error and are close to those observed for other diamagnetic Fe(II) complexes.

Phthalocyaninechloroiron(III).—The oxidation state of the iron in this compound has been shown to be three by quantitative oxidation,[19] and it should have a spin of $^3/_2$. The magnetic moment is low and on the basis of a careful study of its temperature dependence, it has been suggested that dimeric iron–iron interactions occur.[8] No magnetic splitting was observed in the Mössbauer spectrum at 77°K, but one might hope to do so at lower temperatures. The absence of any temperature variation in the quadrupole splitting suggests that no significant depopulation of excited electronic states is occurring in the temperature range covered.

The only other well-authenticated iron(III) compound with a quartet ground state is $Fe[S_2CN(C_2H_5)_2]_2Cl$. The crystal structure has recently been determined[20] and discrete molecules are present. The Mössbauer spectrum of this compound at room temperature shows a quadrupole split doublet with ΔE_Q = 2.54 mm/sec and an isomer shift of +0.64 mm/sec. Similar results have been obtained by Wickman and Trozzolo[21] for the dipropyl and dimethyl derivatives. The quadrupole splitting is almost identical with that observed for phthalocyaninechloroiron(III), but the isomer shift is 0.10 mm/sec more positive. A more detailed comparison is not meaningful because the structure of the dithiocarbamate complex is distorted with the Fe atom 0.63 A above the plane of the four sulfur atoms, whereas that of the phthalocyanine is unknown.

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(19) J. A. Elvidge, *J. Chem. Soc.*, 869 (1961).

(20) B. F. Hoskins, R. L. Martin, and A. H. White, *Nature*, **211**, 627 (1966).

(21) H. H. Wickman and A. M. Trozzolo, *Phys. Rev. Letters*, **15**, 156 (1965); with erratum, *ibid.*, **16**, 162 (1966).

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Raman Study of Aqueous Metal Oxalate Complexes and Related Oxalates[1]

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Raman spectra were measured of concentrated oxalate solutions of Zn(II) and Mg(II). Spectra of the tris complexes were obtained in both cases, and for Zn(II) the bis complex was also detected. No indication of monodentate coordination was observed. For the equilibrium $Zn(C_2O_4)_2^{2-} + C_2O_4^{2-} \rightleftarrows Zn(C_2O_4)_3^{4-}$, an equilibrium quotient of $3.6 \pm 0.6\ M^{-1}$ was determined at 43° in the ionic strength range 8.9–10.2 *M*. Raman intensities and depolarization ratios were quantitatively measured for the three complexes and, for comparison, for oxalate ion, oxalic acid, and dimethyl oxalate. From the intensities of M–O stretching modes, the coordination was shown to be principally ionic (covalent bond orders *ca.* $^1/_4$). Intensities of high-frequency oxalate bands suggest that considerable coupling is apparent, possibly enhanced by increased planarity of oxalate ion on coordination.

Introduction

The oxalate ion represents a simple example of a bidentate, charged ligand. Because of its electronic structure, it presents not only the obvious problems of whether its complexes are essentially ionic, but whether extensive electronic rearrangements may occur on coordination. A Raman spectrophotometric study should not only answer the question of what species are present in solution but also give information on both the character of the metal–oxygen coordination and the subsequent bonding changes within the coordinated ligand. For these reasons the present study was undertaken. The metal ions Zn^{2+} and Mg^{2+} were chosen because of solubility considerations. Of the common divalent cations, only these give colorless oxalate solutions of sufficient concentration for careful Raman studies.

Experimental Section

Analytical reagent grade chemicals were used throughout. Solutions of oxalate complexes were prepared by dropwise addition with vigorous stirring of a concentrated solution of either $Zn(NO_3)_2$ or $Mg(NO_3)_2$ to a solution saturated with $K_2C_2O_4 \cdot H_2O$ and containing an excess of this solid. By maintaining a temperature of *ca.* 40° (the temperature at which all spectra were run), a solution containing as high as 1.0 *M* total Zn(II) and as low as 2.6 *M* total oxalate could be prepared which showed no precipitation for at least 1 day. With Mg in place of Zn(II), the maximum total metal ion concentration so obtainable was 0.4 *M* at a minimum total oxalate concentration of 2.4 *M*. In order to avoid troublesome H_2O Raman bands, some solutions were prepared in 99.9% D_2O, but it was not necessary to remove the H_2O from the initial hydrated salts. Efforts to prepare solutions of suitable concentrations of oxalate complexes of Cd(II), Hg(II), and Mn(II) for Raman studies were not successful.

Stoichiometric oxalate concentrations were determined by standard permanganate titration, and Zn^{2+} or Mg^{2+} concentrations were determined by EDTA titration, after oxidation of the oxalate, using Eriochrome T as indicator.[2] In analyzing dimethyl oxalate solutions, hydrolysis was effected by heating with KOH

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(1) From the Ph.D. thesis of E. C. Gruen (Procter and Gamble predoctoral fellow) and supported by the Office of Saline Water, U. S. Department of the Interior.

(2) G. Schwarzenbach and H. Flaschka, "Die Komplexometrische Titration," Verlag von F. Enke, Stuttgart, 1965.

and the methanol formed was evaporated under reduced pressure, prior to permanganate titration. Nitrate concentration was taken to be twice that of the metal ion, since it was added exclusively as either $Zn(NO_3)_2$ or $Mg(NO_3)_2$.

All Raman spectra were measured with a Cary 81 Raman spectrophotometer. The exciting radiation was usually the 4358-A line of the mercury Toronto arc. However, all absolute intensities were checked using also the 4047-A line and were found to agree within the precision of the 4047-A measurements (±6%, which is somewhat greater uncertainty than for the more intense spectra from the 4358-A line). This agreement shows that the intensities are free from resonance Raman effects. Throughout, an internal standard (either NO_3^- or ClO_4^-) was used for intensity determinations, and in every case the sample tube was surrounded by a Polaroid sheet with the axis of polarization oriented perpendicularly to the axis of the tube. This was done to ensure that the convergence correction for the line being measured is the same as that for the standard. Depolarization ratios were measured by the method of Rank and Kagarise[3] determining a convergence correction of $\rho = 1.09\rho_{\text{exptl}} - 0.21$. For spectral lines below 1000 cm^{-1}, a Wratten 2A gelatin filter was used around the sample tube; above 1000 cm^{-1}, an ethyl violet-*o*-nitrotoluene solution filter was used in an external jacket. All determinations consisted of at least four spectra, each bracketed by spectra of the internal standard. Unless otherwise specified, intensities refer to the total area of a Raman band.

Results

The Raman spectra of the tris-oxalato complexes of Zn(II) and Mg(II) are given in Figure 1 along with that of free oxalate ion. The broad 1650-cm^{-1} H_2O "bending" band has been taken out of the spectra by using D_2O and then subtracting the corresponding 1220-cm^{-1} D_2O "bending" band. Also, the solutions of the tris complexes contained excess free oxalate, the spectrum of which has likewise been subtracted. The principal lines for the complexes are summarized in Table I, which also lists the stronger lines characteristic of the bis-oxalato Zn(II) complex (see below). The depolarization ratios were determined for every line except the shoulder below 900 cm^{-1}, which was too weak for measurement. In every case, the degree of depolarization is correct for the D_3 symmetry assignment made (*i.e.*, all A_1 lines are polarized, E lines are not). This symmetry indicates octahedral coordination to zinc but does not distinguish between planar and nonplanar oxalate ligands. The spectra are complete except for two low-frequency E lines, usually not observed for MO_6 octahedral species. In addition, there is a very weak, polarized line at 1730 cm^{-1} which cannot be attributed either to the bis complex or to hydrogen oxalate ion. It is left unassigned.

For series of solutions containing Zn(II) and oxalate, the spectra in the 1400–1500-cm^{-1} region change as the oxalate/zinc ratio is decreased in the range 4.2–2.6. To determine the reason for this change, a series of experiments was performed following the classical Job method of continuous variation.[4] It was found that for a series of 11 solutions having a total stoichiometric concentration of Zn(II) plus oxalate equal to 3.58 *M*, the Raman intensity at 1448 cm^{-1} showed a well-defined maximum at an oxalate/zinc ratio of 3.3. The Raman intensity at 1475 cm^{-1} continued to increase at the lowest ratio attainable, 2.6. These results are completely consistent with the presence of a tris complex, whose maximum concentration in the presence of lower species should be attained somewhat above the ratio of 3,[5] and a bis complex, whose maximum should be attained below the ratio of 2. These solutions cannot contain significant concentrations of a mono complex, owing to exceedingly low solubility.[6] However, polynuclear species containing more than one (but less than three) oxalate/zinc are not so easily eliminated. The spectrum of the lower species is apparently quite similar to that of the tris complex, as if all oxalate ions contained in it were bidentate. A binuclear complex could be postulated which would meet these criteria, but in view of the equilibrium data discussed below, it seems much less likely than a simple bis complex.

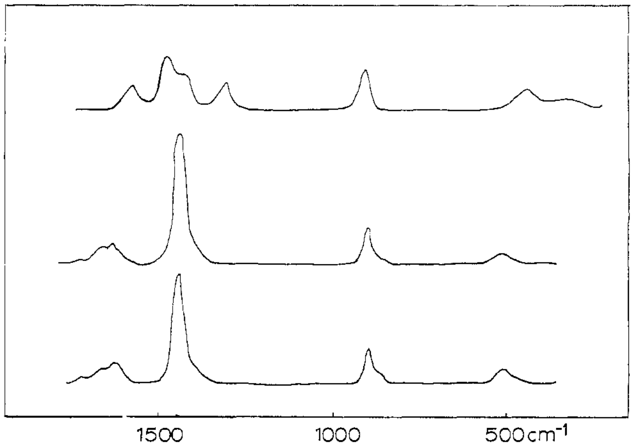

Figure 1.—Raman spectra of oxalate ion, $Zn(C_2O_4)_3^{4-}$, and $Mg(C_2O_4)_3^{4-}$, from top to bottom, respectively.

Table I

Frequencies of Raman Bands for Complexes (cm^{-1})

Symmetry species, D_3	$Zn(C_2O_4)_3^{4-}$	$Zn(C_2O_4)_2^{2-}$	$Mg(C_2O_4)_3^{4-}$
A_1	1448	~1471	1448
	1675		1675
	900		903
	515	515	510
	~868		~881
E	~1405	~1420	~1410
	1630		1623

To arrive at the frequency of the strong lines attributable to a bis complex, the following procedure was adopted. As Figure 2 shows, the spectral region of 1400–1500 cm^{-1} contains a collection of Raman lines. Free oxalate has two overlapping bands in this region (1475 and 1443 cm^{-1}). These can be quantitatively subtracted from the band profile by careful measurement of the isolated free oxalate band at 443 cm^{-1} and knowing the relative band intensities for the free oxalate species. The free oxalate bands so obtained are shown in the figure by the lines of dashes with dots. The residue is then resolved into two symmetric bands at high oxalate/zinc ratio, and into these plus another pair at lower ratio. From curves so resolved, measured

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[3] D. H. Rank and R. E. Kagarise, *J. Opt. Soc. Am.*, **40**, 89 (1956).

[4] P. Job, *Ann. Chim.*, [10] **9**, 113 (1928).

[5] W. Yellin and R. A. Plane, *J. Am. Chem. Soc.*, **83**, 2448 (1961).

[6] W. C. Vosburgh and J. F. Beckman, *ibid.*, **62**, 1028 (1940).

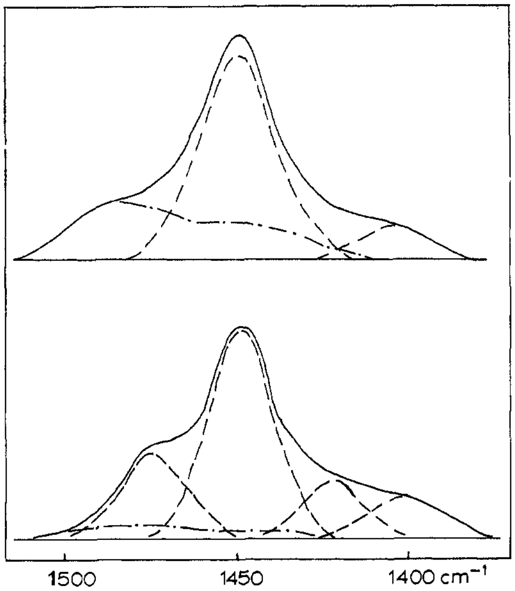

Figure 2.—Overlapping Raman bands of zinc oxalate complexes: top spectrum for a solution having an oxalate-to-zinc ratio of 6; bottom spectrum, 2.7; solid lines, measured spectra; dashes with dots, free oxalate present; dashes, resolved differences.

with parallel and perpendicular Polaroids, it was found that the higher frequency, more intense member of each pair is polarized while the lower frequency member is depolarized. The maxima of the bands so resolved are given in Table I.

From quantitative determination of Raman intensity, which is directly proportional to species concentration, concentrations of the various solute species can be measured. This in turn gives directly equilibrium quotients. For the present zinc solutions, the equilibrium $Zn(C_2O_4)_3^{4-} \rightleftarrows Zn(C_2O_4)_2^{2-} + C_2O_4^{2-}$ is the only one of importance.[6,7] From the over-all stoichiometric concentrations, if any one of the three actual concentrations is determined, the other two are found by difference. In practice, the greatest accuracy was found by measuring the free oxalate concentration from the Raman intensity of the 443-cm^{-1} line, using it to determine the other two concentrations, and hence obtaining the equilibrium quotient. The results of such measurements are shown in Table II. For these solutions, the ionic strength varies between 8.9 and 10.2 *M*. The approximate constancy of the equilibrium quotient tends to confirm the formulation of the lower species. If it were instead $Zn_2(C_2O_4)_4^{4-}$, the quotient would vary by a factor of 3 within this set of experiments. The magnitude of the value determined is orders of magnitude less than the stepwise association constants for the two lower complexes[7] but therefore in reasonable agreement with the early determination of the total dissociation constant of the tris complex.[8]

TABLE II

EQUILIBRIUM STUDIES ON THE COMPLEX ZINC–OXALATE SYSTEM AT 43° AND IONIC STRENGTH OF 8.9–10.2 *M*

[total Zn^{2+}], *M*	1.015	0.94	0.83
[total $C_2O_4^{2-}$], *M*	2.69	2.78	2.84
[free $C_2O_4^{2-}$],[a] *M*	0.20	0.39	0.61
$\dfrac{[Zn(C_2O_4)_3^{4-}]}{[Zn(C_2O_4)_2^{2-}][\text{free } C_2O_4^{2-}]}$, M^{-1}	4.2	3.1	3.6
I_M[b] for $Zn(C_2O_4)_2^{2-}$	2.9	2.5	2.7

[a] Calculated from intensity of 443-cm^{-1} band. [b] Relative to molar intensity of ν_1 of NO_3^-.

A further check on the consistency of the formulation of complex species is given by the last entries in Table II. This quantity is the molar intensity of the (1420 + 1471)-cm^{-1} Raman bands of the bis complex relative to the molar intensity of the 1050-cm^{-1} band of NO_3^-. The value was arrived at by measuring the total area of the 1350–1500-cm^{-1} band envelope, subtracting contributions due to free oxalate and tris complex by using their known molar intensities and determined concentrations, and then dividing by the concentration ascribed to the bis complex. An alternate procedure involving resolution of the peaks and direct measurement of their areas gives identical results. Both the constancy of the result and the magnitude of the value when compared with the corresponding molar intensity of the tris complex (3.6, expected to exceed the bis value by about 50%) indicate that the equilibria are as described.

That the magnesium complex is indeed tris and not bis was shown by measuring the intensity of free oxalate, using this to determine its concentration, and from the stoichiometric total oxalate concentration showing that in fact three oxalate ions are coordinated.

An important objective of this study concerned determination of absolute Raman intensities of both metal to oxygen vibrational bands and of bands due primarily to vibrations within the coordinated ligands. For completely symmetric, A_1, modes, the molecular parameter responsible for Raman intensity is $\partial\bar{\alpha}/\partial Q$, the change of mean molecular polarizability with respect to the normal coordinate. This can be expressed by

$$I = \frac{KI_0M(\nu_0 - \nu_p)^4}{\nu_p[1 - \exp(-h\nu_p/kT)]}\left(\frac{\partial\bar{\alpha}}{\partial Q}\right)^2\left(\frac{6}{6 - 7\rho}\right)$$

where *K* is a collection of physical and instrument constants; I_0, the incident light intensity; *M*, the molarity of the chemical species; ν_0, the frequency of the incident radiation; ν_p, the vibrational frequency; *h*, the Planck constant; *k*, the Boltzmann constant; ρ, the depolarization ratio, *i.e.*, the ratio of intensities of the line for light polarized parallel to the tube axis to that for light polarized perpendicularly to the tube axis, which varies from 0 for completely polarized lines to $^6/_7$ for depolarized lines. Values of the intensity parameter, for the A_1, metal–oxygen bands, are listed in Table III. For comparison, previously determined values for Al(III) and Ga(III) tris-oxalato complexes[9] are included with the values measured in this study. In the last column of the table, values are given for the derivative of mean polarizability with respect to bond extension. In order to calculate this value, it was as-

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(7) "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(8) F. Kunschert, *Z. Anorg. Allgem. Chem.*, **41**, 337 (1904).

(9) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 513 (1964).

TABLE III

DERIVED POLARIZABILITIES FROM RAMAN INTENSITIES

Species	Freq, cm^{-1}	ρ	$(\partial\bar{\alpha}/\partial Q)_{A_1}$, A^2 (amu)$^{-1/2}$	$(\partial\bar{\alpha}/\partial r)_{M-O}$, A^2
$Zn(C_2O_4)_2^{2-}$	515	0.31	0.25	0.50
$Zn(C_2O_4)_3^{4-}$	515	0.31	0.26	0.43
$Mg(C_2O_4)_3^{4-}$	510	0.32	0.23	0.38
$Al(C_2O_4)_3^{3-}$	585	0.57	0.29[a]	0.46
$Ga(C_2O_4)_3^{3-}$	573	0.27	0.44[a]	0.72

[a] R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 513 (1964).

sumed that the M–O vibration is completely decoupled from other vibrations, in which case, $\partial\bar{\alpha}/\partial r = (16/n)^{1/2} \cdot (\partial\bar{\alpha}/\partial Q)$, where n is the number of O atoms coordinated (6 or 4).

Molar intensities of the high-frequency oxalate Raman lines, relative to that of the 1050-cm^{-1} line of nitrate, are recorded in Table IV. In addition to the three complexes, free oxalate ion, oxalic acid, and dimethyl oxalate were all measured in aqueous solutions. Data for them are included for comparison. The depolarization ratios were measured for all polarized lines and are listed in this table. Because solutions containing bis(oxalato)zincate free from the tris species could not be obtained, polarization ratios for bands of this species could not be quantitiatively determined, and in fact only two of its lines in this frequency region were suitable for intensity measurements.

TABLE IV

OXALATE INTENSITIES RELATIVE TO 1050-CM^{-1} LINE OF NITRATE

Species	Freq, cm^{-1}	Polarization	I_M
$C_2O_4^{2-}$	1475	$\rho = 0.28$	0.35
	1582	Depolarized	0.21
$H_2C_2O_4$	1348	$\rho = 0.32$	0.10
	1445	Depolarized	0.11
	1741	$\rho = 0.24$	0.44
$(CH_3)_2C_2O_4$	1348	$\rho = 0.46$	0.17
	1453	Depolarized	0.29
	1724	Depolarized	0.08
	1755	$\rho = 0.18$	0.40
$Zn(C_2O_4)_2^{2-}$	1420	Depolarized	1.0
	1471	Polarized	1.7
$Zn(C_2O_4)_3^{4-}$	1400	Depolarized	0.6
	1448	$\rho = 0.51$	3.0
	1630	Depolarized	0.63
	1675	$\rho \sim 0.34$	0.38
$Mg(C_2O_4)_3^{4-}$	1410	Depolarized	0.34
	1448	$\rho = 0.52$	2.30
	1623	Depolarized	0.84
	1675	$\rho \sim 0.26$	0.33

Discussion

The derived polarizabilities for the metal–oxygen symmetrical stretching modes are of considerable interest. Qualitatively, the values are small, indicating that the coordination does not involve predominantly covalent bond formation. Quantitatively, $\partial\bar{\alpha}/\partial r$, although directly proportional to covalent bond order,[10] depends also on other factors.[11] This dependence is given, to a good approximation, by the equation of Long and Plane[12] which shows the strong dependence of $\partial\bar{\alpha}/\partial r$ on bond length. By using the metal–oxygen distance measured for $K_3Cr(C_2O_4)_3 \cdot 3H_2O$[13] and adjusting the value by amounts corresponding to the ionic radii for the metal cations, covalent bond orders can be calculated for each of the complexes of Table III. These are: $Zn(C_2O_4)_2^{2-}$, 0.25; $Zn(C_2O_4)_3^{4-}$, 0.22; $Mg(C_2O_4)_3^{4-}$, 0.37; $Al(C_2O_4)_3^{3-}$, 0.48; $Ga(C_2O_4)_3^{3-}$, 0.55. These values represent the number of shared pairs of electrons in the M–O bond in each complex. In general, the values are small, especially for the Zn complexes, indicating quite ionic bonding. The group III metals show higher values, but even these are small (about one-third as large) compared to the corresponding values which can be similarly obtained from the $\partial\bar{\alpha}/\partial Q$ values of the acetylacetonate complexes of these same metal cations.[9] Apparently, there is no indication of any π bonding in the oxalato complexes, and even the σ bonding is far from complete.

Also of interest are the higher frequency Raman lines characteristic of vibrations primarily within the oxalate ligands. There are significant differences, in this spectral region, between the free oxalate ion and coordinated oxalate. The data of Table IV show that whereas free oxalate has but one polarized and one depolarized high-frequency line, the tris complex (and presumably also the bis complex of Zn whose complete spectrum could not be obtained) has two polarized and two depolarized lines. This pattern is consistent with the notion that in oxalate ion, all four O atoms are equivalent and hence only one symmetric C–O stretching mode can occur. However, in the bidentate complexes the two coordinated O atoms are distinct from the two which are not coordinated. Thus, a lower frequency pair of lines (one polarized, one not) appears along with a similar high-frequency pair. To substantiate this correlation, spectra of dimethyl oxalate and oxalic acid were also run and included in Table IV. In these cases the separation between the two pairs of lines is even greater than in the complexes, a comparison which has been used in infrared studies to indicate degree of bond covalency.[14] It should be noted that Table IV lists but three bands for oxalic acid; however, the higher frequency, polarized band is noticeably asymmetric, and the polarization ratio measured at intervals across the band is not constant. (The value quoted is the average for the entire band.) Both the asymmetry and the polarizability behavior indicate two overlapping bands—one polarized, one not.

To extend this simple picture for oxalate, the Raman intensities of the polarized, high-frequency bands were examined in order to gain information concerning electron distribution within the C–O regions of oxalate. This procedure immediately breaks down because it is noted that the total intensity of the polarized bands in the complexes is much greater than that in either dimethyl oxalate, oxalic acid, or oxalate ion, even after

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(10) T. Yoshino and H. J. Bernstein, *Spectrochim. Acta*, **14**, 127 (1959).

(11) L. A. Woodward and D. A. Long, *Trans. Faraday Soc.*, **45**, 1131 (1949).

(12) T. V. Long, II, and R. A. Plane, *J. Chem. Phys.*, **43**, 457 (1965).

(13) J. N. van Niekerk and F. R. L. Schoening, *Acta Krist.*, **5**, 196 (1952).

(14) M. J. Schmeltz, T. Miyazawa, S. Mizushima, T. J. Lane, and J. V. Quagliano, *Spectrochim. Acta*, **9**, 51 (1957).

taking account of the different numbers of oxalate groups in the various species. This intensity enhancement in the complexes is not easily explained by simple models. It must involve severe interactions between adjacent bonds. The enhancement for the complexes can come about through coupling either with C–C or with M–O. A normal coordinate analysis of oxalate complexes[15] shows that coupling with C–C is considerable. In fact, the intensity of the *ca.* 900-cm^{-1} band (usually assigned as approximately C–C stretching) is lower in the complexes than in free oxalate. Coordination of the oxalate might enhance this coupling through changing the geometry of the oxalate from D_{2d} when free in solution[16] to something more nearly planar in the complex. Consistent with this is the result for dimethyl oxalate which shows an enhancement of the intensity in the two polarized bands and which has been assigned a structure intermediate between staggered and eclipsed.[17] In any case, the intensity coupling between oxalate modes and the metal–oxalate modes is apparently small and there is a significant difference between metal–oxygen bonding in oxalate complexes and in acetylacetonate complexes.[9]

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(15) J. Fugita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 324, 331 (1962).

(16) G. M. Begun and W. H. Fletcher, *Spectrochim. Acta*, **19**, 1343 (1963).

(17) J. K. Wilmshurst and J. F. Horwood, *J. Mol. Spectry.*, **21**, 48 (1966).

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Proton Magnetic Resonance Studies of the Acetonitrile Complexes of Cobalt(II) and Nickel(II) in Acetonitrile Solutions

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The transverse relaxation rates and the chemical shifts of the bulk solvent protons in acetonitrile solutions of the complexes $Co(CH_3CN)_6^{2+}$ and $Ni(CH_3CN)_6^{2+}$ have been measured at 100 and 60 Mc. From the temperature dependence of the relaxation rates, the parameters k_1 (sec^{-1} at 25°), $\Delta H^{\ddagger}$ (kcal), and $\Delta S^{\ddagger}$ (eu) were calculated for the rate of exchange of acetonitrile between the bulk solvent and the Co(II) and Ni(II) complexes, respectively: 1.4×10^5, 8.1, −7.5; and 3.9×10^3, 10.9, −8.8. The coupling constants, A/h (cps), calculated from the chemical shifts are -2.28×10^4 for the Co(II) complex and -2.63×10^5 for that of Ni(II). It was found that only a single metal ion–solvent complex need be invoked to account for the data obtained over the complete range of temperatures, −45 to +79°. At temperatures below −35°, the proton nmr signal of acetonitrile in the first coordination sphere of Co(II) was distinguished From the relative intensity of this signal the primary solvation number, 5.7 ± 0.3, was calculated. The chemical shifts and transverse relaxation rates of the protons in the primary coordination sphere of Co(II) are consistent with those calculated from the data obtained for the bulk solvent protons.

Introduction

In conjunction with a general study of the kinetic and structural aspects of metal ion solvation in nonaqueous solvents, we have extended our proton nmr measurements of the rates of solvent exchange between the primary coordination spheres of metal ions and the free solvent to the solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ in acetonitrile. The application of this nmr technique to the study of the kinetics and stoichiometry of solvation in a variety of systems has been discussed elsewhere.[2]

One important question concerning the nature of the metal ion–solvent interaction which has arisen is that even if metal ion–solvent complexes can be kinetically distinguished, does a *single* complex exist over the accessible range of temperature and solution compositions in a given system or does an equilibrium exist among kinetically distinguishable complexes of different coordination numbers and geometries?[3] Although the range of systems investigated by the nmr technique is limited, it is interesting, and somewhat surprising, that to account for the nmr relaxation data in a variety of systems, it is only necessary to invoke a single metal ion–solvent complex. These systems include, for example: $M(CH_3OH)_6^{2+}$ in CH_3OH,[4] $M(DMF)_6^{2+}$ in DMF,[2] $Al(DMSO)_6^{3+}$ in DMSO,[5] $Al(DMF)_6^{3+}$ in DMF,[6] $Mg(H_2O)_6^{2+}$ in aqueous acetone,[7] $Mg(CH_3OH)_6^{2+}$ in CH_3OH,[7] $Al(H_2O)_6^{3+}$ and $Be(H_2O)_4^{2+}$ in water,[8] and $Ni(NH_3)_6^{2+}$ in liquid ammonia[9,10] (where M is Co^{2+} and Ni^{2+}, DMSO is dimethyl sulfoxide, and DMF is N,N-dimethylformamide). The data obtained from more inert systems

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(1) To whom inquiries should be addressed.

(2) N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

(3) For a comprehensive and critical discussion of metal ion solvation see: H. Taube, "Steric Problems in the Hydration of Ions in Solution," in "Progress in Stereochemistry," Vol. 3, P. B. D. de la Mare and W. Klyne, Ed., Butterworths, Washington, D. C., 1962, pp 95–137.

(4) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).

(5) S. Thomas and W. L. Reynolds, *ibid.*, **44**, 3148 (1966).

(6) W. G. Movius and N. A. Matwiyoff, *Inorg. Chem.*, **6**, 847 (1967).

(7) N. A. Matwiyoff and H. Taube, unpublished results.

(8) R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **39**, 1349 (1963).

(9) T. J. Swift and H. H. Lo, *J. Am. Chem. Soc.*, **88**, 2994 (1966).

(10) H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965).