The large splittings observed for Ni(Htcaz)₃Cl₂, Ni-(Htscaz)₃Cl₂, and Ni(Hcaz)₃Cl₂ of 1000, 900, and 600 cm⁻¹, respectively, suggest the environments 3N,3S and 3N,3O, as an environment consisting only of nitrogen atoms would be expected to show negligible splitting.

The molar conductance of 10^{-3} M Ni(Htcaz)₃Cl₂ was measured at 25° in aqueous solution and the value of 220 ohm⁻¹ is in agreement with it being a 1:2 electrolyte.

Complexes of Sulfoxides. II. Metal–Oxygen Stretching Vibrations in Complexes of Dimethyl Sulfoxide and Dimethyl Sulfoxide-d_6 and the Point Group of the Cation

By CHARLES V. BERNEY AND JAMES H. WEBER

Consideration of the ways of placing dimethyl sulfoxide (DMSO) ligands around a central metal atom leads to the conclusion that the point group of an $[M(DMSO)_6]^{n+}$ cation must be D_{3d} or S_6. The infrared spectra of several complexes with the formula $[M(DMSO)_6]^{n+}(ClO_4)_n$ have been studied with special emphasis on the region 600–200 cm⁻¹. A band assigned to the metal–oxygen stretching vibration appears in the region 444–415 cm⁻¹ for all the M(II) complexes studied; for Cr-(III) it appears at 529 cm⁻¹. The frequency order found is Cr(III) > Ni(II) > Co(II) > Zn(II) > Fe(II) > Mn(II), in agreement with other studies. Behavior of the C–S–O angle deformation vibrations as bonding strength is increased leads to the conclusion that S_6 is the actual point group of the cation.

Introduction

The use of dimethyl sulfoxide (DMSO) as a ligand in the formation of transition metal complexes was first reported by Cotton and co-workers.[1,2] Following a thorough vibrational analysis of the free ligand,[3] they were able to determine whether bonding in the complex was through the sulfur or the oxygen in DMSO by noting whether ν_{SO}, the S–O stretching frequency, increased or decreased on complexation. It is tempting to extend this method and use the magnitude of the shift in ν_{SO} as a measure of the strength of the coordinate bond, but this approach is open to question, mainly because the vibration labeled ν_{SO} is far from being a pure stretch. The analysis of Horrocks and Cotton[3] indicates that about half of the potential energy of this vibration is associated with methyl rocking motions. The composition of the normal coordinate will change on complexation, effectively masking any trend involving metal–ligand bond strength. Currier and Weber[4] have, in fact, examined the quasi-octahedral complexes of manganese(II), iron(II), cobalt(II), nickel(II), and zinc(II) with DMSO, diphenyl sulfoxide, phenyl methyl sulfoxide, di-n-propyl sulfoxide, and di-n-butyl sulfoxide and have found that little significance could be attached to $\Delta\nu_{SO}$.

A more reliable source of information concerning the strength of the coordinate bond is the set of vibrations which involve this bond directly, *i.e.*, those which (in the first approximation) involve the motion of the DMSO molecule as a whole and thus have no counterpart in the spectrum of the free ligand. If the DMSO molecule is regarded as a single particle, then an octahedral DMSO complex $[M(DMSO)_6]^{n+}$ may be considered as belonging to point group O_h with a vibrational representation $\Gamma_{vib} = A_{1g}$ (Raman) + E_g (Raman) + F_{2g} (Raman) + $2F_{1u}$ (ir) + F_{2u} (inactive).[5]

With due regard for degeneracies, this Γ_{vib} accounts for 15 vibrational degrees of freedom. Internal vibrations of the ligands account for 6 × 24 = 144 degrees of freedom. However, the $[M(DMSO)_6]^{n+}$ complex has 61 atoms, giving it 3(61) − 6 = 177 vibrational degrees of freedom; we have accounted for 159 and are still missing 18. These are the rotations of the free ligands, which are transmuted into rocking, wagging, and twisting modes on complexation. Twelve of these may be incorporated into a model of O_h symmetry by making it 13-atomic, rather than 7-atomic, as, for example, chromium hexacarbonyl.[6] The vibrational representation then becomes $2A_{1g}$ + $2E_g$ + F_{1g} + $2F_{2g}$ + $4F_{1u}$ + $2F_{2u}$, with F_{1u} the only infrared-active species. The normal modes belonging to this repre-

(1) F. A. Cotton and R. Francis. *J. Am. Chem. Soc.*, **82**, 2986 (1960).

(2) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

(3) W. D. Horrocks, Jr., and F. A. Cotton, *Spectrochim. Acta*, **17**, 134 (1961).

(4) W. F. Currier and J. H. Weber, *Inorg. Chem.*, **6**, 1539 (1967).

(5) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, pp 122, 336.

(6) N. J. Hawkins, H. C. Mattraw, W. W. Sabol, and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955).

sentation have been designated[6,7] as ν_6 (CO stretch, 2000 cm^{-1}), ν_7 (MCO deformation, 661 cm^{-1}), ν_8 (M–C stretch, 475 cm^{-1}), and ν_9 (C–M–C deformation, 102 cm^{-1}). If we use this complex as a second-order approximation to [M(DMSO)$_6$]$^{n+}$, ν_6 corresponds to the band observed around 900–1000 cm^{-1} by Cotton, *et al.*,[2] referred to above as ν_{SO}. The greater bulk of the DMSO ligand (compared to CO) probably moves the deformation below the metal–ligand stretch. A study of two DMSO complexes of uranium by Kaufmann and Leroy[8] assigns absorptions at 416 and 420 cm^{-1} to metal–ligand stretching vibrations and absorptions at 264 and 262 cm^{-1} to vibrations involving DMSO rocking or wagging.

Further refinement of the model requires that we consider the shape of the ligands. The DMSO molecule itself has C_s symmetry, and even if the ligands are placed octahedrally around the central atom, the point group of the complex cannot be O_h (though it must be a subgroup of O_h). Let us think of the M(DMSO)$_6$ complex as a superposition of three two-coordinate complexes (CH$_3$)$_2$SO–M–OS(CH$_3$)$_2$ sharing a common M atom. A center of symmetry must be present, or three ligands on one end of the complex will be subject to forces different from the opposite three. This element and the symmetry plane of the ligands themselves define the point group of the (imaginary) two-coordinate component of the complex as C_{2h}. We now merge the three C_{2h} complexes; a quasi-octahedral arrangement requires that the O–M–O axes be mutually perpendicular. Aside from the torsional configuration of the methyl groups (which is beyond the scope of this paper), the only arbitrary parameter left is the orientation of the CSC groups. This may be discussed in terms of the relative orientation of vectors drawn from each sulfur atom to the point midway between the attached pair of carbon atoms (S–C$^1/_2$ vectors). The highest possible symmetry for the complex as a whole is obtained when all of these vectors are directed toward a single C_3 axis of the original octahedron (three vectors will be directed at a point on the axis above the M atom, the other three at a point an equal distance below it); the resultant point group is D_{3d}. If each (CH$_3$)$_2$SO–M–OS-(CH$_3$)$_2$ component is now rotated about its OMO axis by an angle α, the symmetry drops to S_6 (unless $\alpha = 180°$, where it becomes D_{3d} again). Equivalent configurations of special significance are obtained at $\alpha = 45, 135, 225,$ and $315°$. Here each S–C$^1/_2$ vector points toward the OMO axis of a neighboring pair, and the C_2 axes of the three pairs are mutually perpendicular. The top half of this configuration, which may well be the actual one, is shown in Figure 1. Later in this report we will present evidence that the point group of these complexes is S_6 rather than D_{3d}.

Point-group correlation tables[9] show that the effect of reducing the symmetry from O_h to S_6 (or D_{3d}) is to split the triply degenerate F species into A + E. The
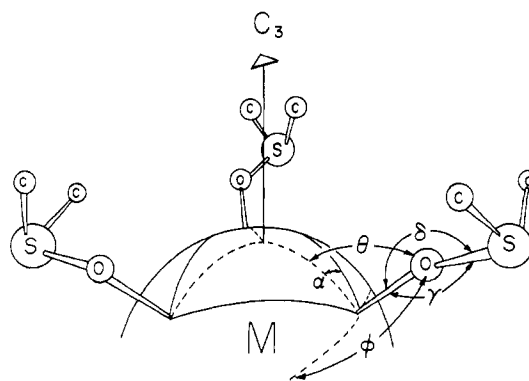

Figure 1.—Suggested structure for half of the [M(DMSO)$_6$]$^{n+}$ complex, point group S_6. Some of the internal coordinates are shown on the right-hand ligand; δ and θ are in the same plane, at right angles to γ and ϕ. The two remaining internal coordinates, r_{MO} and τ, are not shown. α represents the angle formed by the curve connecting the MO bond with the C_3 axis, and the projection of the OSC$_2$ local symmetry plane in its equilibrium position onto the surface of the sphere enclosing the M atom. The figure is for $\alpha = 45°$; the internal coordinate τ represents displacements of α from the equilibrium value.

vibrational representation of [M(DMSO)$_6$]$^{n+}$ under S_6 is $29A_g + 29E_g + 30A_u + 30E_u$ (the E species vibrations are taken to represent two degrees of freedom each, even though they are separably degenerate). If the methyl groups are considered as point masses, Γ_{vib} becomes $11A_g + 11E_g + 12A_u + 12E_u$. Internal vibrations of the ligands now form the representation $6A_g + 6E_g + 6A_u + 6E_u$, leaving $5A_g + 5E_g + 6A_u + 6E_u$ for modes unique to the complex. Symmetry coordinates may easily be constructed with the aid of a character table and the internal coordinates described in Figure 1 and the accompanying caption; since we are not attempting a complete vibrational analysis, they are not given here.

The subject of this report is the application of this model to the interpretation of the infrared spectra of certain complexes of DMSO, particularly in the range 600–200 cm^{-1}. The complexes studied were [M-(DMSO)$_6$]$^{n+}$(ClO$_4$)$_n$ where M is chromium(III), cobalt(II), nickel(II), iron(II), manganese(II), and zinc-(II). The fully deuterated (DMSO-d_6) complexes of chromium(III) and cobalt(II) were also studied.

Experimental Section

Synthesis.—All syntheses have been reported by Currier and Weber[4] or others quoted in that paper.

Infrared Measurements.—All measurements were made on a Beckman IR-12 infrared spectrophotometer. The complexes (all solids) were studied as Nujol mulls; the free ligands DMSO and DMSO-d_6 were examined as liquid films between CsI plates. High dispersion spectra (20 cm^{-1}/in.) in the 600–200-cm^{-1} region were taken using high-density polyethylene mull plates and an equal thickness of polyethylene in the reference beam of the spectrometer. Frequencies of observed bands were calibrated against atmospheric water vapor lines.[10]

Study of the Fe(II) complex was difficult because of its rapid decomposition, which was accompanied by a color change (from light green to orange or yellow), the odor of an organic sulfide, and the appearance of a strong absorption band at 475 cm^{-1}.

(7) H. Murata and K. Kawai, *J. Chem. Phys.*, **27**, 605 (1957).

(8) G. Kaufmann and M. Leroy, *Bull. Soc. Chim. France*, 3770 (1966).

(9) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, Appendix X.

(10) L. R. Blaine, E. K. Plyler, and W. S. Benedict, *J. Res. Natl. Bur. Std.*, **66A**, 223 (1962).

This presumably represents oxidation of the Fe(II) *via* reduction of the DMSO.

Results and Discussion

Since we are interested in identifying the vibrations unique to the complex, it is very helpful to have Horrocks and Cotton's complete infrared–Raman study[3] of the ligands. In the 600–200-cm^{-1} region, these authors[3] found bands at 382 and 333 cm^{-1} (liquid DMSO) and at 340 and 307 cm^{-1} (liquid DMSO-d_6); these bands were assigned to ν_{11} and ν_{23}, described as symmetric and antisymmetric OSC angle deformations. The CSC angle deformation, ν_{12}, was assigned to Raman lines at 308 (DMSO) and 262 cm^{-1} (DMSO-d_6), but was not seen in the infrared. We observed bands at 384, 334, and 311 cm^{-1} (DMSO) and at 340, 306, and 265 cm^{-1} (DMSO-d_6) in good agreement with the earlier results. We did not observe the band at 277 cm^{-1} reported by Johnson and Walton.[11]

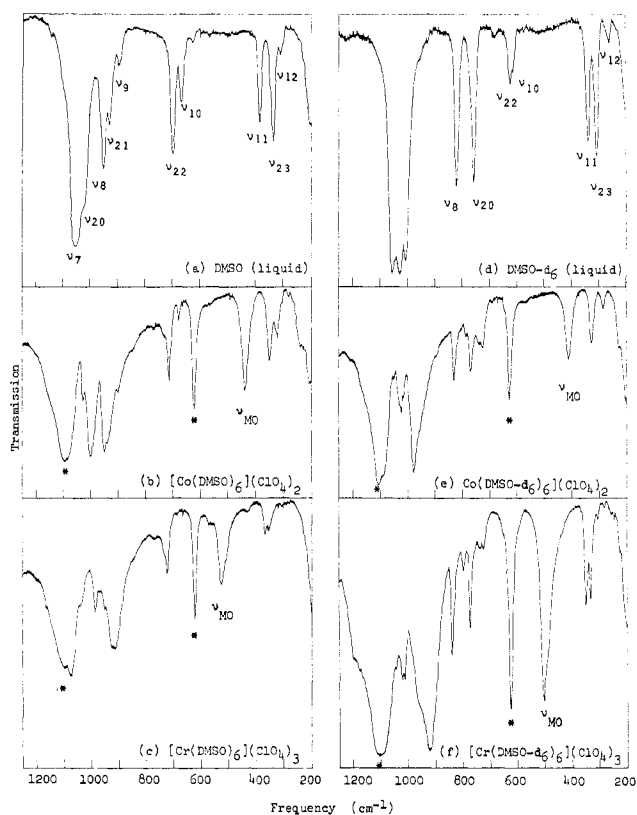Figure 2 shows survey spectra (1250–200 cm^{-1}) of the

Figure 2.—Infrared spectra of DMSO, DMSO-d_6, and their Co(II) and Cr(III) complexes in the region 1250–200 cm^{-1}. Assignments for the free ligands are those of Horrocks and Cotton.[3] Absorptions due to the perchlorate anion are designated with an asterisk. Complexes were run as mulls between CsI plates (which are responsible for the steep absorption at ~200 cm^{-1} in each spectrum).

free ligands DMSO and DMSO-d_6 and their complexes with a divalent ion, cobalt(II), and a trivalent ion, chromium(III). There can be little doubt that the strong band appearing in the 400-cm^{-1} region of the

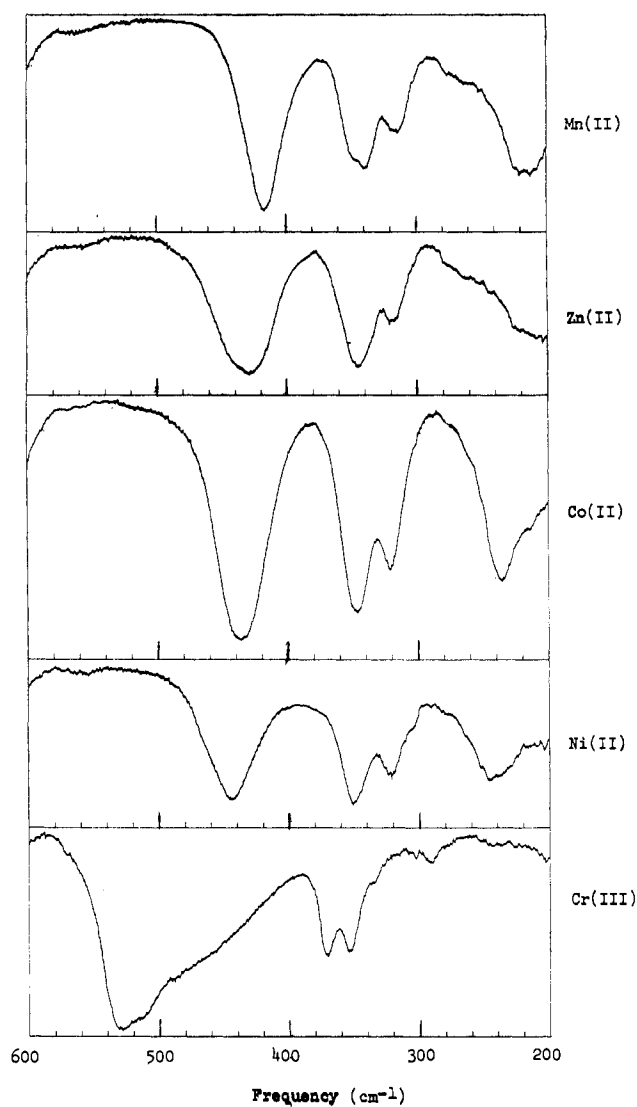(11) B. F. G. Johnson and R. A. Walton, *Spectrochim. Acta*, **22**, 1853 (1966).

Figure 3.—Infrared spectra of the indicated [M(DMSO)$_6$]$^{n+}$-(ClO$_4$)$_n$ complexes in the region 600–200 cm^{-1} (mulls between polyethylene plates). Our data for the Co(II) complex are in disagreement with those of Johnson and Walton.[11] In the present study, we assign the highest frequency peak in each of the above spectra to ν_{MO}, and the doublet in the 380–300-cm^{-1} region to the ligand vibrations δ'_{CSO} and δ''_{CSO} (see text and Table I).

divalent complexes and the 500-cm^{-1} region of the trivalent complexes is due to a metal–ligand vibration. This can be seen by comparing the behavior of this band with that of the pair of bands (348 and 321 cm^{-1} in the [Co(DMSO)$_6$]$^{2+}$ complex) assigned to CSO deformations in the ligand: when the M–O bond strength is increased by substituting a trivalent ion for a divalent one, its frequency is increased by almost 100 cm^{-1}, while the CSO deformation bands change position by only 20–30 cm^{-1}.

It is natural to assign this band as a metal–oxygen stretching vibration, that is, one for which the normal coordinate consists largely of a translational displacement of the ligand as a whole with respect to the metal atom. This may be roughly confirmed by looking at the ratios of the frequencies for the light and heavy ligands: 436/409 = 1.07 for cobalt(II) and 529/506 =

Table I

Infrared Absorptions of $[M(DMSO)_6]^{n+}(ClO_4)_n$ Complexes in the Region 600–200 CM^{-1} [a]

	Free ligand	Fe(II)	Mn(II)	Zn(II)	Co(II)	Ni(II)	Cr(III)
DMSO Complexes							
Frequency of MO stretch, cm⁻¹		{438, 415}	418 s	431 s	436 s	444 s	529 s
Band width at half-height, cm⁻¹		18 + 14	36	52	46	48	110
"Symmetric" CSO deformation, δ'cso	384 (ν_{11})	340[b]	340 ms (347 sh)	345 s	348 s	350 s	370 m
"Antisymmetric" CSO deformation, δ''cso	334 (ν_{23})	320[b] sh	315 m	318 m	321 m	321 m	354 m
δ'cso − δ''cso	50	~20[b]	25 (32)	27	27	29	16
½[(ν_{11} + ν_{23}) − (δ'cso + δ''cso)]	(0)	29	32 (28)	33	25	24	−3
Other bands	311 (ν_{12})	262 m?	277 w	279 w	276 w	280 w	334 w
		225 w?	215 ms	220 ms	236 ms	246 ms	291 w
DMSO-d_6 Complexes							
Frequency of MO stretch, cm⁻¹					409 s		506 s
Band width at half-height, cm⁻¹					40		
"Symmetric" CSO deformation, δ'cso	340 (ν_{11})				323 s		350 m
"Antisymmetric" CSO deformation, δ''cso	306 (ν_{23})				281 m		333 m
δ'cso − δ''cso	36				42		17
½[(ν_{11} + ν_{23}) − (δ'cso + δ''cso)]	(0)				31		−19
Other bands	265 (ν_{12})				226 s		303 w

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] The two peaks (δ'cso and δ''cso) are not well resolved.

1.045 for chromium(III). If the motion were pure M–O stretch, the expected ratio would be that of the square roots of the molecular weights of the isotopic species: $(84/78)^{1/2} = 1.035$. This indicates that the vibration in the chromium(III) complex is almost pure M–O stretch, with a slightly higher proportion of angle deformation in the cobalt(II) complex. In both cases we are justified in labeling the band as ν_{MO}.

Data from the high-dispersion spectra of all complexes included in this study are collected in Table I. The metal ions are arranged in order of increasing ν_{MO}, but first we note there is an ambiguity in the case of iron-(II). As was mentioned above, study of this complex was hindered by its rapid decomposition, but the peaks at 438 and 415 cm⁻¹ (plus a shoulder at 402 cm⁻¹) were strong in freshly prepared samples, and their intensity diminished as decomposition progressed. If we assign them both to $\nu_{MO}[Fe(DMSO)_6^{2+}]$, we can explain the splitting by remembering that the over-all symmetry of the complex is S_6 (or D_{3d}) and the infrared-allowed species of ν_{MO} are $A_u + E_u$ (or $A_{2u} + E_u$) rather than F_{1u}. This leaves the problem of why the splitting is observed with iron(II), but not with any of the other divalent ions. We can partly explain this by noting that the other ν_{MO} bands are all rather broad (band widths are given in Table I), and the widths are equal to or greater than the sum of the widths of the iron(II) doublet. This suggests that the ν_{MO} bands are in fact all split, but only in the case of iron(II) is the splitting resolved.

Positions of CSO deformations (largely localized in the ligand) are also given in Table I. They are labeled "symmetric" and "antisymmetric" to agree with their order in the free ligands[3] (we see no indication of any interaction strong enough to reverse their positions). The terms "symmetric" and "antisymmetric" are in quotes because if the point group of the complex is S_6, the local plane of symmetry in the ligand (even assuming no geometrical distortion on complexation) is no longer a symmetry element of the complex as a whole. This means that deformations of the two CSO angles on a given ligand must go into separate symmetry coordinates. The symmetry coordinates themselves will go into plus and minus combinations to form the normal coordinates, but the coefficients will no longer be ±1. The effect might be described as a "mixing" of ν_{11} and ν_{23} (notation of ref 3), but is more accurately thought of as a reduction of the complete mixing (*i.e.*, an uncoupling) of the two CSO coordinates which in the free ligand is required by the plane of symmetry. Table I shows the trend: the free ligand vibrations (384 and 334 cm⁻¹) are 50 cm⁻¹ apart, the corresponding M(II) vibrations are 25–29 cm⁻¹ apart, and the vibrations in the strongly bonded chromium(III) complex are separated by only 16 cm⁻¹. Since the local plane of symmetry would be preserved in a D_{3d} configuration, we may now conclude that the actual configuration of these complexes is S_6, rather than D_{3d}.

The mean decrease in CSO deformation frequency on complexation is given in Table I as ½[(ν_{11} + ν_{23}) − (δ'cso + δ''cso)]. This quantity is positive (that is, the vibrations are higher in the free ligand) for all of the M(II) complexes. This is readily understandable: these motions in the free ligand involve both the oxygen and the methyl groups; when the oxygen is tied down by complexation, the bulkier methyl groups must account for more of the action and the frequency decreases (note that the decrease goes from 25 to 31 cm⁻¹ in the cobalt(II) complex when the DMSO is deuterated). Somewhat more surprising is the "negative decrease" exhibited by the Cr(III) complexes—the mean values of the CSO deformations are higher in the complex than in the free ligand. This is presumably due to changes in force constants brought about by hybridization changes associated with tighter bonding, to steric crowding associated with shortening of the M–O bond, to increased mixing with O–M–O and M–O–S deformation vibrations, or to a combination of these effects.

A series of broad peaks increasing in frequency from 215 cm^{-1} for the Mn(II) complex to 246 cm^{-1} for Ni(II) can be seen in Figure 3. These may be M–O–S angle deformations; if so, the weak band at 291 cm^{-1} in the Cr(III) spectrum is the same vibration and its low intensity is puzzling. An alternative explanation is that the 215–246-cm^{-1} bands in the M(II) complexes represent lattice vibrations, all at approximately the same frequency (since the M(II) complexes are expected to be isostructural) but increasing slightly as the shorter M–O bonds allow tighter packing in the lattice. The Cr(III) complex cannot be isostructural with the M(II) complexes and the corresponding lattice vibration may well be below 200 cm^{-1}. If this is true, the angle deformations may be the very weak, diffuse features seen around 280 cm^{-1} for all of the M(II) complexes in Figure 3.

The results of this study may be compared with an infrared study of the quasi-octahedral pyridine N-oxide–metal perchlorate complexes by Kakiuti, Kida, and Quagliano.[12] The positions (in cm^{-1}) of the peaks assigned to M–O stretching vibrations by these authors[12] for complexes analogous to those we have studied are as follows: Fe(II), 320 s, ∼304 w, sh; Mn(II), 311 s; Zn(II), 319 s; Co(II), 331 s; Ni(II), 342 s; Cr(III), 431 vs, 402 w. Not only is there excellent agreement in the order of the metals with respect to the strength of the M–O bond (judged by the frequency of ν_{MO}), but other spectral features such as the appearance of shoulders or splitting for Fe(II) and Cr(III) are re-

produced. This is strong evidence for the validity of the assignments. The relative M–O bond strength in six-coordinate DMSO complexes is: Ni(II) > Co(II) > Zn(II) > Fe(II) > Mn(II). The order in the six-coordinate pyridine N-oxide series is: Cu(II) > Ni(II) > Co(II) > Zn(II) > Fe(II) ∼ Mn(II). In both series the order is in agreement with the usual stability order toward oxygen donors. We also note that the ratio ν_{MO}(DMSO)/ν_{MO}(pyridine N-oxide) is 1.30–1.35 for corresponding M(II) complexes and is 1.23 for the Cr(III) complexes. If the M–O stretching force constant were the same for both types of complexes, the maximum value possible for this ratio would be 1.12. We can thus make the qualitative statement that pyridine N-oxide is a weaker ligand than DMSO for the metals included in this study (a quantitative statement would require knowledge of the quasi-F_{1u} bending frequencies). This conclusion is in conflict with the results of ligand field studies.[13] In nickel(II) and cobalt(II) complexes of the form [ML$_6$](ClO$_4$)$_n$ pyridine N-oxide has the larger Δ_0 value, but DMSO has the larger value in chromium(III) complexes. The conflict between the infrared and ligand field results merits further study.

(12) Y. Kakiuti, S. Kida, and J. V. Quagliano, *Spectrochim. Acta*, **19**, 201 (1963).

(13) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

CONTRIBUTION FROM THE PENNSYLVANIA STATE UNIVERSITY,
UNIVERSITY PARK, PENNSYLVANIA

Evidence for a Trigonal-Prismatic Activated Complex in the Solid-State Racemization of Potassium Trioxalatocobaltate(III)[1]

BY C. D. SCHMULBACH, J. BRADY,[2] AND F. DACHILLE

The volume of activation, ΔV^*, and the energy of activation were determined for the racemization of crystalline potassium trioxalatocobaltate(III) and found to be -1.66 ± 0.33 cm^3 mole^{-1} and 1.9 $\pm$ 0.7 kcal mole^{-1}, respectively. The solid-state racemization was established to be first order with respect to the complex, and the specific rate constant for racemization at 34.0×10^3 atm and room temperature was determined to be 6.4×10^{-7} sec^{-1}. Water of hydration was found to decrease the rate of racemization. A trigonal-prismatic structure for the activated complex is favored.

Introduction

In a previous communication it was reported that the rate of the solid-state racemization of several inorganic salts is increased by pressure.[3] A negative volume of activation for racemization was determined for potas-

(1) Abstracted in part from the doctoral thesis of J. Brady, The Pennsylvania State University, 1963.

(2) National Science Foundation Cooperative Fellow, 1961–1962 and 1962–1963. Address inquiries to this author at Department of Chemistry, St. John's University, Jamaica, N. Y.

(3) J. Brady, F. Dachille, and C. D. Schmulbach, *Inorg. Chem.*, **2**, 803 (1963).

sium trioxalatocobaltate(III), and trigonal-prismatic structures, E and F in Figure 1, were considered the most likely for the activated complex in this racemization process. Structure C, or for that matter any structure containing water in the coordination sphere, could not be ruled out as possible structures for the activated complex. We report here the results of an extended investigation of the K$_3$[Co(C$_2$O$_4$)$_3$] system which was undertaken in an attempt to provide further evidence for the existence of the trigonal-prismatic ac-