalent emitting species exist in solution. This latter conclusion was also obtained from the NMR studies. The luminescence techniques cannot permit one to determine the structures of the DOTMA or DOTA complexes in solution, but through the use of NMR spectroscopy it was possible to propose a structure for each isomer present in the solutions. One must remember, however, that the results are only suggestive of the nature of the two species yielding the highest values of the *R* agreement factors. In addition, it was demonstrated that the compounds experience a considerable degree of steric crowding and that all the isomers were rigid on the NMR time scale.

Acknowledgment. This work was supported by the Camille and Henry Dreyfus Foundation, through a Teacher-Scholar award to H.G.B. J.F.D. is Chercheur Qualifie at the University of Liege and gratefully acknowledges research support from the Fonds National de la Recherche Scientifique of Belgium. The authors thank Dr. Cl. Houssier (University of Liege) for recording some of the CD spectra and Dr. R. W. White (Chemical Abstracts Service, Columbus, OH) for help in naming the DOTMA ligand.

Supplementary Material Available: Total luminescence and circularly polarized luminescence spectra obtained within the $^5D_0 \rightarrow {}^7F_2, {}^7F_3, {}^7F_4$ transitions of EuDOTMA and within the $^5D_4 \rightarrow {}^7F_5, {}^7F_4, {}^7F_3$ transitions of TbDOTMA (6 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratory of Inorganic Chemistry, College of General Education,
and Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464, Japan

Structural Study of Copper(II) Sulfate Solution in Highly Concentrated Aqueous Ammonia by X-ray Absorption Spectra

MITSURU SANO,*[†] TETSUYA MARUO,[‡] YUICHI MASUDA,[‡] and HIDEO YAMATERA[‡]

Received February 24, 1984

The structural study of a concentrated ammoniacal solution of copper(II) sulfate has been carried out with X-ray absorption techniques. The EXAFS spectra were obtained for solid $[Cu(en)_2]Cl_2 \cdot 2H_2O$ and the copper(II) solution in concentrated aqueous ammonia. A comparison of the spectra gives the structural parameters of the copper complex in solution; the Cu–N distance is 2.02 Å, and the coordination number is about 4 as determined by EXAFS. The XANES of the solution suggests a square-pyramidal structure, $[Cu(NH_3)_5]^{2+}$. The absorption spectrum has also been considered by using the angular-overlap model. It is concluded that the copper(II) species existing in concentrated aqueous ammonia is a square-pyramidal $[Cu(NH_3)_5]^{2+}$ with the bond distance 2.02 Å between copper and equatorial nitrogen atoms.

Introduction

Addition of aqueous ammonia to an aqueous copper(II) solution results in successive replacements of coordinated water by ammonia according to

$$[Cu(NH_3)_{n-1}(H_2O)_{6-n+1}]^{2+} + NH_3 = [Cu(NH_3)_n(H_2O)_{6-n}]^{2+} + H_2O$$

The successive formation constants have been given for each step of the reactions. K_5 is very small (0.3), and K_6 is practically zero.[1] The electronic spectrum of the aqueous copper(II) solution changes on the addition of aqueous ammonia. The wavenumber and the molar absorption coefficient increase with increasing ammonia concentration until $[Cu(NH_3)_4]^{2+}$ is formed. However, further addition of ammonia results in a substantial decrease in the wavenumber of the absorption maximum and a substantial increase in the intensity.

An X-ray diffraction study of solid $K[Cu(NH_3)_5](PF_6)_3$ has shown a square-pyramidal form for the pentaamminecopper(II) ion with $Cu–N_{eq}$=2.010 and 2.048 and $Cu–N_{ax}$=2.193 Å.[2] (N_{eq} and N_{ax} denote the equatorial and axial nitrogen atoms.) It is reported from an EXAFS study that $[Cu(NH_3)_5](BF_4)_2$ has five equal Cu–N bond lengths.[3] An X-ray diffraction study of the copper(II) species in highly concentrated ammoniacal solution has been carried out by Yamaguchi et al., who showed a tetragonal structure: $Cu–N_{eq}$ = 1.93, $Cu–N_{ax}$=2.30, $Cu–X_{ax}$=2.30 Å (X = N, O).[4] This structure is considerably different from that in the crystal.

Extended X-ray absorption fine structure (EXAFS) is well-known to be one of the most powerful tools to study the local environment of a concerned atomic species.[5] X-ray absorption near-edge structure (XANES) also gives useful information for the molecular geometry.[6] In this paper, we report a structural study of a copper(II) solution in highly concentrated aqueous ammonia by the X-ray absorption techniques.

Experimental Section

Sample Preparation. An ammoniacal copper solution of high ammonia concentration was prepared by introducing gaseous ammonia into a tetraamminecopper(II) sulfate solution to saturation (the NH_3/Cu mole ratio was about 47). The concentration of the cop-

---

[†] Laboratory of Inorganic Chemistry, College of General Education.
[‡] Department of Chemistry.

(1) Hathaway, B. J.; Tomlinson, A. A. G. *Coord. Chem.* **1970**, *5*, 1–45.
(2) Alagna, L.; Prosperi, T.; Tomlinson, A. A. G.; Vlaic, G. *J. Chem. Soc., Dalton Trans.* **1983**, 645–648.
(3) Duggan, M.; Ray, N.; Hathaway, B. J.; Tomlinson, A. A. G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton Trans.* **1980**, 1342–1348.
(4) Yamaguchi, T.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 415–419.
(5) Sandstrom, D. R.; Lytle, F. W. *Annu. Rev. Phys. Chem.* **1979**, *30*, 215–238.
(6) Glen, G. L.; Dodd, C. G. *J. Appl. Phys.* **1968**, *39*, 5372–5377.

0020-1669/84/1323-4466$01.50/0

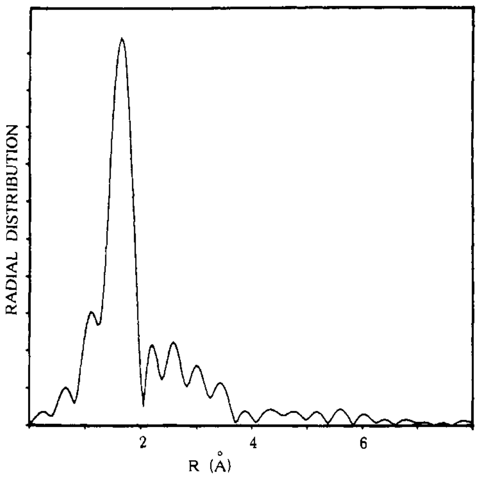

Figure 1. Fourier transformation of the EXAFS spectrum of a copper(II) sulfate solution in concentrated aqueous ammonia.

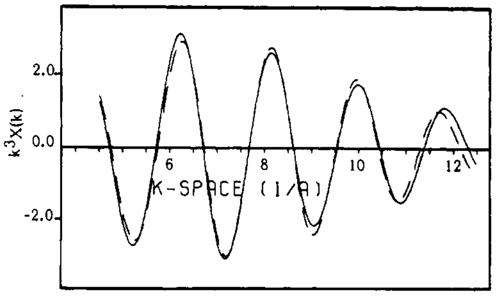

Figure 2. Curve-fitting results of structure determination for the species in solution by use of a set of parameters obtained from the spectrum of solid [Cu(NH$_3$)$_4$]SO$_4$·H$_2$O. The solid line is the filtered EXAFS spectrum, and dashed line is the least-squares fit.

per(II) ion was determined by EDTA titration (0.323 M). The concentration of total ammonia was determined by titration with hydrochloric acid (15.3 M). The solid samples as reference compounds were prepared by the literature methods.[7]

Measurements. Measurements were carried out on the EXAFS port at the Photon Factory (2.5 GeV) of the National Laboratory of High-Energy Physics (KEK). The operation current was 150–80 mA. The spectra were registered in a transmission mode. A small volume of the sample solution was contained in a plastic cell between Mylar windows spaced 1.0 mm apart. The solid compounds were powdered and enclosed between adhesive tape in a polyethylene bag to protect them from moisture and to form a uniformly thin film. The absorption spectra were measured at room temperature in the range of photon energy extending from 8600 to 10000 eV. Intensity at each energy was measured with an ionization chamber for 2 s. The spectra have been taken with a resolution of 0.5 eV and a statistical error within 0.05%.

Data Analysis. The EXAFS was obtained by using standard procedures of the preedge subtraction, cubic-spline removal, and Fourier filtering.[8] The curve-fitting analysis was performed according to the method of Cramer et al.[9] using the following formula for $k^3\chi(k)$:

$$k^3\chi(k) = \sum c_0 N r^{-2}[\exp(-c_1 k^2)]k^{-c_2}[\sin\,[a_0 + (a_1 + 2r)k + a_2 k^2]] \tag{1}$$

where N and r represent respectively the coordination number and the interatomic distance, c'_0, c_1, and c_2 are the parameters for amplitude functions, and a_0, a_1, and a_2 are the parameters for the phase shift. These parameters were determined by fitting to the EXAFS spectrum a model compound with a known structure and transferring to the analysis of the spectrum of the solution.

Table I. Results of Curve-Fitting Analysis of the EXAFS Spectra for Copper(II) Solution in Highly Concentrated Aqueous Ammonia and for the Crystalline Tetraamminecopper(II) Complex Salt (for Comparison)

	fitting	coord no.[a]	Cu–N dist,[a] Å
[Cu(NH$_3$)$_5$]$^{2+}$	one shell	3.6 ± 0.1	2.018 ± 0.002
	two shell	3.6 ± 0.1	2.017 ± 0.002
		−0.2 ± 0.1	2.372 ± 0.002
[Cu(NH$_3$)$_4$]SO$_4$·H$_2$O	one shell	3.5 ± 0.1	2.000 ± 0.002
	two shell	3.4 ± 0.1	2.000 ± 0.002
		0.2 ± 0.2	2.513 ± 0.006 (2.03)[b]

[a] The errors given here are only those concerned with the curve-fitting procedure. (Parameters for the curve fitting were transferred from [Cu(en)$_2$]Cl$_2$·2H$_2$O as the model compound.) Experimental errors and/or errors due to misfit of the model compound and of the method of analysis to the quality of experimental data are not included. [b] The value in parentheses is the result from an X-ray diffraction study.[16]

Results and Discussion

The results of Fourier transformation from the k space to the r space are shown in Figure 1; the transformation is applied to the $k^3\chi(k)$ values in the k range of 4.0–13.0 Å^{-1}. In order to determine the c_n and a_n parameters (n = 0–2), we first examined the spectra of crystalline [Cu(en)$_2$]Cl$_2$·2H$_2$O, of which the structure is known: $r_{\text{Cu–N}_{\text{eq}}} = 2.00$, $r_{\text{Cu–O}_{\text{ax}}} = 2.62$, $r_{\text{Cu–Cl}_{\text{ax}}} = 2.81$ Å.[10] Since the Cu–N bond distance is isolated from the other bonds, the compound is proper for obtaining the parameters for Cu–N interaction. With fixed N and r values, we obtained the c_n and a_n parameters by curve fitting the Fourier-filtered spectra in the k range of 4.5–12.5 Å^{-1} for the isolated Cu–N interaction (1.0 ≤ r ≤ 2.20 Å). In order to obtain the structure, the curve-fitting analyses have been carried out on the assumptions of a single Cu–N distance and two different Cu–N distances. The numerical results are summarized in Table I. The coordination numbers for the concerned complex obtained from both fitting procedures are about 4 with Cu–N = 2.02 Å. However, the calculation for the two-shell type gives negative coordination number with Cu–N = 2.38, which is not real. Since the c_1 parameter is correlated with the Cu–N vibration, the curve-fitting analysis with a fixed c_1 value gives a smaller coordination number for Cu–N bonds vibrating with a larger amplitude. Considering that the amplitude of the Cu–N vibration in the solid en complex is expected to be smaller than those in the ammine complexes, the coordination number in the ammine complexes is very likely to be 4, which corresponds to the equatorial nitrogen atoms.

We did not find the axial nitrogen atom in the concerned ammine complex and in the axial oxygen atom in the solid tetraammine complex. It is consistent with some other EXAFS studies where axial ligands of Cu^{2+} were not detected (for solid CuSO$_4$·5H$_2$O and for an aqueous CuSO$_4$ solution).[11-13]

We deduced the shape of the copper(II) complex existing in concentrated ammoniacal solutions from XANES and absorption spectra.

The XANES spectra give information about the symmetry of the environment of the absorbing atom. The XANES spectra for the copper(II) complexes in solid and solution (Figure 3) show the preedge (A), the midedge (B), and the

---

(7) "Shin Jikken Kagaku Koza"; Maruzen: Tokyo, 1977; Vol. 8, pp 1365–1366.

(8) Cramer, S. P.; Hodgson, K. O. *Prog. Inorg. Chem.* **1979**, *25*, 1–39 and references therein.

(9) Cramer, S. P.; Hodgson, K. O.; Stiefel, E. I.; Newton, N. E. *J. Am. Chem. Soc.* **1978**, *100*, 2748–2761.

(10) Ball, R. D.; Hall, D.; Richard, C. E. F.; Waters, T. N. *J. Chem. Soc. A* **1967**, 1435–1437.

(11) Joyner, R. W. *Chem. Phys. Lett.* **1980**, *72*, 162–164.

(12) Sham, T. K.; Hastings, J. B.; Perlman, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 5904–5906.

(13) Sano, M.; Maruo, T.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3287–3290.

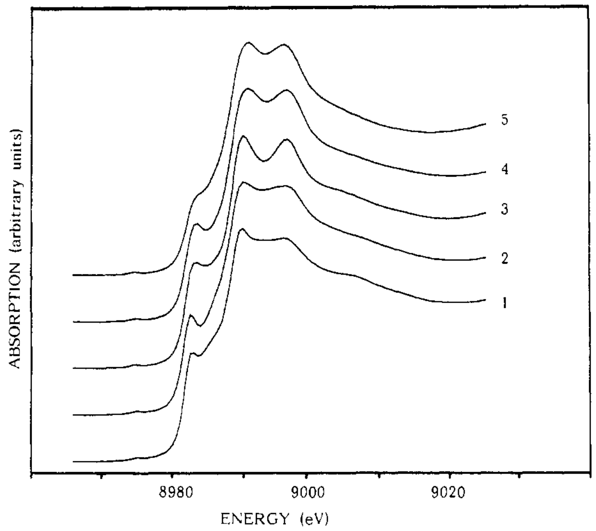

Figure 3. X-ray absorption near-edge structure (XANES) data showing structure near the copper *K* edge: 1, $[Cu(NH_3)_4]SO_4{\cdot}H_2O$ in solid; 2, $[Cu(NH_3)_4]^{2+}$ in solution; 3, $[Cu(en)_2]Cl_2{\cdot}H_2O$ in solid; 4, $[Cu(en)_2]^{2+}$ in solution; 5, copper(II) solution in concentrated aqueous ammonia.

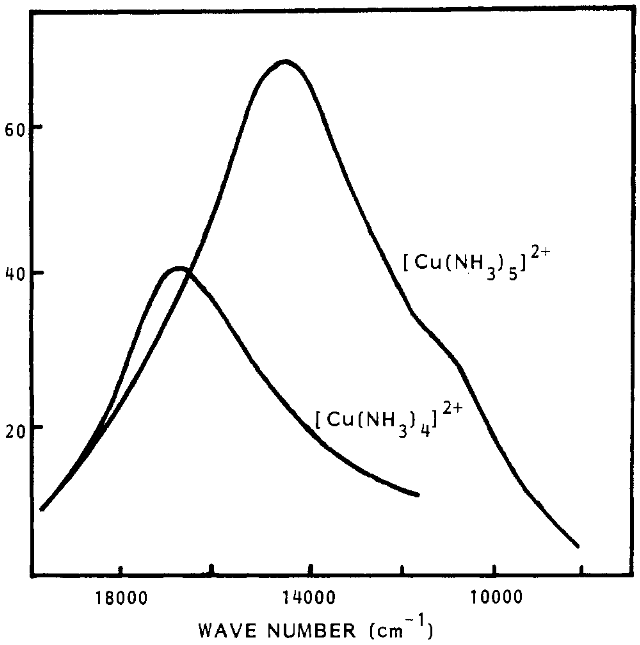

Figure 4. Visible absorption spectra of amminecopper(II) solutions.

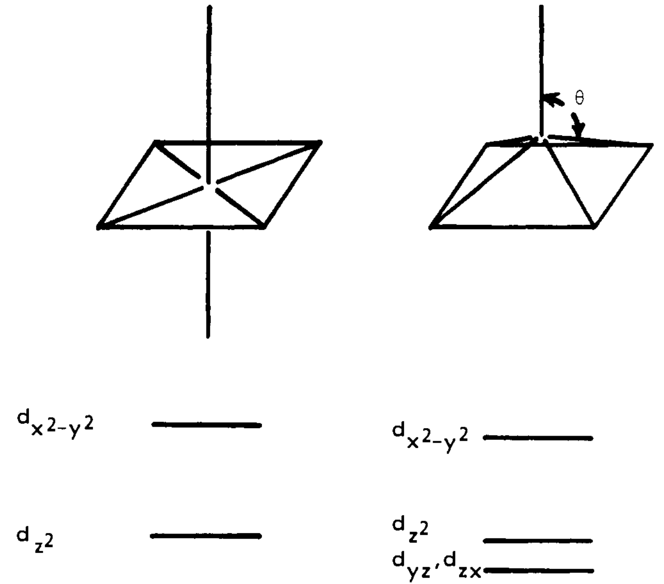

Figure 5. Orbital energy levels for complexes of D_{4h} and C_{4v} symmetries.

Table II. Calculated d-Orbital Energies by the Angular-Overlap Model

orbital	D_{4h} (4 N_{eq})^a	D_{4h} (4 N_{eq} + 2 N_{ax}')^a	C_{4v} (4 N_θ + N_0)^b
d_{xy}	0	0	0
d_{yz}	0	0	$^3/_2 \sin^2 (2\theta e_\sigma)$
d_{zx}	0	0	$^3/_2 \sin^2 (2\theta e_\sigma)$
d_{z^2}	e_σ	$e_\sigma + 2e_\sigma'$	$^1/_4(1 + 3 \cos (2\theta))^2 e_\sigma + e_\sigma'$
$d_{x^2-y^2}$	$3e_\sigma$	$3e_\sigma$	$^3/_4(1 - \cos (2\theta))^2 e_\sigma$

[a] N_{eq} represents a N donor atom at an equatorial site. N_{ax}' represents a N or O donor atom at an axial site. [b] $N_\theta = N_{eq}$ when $\theta = 90°$. $N_0 = N_{\theta=0°} = N_{ax}$.

main peaks (C and D). The strong similarities between the tetraammine and bis(ethylenediamine) complexes (curves 1–4) are evident. This is to be expected since the first coordination shell of nitrogen atoms around Cu^{2+} is approximately tetragonal in the tetraammine and bis(ethylenediamine) complexes. The midedge feature (B) for the concentrated ammoniacal solution is less pronounced than those of other spectra. Bair et al.[14] and Kuroda et al.[15] reported the assignment of the XANES of Cu^{2+} and $[CuCl_4]^{2-}$ on the basis of MO calculations, respectively. Both results showed that the first preedge feature (A) is attributed to the 1s–3d transition. The main peaks (C and D) are interpreted as 1s–4p and 1s–5p transitions, and the midedge feature (B) is interpreted as a 1s–4p plus shakedown transition. The shakedown transition occurs as follows. The effective nuclear charge of the Cu atom increases on an electronic transition from 1s to an outer shell, the valence orbitals are stabilized, and a ligand σ electron transfers to the hole in the stabilized metal d orbital. Then, the probability for the shakedown transition to occur depends upon the overlap between the lone pair orbital of the ligand and the vacant d orbital of the metal. The lower intensity of the B feature for the solution complex can be an indication of a smaller overlap between those orbitals. The smaller σ overlap will come from the following two reasons: (1) the longer Cu–N distance; (2) the displacement of the nitrogen atoms from the $d_{x^2-y^2}$ plane. The EXAFS results show that the Cu–N bond distance in the concerned complex is almost the same as those in the other complexes. This excludes the possibility of (1). The second reason is possible. The σ overlap is proportional to 1 − cos 2θ. (θ is defined in Figure 5). The aqueous tetraammine and both en complexes have planar nitrogen atoms lying at 90°. Although the copper atom in the solid ammine complex lies 0.2 Å above the basal plane of four nitrogen atoms,[16] this displacement will cause a decrease of only 2% in the energy of absorption maximum. On the other hand, if the concerned complex has an out-of-plane copper atom at θ = 103°, the decrease in the overlap will exceed 10%. Such a tetragonal-pyramidal form may possibly

---

(14) Bair, R. A.; Goddad, W. A., III *Phys. Rev. B: Condens. Matter* **1980**, *22*, 2767–2776.

(15) Yokoyama, T.; Asakura, K.; Kosugi, N.; Kuroda, H., to be submitted for publication.

(16) Morosin, B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B25*, 19–30.

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%).

Acknowledgment. We thank the staff of the Photon Factory at KEK for providing beam time and kindly giving us useful advice and assistance.

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.

---

[17] Schäffer, C. E.; Jørgensen, C. K. *Mol. Phys.* **1965**, *9*, 401–415.

[18] Smith, D. W. *Struct. Bonding (Berlin)* **1978**, *35*, 87–118.

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[‡]

Received March 27, 1984

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

---

[†] University of East Anglia.

[‡] Universita di Torino.

[1] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed; Wiley: New York, 1980; p 1217 ff.

[2] Raymond, K. N.; Corfield, P. W. R.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1362. See also, for example: Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1104.

[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.

[4] Cartner, A.; Kettle, S. F. A.; Rakshit, S.; Willis, D. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 369.

[5] Churchill, M. R.; De Boer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

[6] Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

[7] Halford, R. S. *J. Chem. Phys.* **1946**, *14*, 8.

0020-1669/84/1323-4469$01.50/0