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Complexes of Sulfoxides. IV. Vibrational Spectra of Tetramethylene Sulfoxide Complexes

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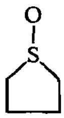
A vibrational spectroscopic study of tetramethylene sulfoxide (TMSO) and its hexacoordinate complexes with Al^{III}, Cr^{III}, Fe^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, *and* Zn^{II} *has been carried out. The frequency order of* ν_{MO} *corresponds to that found for DMSO complexes. Splitting in the* ν_{SO} *bands is interpreted as further evidence for* S_6 *symmetry of the cation. Simplified vibrational models have been used to estimate the force constants involved, and the order determined by the MO stretching force constant is found to differ from the* ν_{MO} *frequency order for* Zn^{II} *and* Al^{III}.

Introduction

A previous paper in this series[1] dealt with the infrared spectra of a series of dimethyl sulfoxide (DMSO) complexes. A strong band appeared in the region 444-415 cm^{-1} for each of the M^{II} complexes and at 529 cm^{-1} for the Cr^{III} complex; these bands were assigned as metal-oxygen stretching vibrations, ν_{MO}. Increasing M–O bond strength should increase the M–O stretching force constant in this series of complexes, leading to increases in ν_{MO}–hence the interest in the observed ν_{MO} frequency order ($Mn^{II} < Fe^{II} < Zn^{II} < Co^{II} < Ni^{II} < Cr^{III}$). However, vibrational frequency is a function of the masses of the vibrating atoms as well as the force constants, and the masses of the metal atoms in the above series vary from 52 to 65 amu. Thus an ordering of the metals with respect to the M–O force constant of the complex is of more fundamental significance than an ordering with respect to frequency.

The present study reports infrared observations of complexes of tetramethylene sulfoxide, TMSO,



a ligand closely related to DMSO. Complexes of Al^{III} and Fe^{III}, in addition to the metals mentioned above, were prepared. Simplified vibrational models have been used to estimate relative force constants for these complexes, giving an ordering of the metals which does, in fact, differ from the frequency order.

Experimental Section

Syntheses. All syntheses have been reported by van Leeuwen and Groeneveld[2] or others quoted in that paper.

Infrared Measurements. Spectra were obtained on Beckman IR-11 and -12 spectrophotometers. The complexes (all solids) were studied as Nujol mulls supported between NaCl, CsI, or high density polyethylene plates. TMSO was taken as a liquid film. Frequencies of observed bands were calibrated against polystyrene or atmospheric water vapor lines.[3] Spectral resolution was about 1 cm^{-1}.

After the experimental work was completed, a paper[4] appeared which reports M–O stretching frequencies for these and several other TMSO complexes. Our frequencies are given in Table I; those of Reedijk *et al.* differ by 0-8 cm^{-1} (average 4.4, or about 1%). Discrepancies may be due to the differing resolution of the spectrometers used, since the band shapes are somewhat asymmetric.

Raman Measurements. Spectra of the ligand were run by Dr. Chris W. Brown of the University of Rhode Island, using a Cary 81 instrument with He-Ne laser excitation.

Preliminary Remarks

The Ligand. In our previous study[1] we were able to use the results of Horrocks and Cotton's thorough vibrational analysis of the ligand.[5] In the present case, we fall heir to no such benefits. Klaeboe[6] has reported the infrared and Raman spectra of TMSO, but has given only tentative assignments. We agree with his approximate descriptions of several of the bands, but must disagree with his postulated molecular structure, «a puckered ring with C_2 symmetry...» Such a structure would require the oxygen, sulfur and alpha carbons to be coplanar, a configuration which leaves the lone pair of electrons on the sulfur with no place to go. Experimental evidence supporting a pyramidal configuration about the sulfur in sulfoxide

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(1) C.V. Berney and J.H. Weber, *Inorg. Chem.*, *7*, 283 (1968).
(2) P.W.N M. van Leeuwen and W.L. Groenveld, *Rec. Trav. Chim.*, *86*, 721 (1967).
(3) L.R. Blaine, E.K. Plyler, and W.S. Benedict, *J. Res. Natl. Bur. Std.*, *66A*, 223 (1962).
(4) J. Reedijk, P.W.N.M van Leeuwen, and W.L. Groeneveld, *Rec. Trav. Chim.*, *87*, 1073 (1968).
(5) W.D. Horrocks and F.A. Cotton, *Spectrochim. Acta*, *17*, 134 (1961).
(6) P. Klaeboe, *Acta Chem. Scand.*, *22*, 369 (1968).

Table I. Observed Frequencies (cm^{-1}) of Selected Vibrations in $[M^{n+}(TMSO)_6](ClO_4^-)_n$ Complexes

	ν_{SO}	δ_{ring}	ν_{MO}	δ_{SO}	φ	δ_{ML}
TMSO (free ligand)	1022	540	—	341,325	240	—
Mn^{II}	974,948sh	544	388	340,331	277	211
Fe^{II}	967		397	346,337		225,205
Zn^{II}	973,949sh	553	399	346,334	277	191
Co^{II}	968,942sh	553	406	346,336	288	220
Ni^{II}	970,947	555	413	336	290	228
Fe^{III}	921	559	443	343	282	251
Cr^{III}	932sh,911	573	484	354	290	316
Al^{III}	953,920sh	589	499	373	278	330

compounds exists for a wide variety of compounds, and comes from several sources (*e.g.*, microwave spectroscopy,[7] x-ray diffraction,[8] and the existence of stable enantiomers).[9] This feature destroys the C_2 axis possible for the puckered ring, leaving only the trivial element C_1.

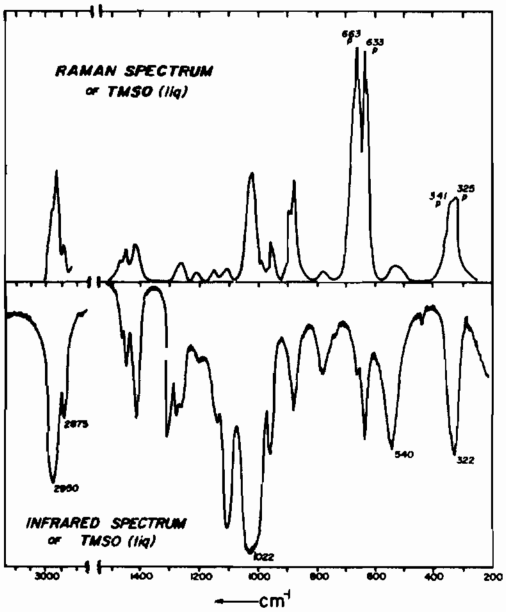

Figure 1. Raman and infrared spectra of liquid TMSO. ν_{SO} is at 1022 cm^{-1}.

Figure 1 displays the infrared and Raman spectra of liquid TMSO. The strongest infrared peak (1022 cm^{-1}) is certainly the S–O stretch. The two strongest Raman peaks (663 and 633 cm^{-1}) are reasonably interpreted as the two C–S stretching vibrations; that they are both polarized is in accord with the postulated C_1 symmetry of the molecule. The broad peak in the 500 cm^{-1} region represents two or three different vibrations, probably including in-phase and out-of-phase ring-bending modes (δ_{ring}). The strong peak in the 300 cm^{-1} region contains vibrations at 341 and 325 cm^{-1} which we assign as the O–S–C angle deformation vibrations (δ_{SO}). A weak band at 240 cm^{-1} is probably a ring-folding motion which we will designate φ, precise description of which is rendered difficult by the low molecular symmetry.

The Complex. Compounds treated in the present study all have the general formula $[ML_6]^{n+}(ClO_4^-)_n$, where M is the central metal ion, and L=TMSO. Survey spectra of the complexes are presented in Figure 2. As in the case of DMSO,[10] the bonding is through the oxygen, and the ligands are octahedrally disposed. In our previous study,[1] we concluded that the likely point groups for the DMSO complexes (where the ligand had C_s symmetry) were D_{3d} and S_6, the latter possibility being favored by certain features of the infrared spectrum. With a C_1 ligand, the highest symmetry possible is S_6, and we will assume that this is the actual point group. However, it is useful to initially regard the vibrations of the cation in the O_h approximation, taking full advantage of the skeletal symmetry of the complex before moving on to the S_6 model.

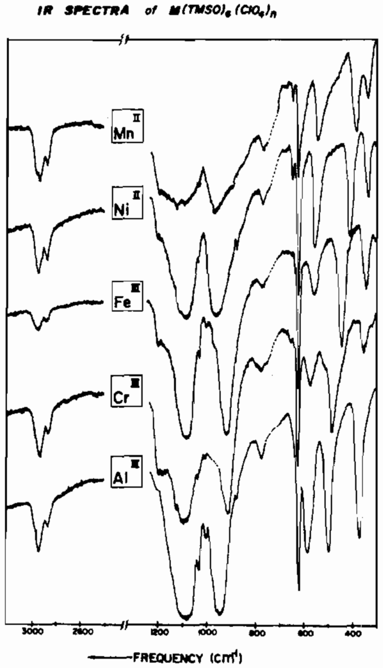

Figure 2. Infrared spectra of $M(TMSO)_6(ClO_4)_n$. Broad peaks at ~ 1100 cm^{-1} and sharp peaks at 620 cm^{-1} are ν_3 and ν_4 of ClO_4^-. Prominent peaks going from 388 cm^{-1} (Mn^{II}) to 499 cm^{-1} (Al^{III}) are assigned as ν_{MO}. Other peaks in this region are ligand vibrations δ_{ring} (544-589 cm^{-1}) and δ_{SO} (341-373 cm^{-1}).

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[7] H. Dreizler and G Dendl, *Z. Naturf. 20 (A)*, 1431 (1966).
[8] H.M.M. Shearer, *J. Chem. Soc.*, 1394 (1959).
[9] K.K. Andersen, *Tetrahed. Lett.*, *3*, 93 (1962).
[10] F.A. Cotton, R. Francis, and W.D. Horrocks, *J. Phys. Chem.*, *64*, 1534 (1960).

Classification of Vibrations. The number of normal modes of the ML_6 cation is easily calculated from the formula 3N-6, where N is the appropriate number of atoms. If n_L is the number of atoms in the ligand (assumed nonlinear), each free ligand will have $3n_L-6$ normal modes. If the coupling between the ligand and the central atom is not too strong, these vibrations will be essentially unchanged on complexation; that is, their frequencies and descriptions in terms of internal coordinates will be perturbed but not distorted beyond recognition. Thus $6(3n_L-6)$ modes of the complex can be identified with internal ligand modes. Since $N = Nn_L + 1$, the number of modes unique to the complex is 33 regardless of the nature of the ligand (so long as it is nonlinear). The representation Γ_{ex} of these external modes, which in the first approximation will correspond to rigid-body motions of the ligand, can be derived by considering the case where the ligand is diatomic.

The vibrational representation for an octahedral $M(XY)_6$ complex is

$$\Gamma_{vib} = 2A_{1g} + 2E_g + F_{1g} + 2F_{2g} + 4F_{1u} + 2F_{2u}$$

The representation for either the X–Y (internal) or M–X (external) stretching mode is

$$\Gamma_{str} = A_{1g} + E_g + F_{1u}$$

Subtracting 2 Γ_{str} from Γ_{vib} leaves Γ_{def}, the representation of the deformation modes.

$$\Gamma_{def} = F_{1g} + 2F_{2g} + 2F_{1u} + 2F_{2u}$$

Since the ligand is diatomic, all the deformation modes in this representation are external. They can further be classified as «gear» or «antigear» deformations by the relative motion of the X and Y atoms.

$$\begin{array}{c} Y\rightarrow \\ | \\ X\rightarrow \\ | \\ M \end{array} \qquad\qquad \begin{array}{c} Y\rightarrow \\ | \\ \leftarrow X \\ | \\ M \end{array}$$

gear deformation antigear deformation

Actual twisting motions are not possible for a linear ligand bonded along the molecular axis, but the representation of this motion under O_h can still be obtained by forming the symmetry coordinates of an appropriate vector by the usual procedure.[11] The result is

$$\Gamma_{twist} = A_{1u} + E_u + F_{1u}$$

so that, adding, we obtain

$$\Gamma_{ex}(O_h) = \Gamma_{str} + \Gamma_{def} + \Gamma_{twist}$$
$$= A_{1g} + E_g + F_{1g} + 2F_{2g} + A_{1u} + E_u + 4F_{1u} + 2F_{2u}$$

This result, with Raman and infrared activities, is displayed in Figure 3, together with the correlations required when the symmetry is lowered to D_{3d} and to S_6.

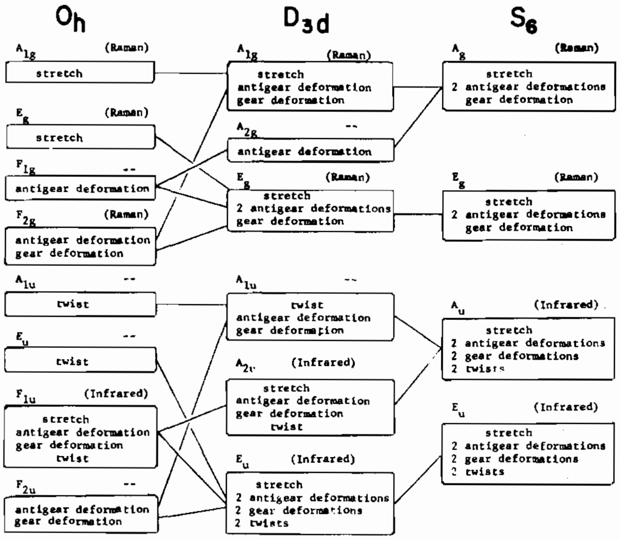

Figure 3. Correlation of external ligand vibrations for O_h, D_{3d} and S_6 conformations of an ML_6 complex.

Since any ligand with a symmetry lower than C_{4v} will disrupt the O_h symmetry of an octahedral complex, it is meaningless to discuss the internal vibrations of $M(TMSO)_6$ under O_h. A D_{3d} structure requires that the ligand have a plane of symmetry coinciding with one of the symmetry planes of the complex. In this case, representations of each internal ligand vibration symmetric (A′) or antisymmetric (A″) with respect to the plane are

$$\Gamma_{Q(A')} = A_{1g} + E_g + A_{2u} + E_u$$
$$\Gamma_{Q(A'')} = A_{2g} + E_g + A_{1u} + E_u$$

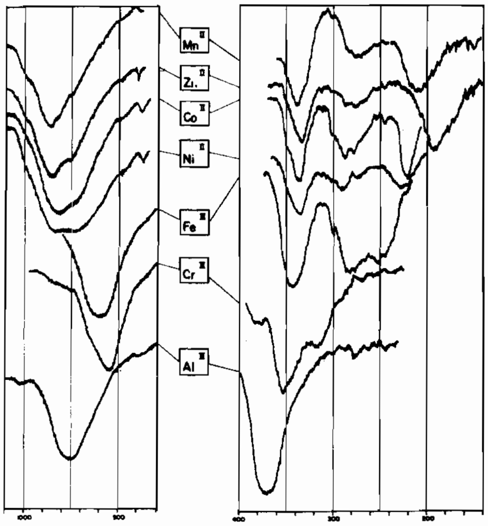

Figure 4. High-resolution infrared spectra of the ν_{SO} and δ_{ML} regions of $M(TMSO)_6(ClO_4)_n$ complexes. Prominent peaks running from 341 cm^{-1} (Mn^{II}) to 373 cm^{-1} (Al^{III}) are assigned to the internal ligand vibration δ_{SO}. The external mode δ_{ML} is well separated for the divalent metals shown (211, 191, 220 and 228 cm^{-1}), but becomes mixed with other vibrations for the trivalent metals.

In an S_6 complex, the ligand has effective C_1 sym-

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[11] E.B. Wilson, Jr., J.C. Decius, and P.C. Cross, *Molecular Vibrations*, McGraw-Hill, New York (1955), p. 118.

metry whether it started that way or not, and the representation for each vibration is

$$\Gamma_Q = A_g + E_g + A_u + E_u$$

Since S_6 has a center of symmetry, the mutual exclusion rule holds; only the A_g and E_g components will be seen in the Raman, and A_u and E_u in the infrared. A_u and E_u in the S_6 model derive from F_{1u} in the O_h approximation and so are initially degenerate. Most of the observed bands (Figure 2) are thus unresolved A_u, E_u pairs, but the degeneracy can be lifted by interligand coupling. Some evidence for such splitting can be seen in Figure 4, where portions of the spectra are shown under conditions of higher resolution. The splitting is particularly pronounced in the ν_{SO} bands (around 950 cm^{-1}). This is what one would expect from the structure postulated for the cations (Figure 5). The set of MO bonds has strict O_h symmetry, while it is the placement of the SO bonds which requires the point group to be S_6. Other sets of equivalent bonds (*e.g.* S–C, C–C) are in nonoctahedral positions, but are not in a position to interact as strongly as the SO bonds.

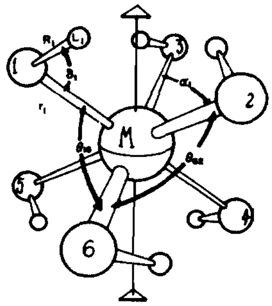

Figure 5. S_6 structure assumed for the $M(OL)_6$ model. The numbered medium-size spheres represent the oxygen atoms and the small spheres represent the SC_4H_8 moieties. Representative examples of internal coordinates are shown, except for the τ_i, which are torsions about the $M\text{-}O_i$ bonds.

Results

Frequencies of some readily identifiable vibrations are given in Table I, where the metals have been listed in order of increasing ν_{MO}. This order is the same as that found for DMSO complexes,[1] with the additional ions Al^{III} and Fe^{III} coming higher and lower than Cr^{III}. In fact, the ratio of ν_{MO} for the TMSO and DMSO complexes of a given metal is very nearly constant (at 0.93), adding considerable support to the assignment. The vibration labeled δ_{ML} is clearly recognizable in the spectra of most of the complexes (Figure 4), although in the case of Al^{III} it seems to be blended with the absorption assigned to ν_{MO}. Its assignment as an external (interligand) deformation results from its absence in the spectrum of the free ligand, and from its position below ν_{MO}. It is even more strongly dependent on the metal ion than ν_{MO}, although its position in the case of the Zn^{II} complex is anomalous.

The S–O stretching vibration is of special interest because of its sensitivity to complex formation. Cotton and Francis[12] have pointed out that draining electrons from the oxygen (to form the M–O bond) should lower the S–O bond order and the S–O stretching frequency. Thus, the tighter the M–O bond, the larger ν_{MO}, and the greater the decrease in ν_{SO} from its value in the free ligand. It is clear from Figure 4 that this relationship holds until we get to Al^{III}, where ν_{SO} goes up again. If ν_{MO} is used as a criterion of M–O bond strength, Al^{III} ranks first in the present series of metals; if $\Delta\nu_{SO}$ is used, it comes between Ni^{II} and Fe^{II}.

So we have an anomaly (the low position of δ_{ML} in the Zn complex) and an ambiguity (the position of Al^{III} in an M–O bond-strength ordering). Either of these difficulties might be due to the mass of the central metal ion, since Zn is the heaviest of the metals investigated and Al is the lightest. To answer these questions, and more fundamentally, to obtain a ranking of the metals with respect to MO force constants rather than frequencies, we have carried out normal-coordinate calculations on a number of simplified models. These calculations are described in the next section.

Calculations

Since an $M(TMSO)_6$ cation has 249 vibrational degrees of freedom, a rigorous normal-coordinate analysis is impractical. We have therefore examined a series of progressively more realistic vibrational models to see how the derived force constants depend on the model assumed. The results for all these calculations are compiled in Table II.

ML (Diatomic) Model. The simplest model we can possibly assume is that of a diatomic molecule ML, where M is the metal and L represents the TMSO ligand. The force constant, f_{MO}, can be found directly from the expression $(\nu_{MO}/1303.16)^2\mu$, where μ is the reduced mass, calculated using the mass of L as 104 amu and the mass number of the most abundant isotope for the mass of M.

ML_6 Model (O_h symmetry). The vibrational representation for this model is

$$\Gamma_{vib} = A_{1g} + E_g + F_{2g} + 2F_{1u} + F_{2u}.$$

The two vibrations in F_{1u} are the only IR-active modes. They can be approximately described as a stretch and a bend, although some mixing of these internal coordinates will occur (a diagram is given on p. 118 of Nakamoto).[13] G-matrix elements were calculated assuming an M–L bond distance[14] of 2.00 Å, and masses as quoted above. A diagonal F matrix was assumed. The secular determinant was solved as a quadratic equation with the roots chosen to give a stretching force constant greater than the bending force constant. The spectrum of the Fe^{II} complex

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(12) F.A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, *82*, 2986 (1960).
(13) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, New York (1963).
(14) M.J. Bennett, F.A. Cotton, and D.L. Weaver, *Acta Cryst.*, *23*, 581 (1967).

Table II. Force constants (millidynes/Å) calculated for $M(TMSO)_6$ complexes using simplified vibrational models.

	ML model	ML_6 model		bent MOL model[a]		bent LOMOL model[a]			$M(OL)_6$ model[b]		
	f_{MO}	f_{MO}	f_{bend}	f_{SO}	f_{MO}	f_{SO}	f_{MO}	f_{OMO}	f_{SO}	f_{MO}	f_{OMO}
Mn^{II}	3.19	1.69	0.90	7.28	1.16	7.11	0.84	0.86	7.223	1.055	0.283
Fe^{II}	3.38	1.73[c]	1.09[c]	7.16	1.23	6.92[c]	0.87[c]	1.11	7.084	1.112	0.363
		1.83[d]	0.86[d]			7.01[d]	0.92[d]	0.77	7.101	1.122	0.234
Co^{II}	3.65	1.90	0.99	7.15	1.32	6.94	0.95	1.05	7.078	1.201	0.327
Ni^{II}	3.74	2.02	1.23	7.17	1.37	6.93	0.98	1.16	7.088	1.245	0.370
Zn^{II}	3.71	2.03	0.90	7.24	1.29	7.12	0.99	0.68	7.178	1.198	0.163
Fe^{III}	4.21	2.25	1.13	6.36	1.61	6.05	1.11	1.51	6.259	1.436	0.312
Cr^{III}	4.78	(no real solution)		6.11	1.97	—	—	—	5.894	1.677	0.880
Al^{III}	3.14	1.66	0.91	6.80	1.61	6.54	1.06	1.39	6.728	0.925	0.866

[a] $f_{bend} = f_{MOL}$ held at 0.35. [b] $f_{MOL} = 0.35$, $f_{OMO'} = 0.10$, interaction constant $f_{MO,OMO} = 0.025$. [c] δ_{ML} taken as 225 cm^{-1}. [d] δ_{ML} taken as 205 cm^{-1}.

shows peaks at 225 and 205 cm^{-1}, due to mixing of δ_{ML} and an internal vibration of the ligands, or to a weak Jahn-Teller effect in the t_{2g} orbitals. Since the assignment is uncertain, the calculations are carried through for both frequencies. No real solution of the secular equation was obtained for the Cr^{III} complex.

Bent MOL model (C_s symmetry). One disadvantage of the previous models is that they give no information at all about the S–O bond. The simplest system that offers any hope of doing this is a linear M–O–L model ($C_{\infty v}$ symmetry), with a representation $\Gamma_{vib} = 2A_1 + E_1$. The L now stands for SC_4H_8. The two stretches are in A_1, and it proves impossible to find real force constants that will reproduce observed values for ν_{SO} and ν_{MO}. If the molecule is bent, the symmetry becomes C_s, and all three vibrations are in A′; it is then possible to fit the two stretching frequencies, letting the bending frequency vary arbitrarily. The G matrices were calculated using $r_{MO} = 2.00$ Å, and 88 amu as the mass of L. An F matrix with diagonal elements f_{SO}, f_{MO} and f_{bend} was assumed, and a computer program written to solve the 3×3 secular equation and perturb the trial F until the two highest eigenvalues matched ν_{SO} and ν_{MO}. The bending force constant was held constant during this calculation. The sensitivity of f_{SO} and f_{MO} to the value of f_{bend} assumed was determined by varying this quantity from 0.32 to 0.70; f_{SO} changed by less than a percent over this range, while f_{MO} decreased by almost 30%. The order of the metals with respect to f_{SO} or f_{MO} was unchanged, however.

Bent LOMOL model (C_{2h} symmetry). An octahedral complex ML_6 can be thought of as three linear LM′L units superimposed in such a way that the LML axes are orthogonal and the three M′ atoms are merged to form a single M. Thus the next step in developing a more accurate model (including both M–O and S–O bonds) would be to put an O–L group on both sides of the M atom. If the units are collinear, the model has $D_{\infty h}$ symmetry and the two IR-active stretches comprise the Σ_g^- part of the vibrational representation. As in the linear MOL case, it proves impossible to find real force constants that will reproduce the observed frequencies. Hence we go to a bent, C_{2h} model, for which

$$\Gamma_{vib} = 3A_g + 2A_u + 4B_u.$$

B_u contains the infrared-active stretching vibrations ν_{SO} and ν_{MO}, plus two deformations, δ_{MOS} and δ_{OMO}.

The program written for this phase of the study was designed to accept the 4×4 B_u block of the symmetry-factored G matrix, a trial (diagonal) F matrix, and three observed frequencies (ν_{SO}, ν_{MO}, and δ_{ML}) as input for each complex. One of the four force constants was held fixed while the other three were perturbed until agreement with the observed frequencies was achieved. Originally the fixed force constant was f_{OMO}. It turned out to be impossible to converge on the observed frequencies unless f_{OMO} was varied, and the resulting eigenvectors indicated that the vibration designated δ_{ML} is, in terms of this model, best interpreted as δ_{OMO}. As in the case of the ML_6 model, it proved impossible to find a real, diagonal, force field that would reproduce the frequencies for the Cr complex.

$M(OL)_6$ model (S_6 symmetry). The gross geometry of the model and the internal coordinates selected are shown in Figure 5. The MOL angle was taken as 124°, to correspond with the MOS angle in the Fe^{III}–DMSO complex investigated crystallographically by Bennett *et al.*[14] The LO bond length was assumed to be 1.54 Å, and the MO bond length was taken as 1.476 Å plus the (Goldschmidt) ionic radius of the metal ion (this reproduces the Fe–O distance observed in Ref. 14). Average atomic weights, rather than isotopic masses, were used in these calculations. The G matrix was obtained from GMAT, an adaptation of a program due to Schachtschneider.[15]

The vibrational representation for this model is

$$\Gamma_{vib} = 5A_g + 5E_g + 6A_u + 6E_u$$

(this differs from the Γ_{vib} given in Figure 3 because six internal stretches are included and six twists are left out, since the ligand is assumed diatomic and therefore linear). Calculations were done only for the A_u block, symmetry coordinates for which are given in Table III. Coupling between the torsion and other vibrations is usually small, so S_τ was left out of the calculation, reducing the block to 5×5.

A trial F matrix was entered, and the force constants f_{SO}, f_{MO}, and f_{OMO} were varied (using a Jacobian matrix) until agreement with the observed values of

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(15) J.N. Schachtschneider, Technical Report 231-64, Shell Development Company, Emeryville, California.

Table III. Symmetry Coordinates for the A_u Block, $M(OL)_6$ Model

$S_{SO}=6^{-1/2}[R_1+R_2+R_3-R_4-R_5-R_6]$	(S-O stretch)
$S_{MO}=6^{-1/2}[r_1+r_2+r_3-r_4-r_5-r_6]$	(M-O stretch)
$S_{MOL}=6^{-1/2}[\delta_1+\delta_2+\delta_3-\delta_4-\delta_5-\delta_6]$	(MOL deformation)
$S_{\rho MO}=6^{-1/2}[\alpha_1+\alpha_2+\alpha_3-\alpha_4-\alpha_5-\alpha_6]$	(antisymmetric umbrella mode)
$S_{\rho MO}'=6^{-1/2}[\theta_{16}+\theta_{24}+\theta_{35}-\theta_{43}-\theta_{51}-\theta_{62}]$	(L_3ML_3 pseudotorsion)
$S_\tau=6^{-1/2}[\tau_1+\tau_2+\tau_3-\tau_4-\tau_5-\tau_6]$	(MOL torsion)

ν_{SO}, ν_{MO}, and δ_{ML} was obtained. These frequencies could be fitted with a diagonal F matrix for all complexes except Al^{III}, for which an S_{MO}, S_{OMO} interaction element of 0.025 was required. To keep the results comparable, calculations were repeated for all the other complexes using this value. The force constants f_{MOL} and f_{OMO}' were held at 0.35 and 0.10 throughout the calculations.

The potential energy distributions derived from these calculations indicate that the vibrations ν_{SO} and ν_{MO} are well described by the symmetry coordinates S_{SO} and S_{MO}. In this model, the vibration labeled δ_{ML} consists of mixtures of S_{MOL} varying with the complex, and sometimes including an infusion of S_{OMO}'. In the Al complex, ν_{MO} and δ_{ML} were strongly mixed.

Discussion

Divalent Complexes. All of the models show f_{MO} increasing from Mn to Ni; Zn then either shows a slight increase over Ni (ML_6, LOMOL), or drops back slightly, to between Co and Ni for $M(OL)_6$, the most realistic of the models. The force-constant ranking for Zn thus differs from the ν_{MO} ranking, an effect attributable to its high mass. The order of the metals with respect to f_{MO} is in very close agreement with the order of stability of their complexes, as determined by Irving and Williams,[16] and with the order of ligand-field stabilization energies.[17] This order suggests that the increasing nuclear charge of the metal is effective in increasing f_{MO} in spite of the decreasing number of vacancies in the *d* subshell until, with Zn, the *d* subshell is completely filled. Completion of the *d* subshell reduces the covalent component of the MO bond, resulting in (i) a decrease in its directional character (reflected in the sudden drop in f_{OMO} from Ni to Zn) and (ii) a decrease in the drainage of electrons from the SO bond (reflected in the increase of f_{SO} from Co to Zn). Effect (i) explains the anomalous position of δ_{ML} for Zn (Figure 4). Effect (ii) means that Δf_{SO} (the decrease in f_{SO} from its value in the free ligand) is not a single-valued function of the MO bond strength, but depends in a more complicated way on the type of bonding involved. These ideas will be discussed in more detail elsewhere.[18]

Trivalent Complexes. Cr^{III} exhibits the largest f_{MO} and smallest f_{SO} of any of the metals studied in all cases for which solutions were obtained. This suggests a comparatively large covalent component in the Cr–O bond and is consistent with the electron configuration of the ion ($t_{2g}^3e_g^0$), which leaves the octahedrally-disposed orbitals completely vacant. Force constants for Fe^{III} indicate weaker bonding than for Cr^{III}, but stronger than is found in any of the divalent complexes.

Results for Al^{III} are the most model-sensitive of all, due to the small mass of the ion. The MOL and LOMOL models rank it with or just below Fe^{III} (in terms of the f_{MO} criterion), while the ML, ML_6, and $M(OL)_6$ models all give it a force constant smaller than any of the divalent metals. Models supplying values for f_{SO} all put Al between the divalent metals and Fe^{III} for this parameter. Since Al^{III} is a d^0 ion, this is again consistent with the idea of a relatively large covalent contribution (effective in attracting electrons from the SO bond) which does not lead to a large f_{MO} because of a smaller effective nuclear charge. More sophisticated calculations will be required to get a reliable comparison for Al^{III}. Observation by Raman spectroscopy of the totally symmetric ν_{MO} mode in this series of complexes would provide even more reliable information.

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[16] H. Irving and R.J.P Williams, *Nature, 162*, 746 (1948); *J. Chem. Soc., 1953*, 3192.

[17] J.S. Griffith and L.E. Orgel, *Quart. Revs.* (London), *11*, 381 (1957).

[18] C.V. Berney, to be published.