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Spectra of Manganese(III) Complexes. The Origin of the Low-Energy Band[1]

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The solution and solid-state spectra of 11 representative manganese(III) complexes and acidic, aqueous solution spectra of the manganese(III) ion were examined. In each case two bands in the near-infrared and visible portions of the spectra were found under suitable experimental conditions. The consequences of Jahn–Teller effects on manganese(III) complexes are discussed and the low-energy band ($\sim$10,000 cm^{-1}) is assigned generally to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition for a D_{4h} symmetry complex. Further refinement of the X-ray crystal structure[3] of manganese(III) acetylacetonate confirms the fact that no sizable static distortions of the Mn–O bond are present. However, the data are insufficiently good to rule out pseudorotation or small static distortions with molecular disorder in the crystal. The electronic spectrum of the complex in the visible and near-infrared spectral regions is consistent only with a band assignment which assumes a splitting of $\sim$9000 cm^{-1} for the ^5E_g (in O_h) state.

Introduction

The electronic and structural properties of high-spin manganese(III) complexes are of unusual interest since the ground electronic state anticipated in octahedral complexes, ^5E_g, is subject to strong Jahn–Teller forces.[4,5] A similar electronic ground state has been observed[6] in complexes of chromium(II).

Despite several recent reports[7-14] of the preparation and optical properties of manganese(III) complexes, difficulties have arisen in the assignment of the electronic transition appearing in the near-infrared spectral region. The relationship of the presence of this band to the structure of the complex in question has not been clarified. In particular, this band has been variously assigned to a spin-forbidden transition[15,16] from the ground state to $^3T_{1g}$ (in O_h), as a low-energy "charge-transfer"[10,14] transition, as a transition from the ^5E_g ground state to a trigonally split $^5T_{2g}$ excited state,[17] and as a spin-allowed transition between components of the ^5E_g (in O_h) ground state split by Jahn–Teller phenomena.[5,18]

In this paper we report the results of a rather exhaustive study of the electronic spectra of a wide variety of manganese(III) complexes and attempt to correlate and systematize the available data. We also report the results of a reexamination of the structural data[3] for manganese(III) acetylacetonate. We have examined the possibility that the electronic spectrum of this complex is consistent with a pseudorotating structure, both in solution and for the room-temperature solid.

Experimental Section

Since complexes of manganese(III) are readily subject to decomposition[19,20] it is necessary to use special care in preparing samples and observing spectra.

Preparation of Complexes. Bis(2,4-pentanedionato)diaquomanganese(III) Chloride Dihydrate, $Mn(acac)_2(H_2O)_2Cl \cdot 2H_2O$.—Preparative procedures were followed as given in the literature.[21] *Anal.* Calcd for $MnC_{10}H_{22}O_8Cl$: C, 33.24; H, 6.1. Found: C, 33.00; H, 6.04.

Ammonium Bis(5-Chlorosalicylato)diaquomanganese(III) Dihydrate, $NH_4[Mn(5\text{-}Cl\text{-}Sal)_2(H_2O)_2] \cdot 2H_2O$.—Literature methods of preparation[22] gave very satisfactory yields of this complex. *Anal.* Calcd for $MnC_{14}O_{10}H_{20}NCl_2$: C, 34.3; H, 3.67. Found: C, 34.35; H, 3.56.

Other complexes prepared using existing procedures were: manganese(III) acetate dihydrate;[23] tris(1,2-propanediamine)cobalt(III) hexachloromanganese(III), $[(1,2\text{-pn})_3Co][MnCl_6]$;[7] potassium pentachloromanganese(III), K_2MnCl_5;[24] potassium pentafluoromanganese(III), K_2MnF_5;[25] potassium tris(oxalato)manganese(III) trihydrate, $K_3Mn(Ox)_3 \cdot 3H_2O$;[26] and cesium–manganese alum, $CsMn(SO_4)_2 \cdot 12H_2O$.[23]

Both manganese(III) acetate (contaminated with MnO_2 and manganese(II) acetate) and $K_3Mn(Ox)_3 \cdot 3H_2O$ (contaminated with potassium oxalate) were judged to be impure but usable. The other complexes were freshly prepared and/or recrystallized immediately prior to use and were taken to be pure.

Bis(tetraethylammonium)pentachloromanganese(III), $[(C_2H_5)_4N]_2MnCl_5$.—The preparation of this compound has been reported by Goodwin and Sylva.[11] It was found that, although this preparative procedure is suitable, it is more convenient to alter certain portions of it.

A suspension of manganese dioxide in absolute ether was treated carefully with acetyl chloride (99% CH_3COCl, J. T. Baker Chemical Co.) to produce an intensely purple solution which was

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(1) Abstracted in part from the Ph.D. thesis of T. S. Davis.

(2) National Defense Education Act Fellow, 1962–1965.

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then filtered to remove unreduced manganese dioxide. The reaction usually was initiated by adding a small amount of solid manganese(III) acetate. Small portions of an ethanol solution of $(C_2H_5)_4NCl$ were added to the purple ether solution until precipitation of the green, finely divided complex was complete. The product was filtered, washed with ethanol and ether, and dried over sodium hydroxide in a desiccator. The complex may be prepared in solvents other than ether (*e.g.*, ethanol, CCl_4, 1-butanol, methanol) but photodecomposition appears slower in ether.

Mixed Manganese–Aluminum Alum, $NH_4Al[Mn](SO_4)_2 \cdot 12H_2O$.—This mixed alum is the only one reported which contains manganese(III)[27] and may be prepared over quite a large range of manganese(III) concentrations. In a typical preparation 2.5 g of manganese(III) acetate was dissolved in a minimum amount of cooled 30% (by volume) H_2SO_4. Because of solubility problems in dilute acid, the required 4.85 g of $Al_2(SO_4)_3$ was first dissolved in ~35 ml of warm water and then acidified to 30% H_2SO_4, cooled, and added to the manganese(III) acetate solution. The cation was added as 1.98 g of $(NH_4)_2SO_4$ which was also dissolved in 30% H_2SO_4 and cooled before addition to the manganese(III) solution. The mixed alum was obtained in at least two crystalline forms after being allowed to stand in a refrigerator from 1 day to 1 month. These crystals were isolated by filtering rapidly on a coarse frit, washed quickly with absolute alcohol, and stored in loosely stoppered glass vials. To limit photodecomposition and dehydration, the vials were stored over 30% H_2SO_4 in a darkened desiccator.

Tris(tropolonato)manganese(III), $Mn(tp)_3$.—Although this compound apparently has not been previously prepared, adaptation of a procedure given by Donaruma[28] gives the desired complex easily. Tropolone (0.01 mol or ~1.22 g) and manganese(III) acetate (~0.0027 mol or ~0.724 g) were finely powdered and dissolved in 50 ml of dry toluene. The solution was placed in an appropriate flask and heated with magnetic stirring until ~30 ml of a toluene–acetic acid azeotrope had distilled over, at which point a dark green precipitate had formed. The reaction mixture was cooled and the product was filtered and washed four times with toluene. The product was recrystallized from chloroform and washed with ether. The green needles obtained decomposed without melting at ~235° (uncorrected). *Anal.* Calcd for $MnC_{21}H_{15}O_6$: C, 60.30; H, 3.59. Found: C, 59.59; H, 3.69. The compound was not thoroughly dried prior to analysis.

Tris(1,1,1,6,6,6-hexafluoro-2,4-pentanedionato)manganese(III).—Oxidation of manganese(II) in the presence of sodium acetate and hexafluoroacetylacetone (HF_6acac) with $KMnO_4$ gives MnO_2 or Mn_2O_3. Ligand-exchange techniques are required to prepare the complex. We found it feasible to exchange the trifluoroacetylacetonate ligand for the hexafluoro derivative starting with $Mn(F_3acac)_3$.

In a typical experiment, HF_6acac (the hydrate must be avoided) was added to $Mn(F_3acac)_3$ in slight excess of the quantity necessary to dissolve the complex. Ligroin (bp 60–90°) was added to increase the volume approximately fourfold and the solution was cooled to ~0°. After about 2 hr, the impure product was filtered off and again treated to the HF_6acac plus ligroin procedure. The product subsequently was sublimed at 30° (250 mm) pressure onto a cold finger, mp 57–58° (uncorrected). The complex readily formed a coating of what appeared to be $Mn(F_6acac)_2 \cdot 2H_2O$ in moist air and decomposed in moist solvents. *Anal.* Calcd for $MnC_{15}H_3O_6F_{18}$: C, 26.7; F, 50.7; Mn, 8.1. Found: C, 28.7; F, 47.7; Mn, 8.4.

Tris(3-cyano-2,4-pentanedionato)manganese(III).—Like $Mn(F_6acac)_3$, this compound could not be prepared by conventional procedures. Ligand exchange with $Mn(DPM)_3$ or $Mn(DIBM)_3$ (DIBM is the anion of diisobutyrylmethane, and DPM is the anion of dipivaloylmethane) produced the desired product. In a typical experiment, 1.0 g of $Mn(DIBM)_3$ or $Mn(DPM)_3$ was dissolved in 20 ml of cyclohexane. To this black solution, 1.2 g of 3-cyano-2,4-pentanedione[29] was added in small amounts with stirring. After complete addition of the ligand, approximately 1 g of a black precipitate was formed which was filtered from the solution and washed with cyclohexane. The product was purified by recrystallization from benzene upon addition of cyclohexane and was found to melt at 165° (uncorrected) with decomposition. *Anal.* Calcd for $MnC_{18}H_{18}O_6N_3$: C, 50.6; H, 4.2; N, 9.8; Mn, 12.9. Found: C, 50.6; H, 4.4; N, 9.9; Mn, 12.9.

Acid Solutions of Manganese(III) Ion.—Solutions containing manganese(III) in dilute hydrochloric,[14,30] sulfuric,[8,14,31] and perchloric[5,8] acids have been reported previously. However, it was found that sulfuric acid solutions prepared by some literature methods[31] were unstable and too concentrated for spectral studies. In essence, the procedure given by Vogel[31] was used with the concentrations of $Mn(ClO_4)_2 \cdot 6H_2O$ and $KMnO_4$ cut by a factor of 10. The solutions were protected from photodecomposition throughout preparation and stored for several hours in the dark prior to taking the spectra.

Solutions of manganese(III) in hydrochloric acid were produced using the above procedure. It was found that hydrochloric acid solutions of manganese(III) ion are more unstable to light and decompose faster, even in the dark, than sulfuric acid solutions. It was also found that a spectroscopically identical solution could be prepared simply by dissolving manganese dioxide in dilute HCl.

Spectroscopic Studies.—A Cary Model 14 spectrophotometer was used to obtain solution and transmission mull spectra of the complexes. Solution spectra were obtained in matched silica cells and the solvents employed were of the highest practical purity. Samples for transmission mull spectra were prepared by dispersing the particular complex in a suitable medium (Nujol or hexachlorobutadiene), then pressing between silica plates, and sealing the edges.

The reflectance spectra of several complexes were obtained from a Beckman Model DK-2 equipped with a standard reflectance attachment. Reflectance spectra at low temperatures were obtained using apparatus described by Fackler and Holah.[6]

X-Ray Structure of Manganese(III) Acetylacetonate.—The data of Morosin and Brathovde[3] (M–B) were weighted according to the Hughes scheme.[32] Refinement of the data[33] using isotropic thermal parameters in a number of least-squares cycles was conducted to minimize *R*. M–B used the differential method. Changes in atom positions from those found by M–B were small though these changes did lead to somewhat lower thermal parameters. A slightly larger trigonal twist, 8.5° compared with the 7.5° of M–B, was concluded. Interatomic distances and isotropic temperature factors as determined are presented in Table I for the structure of Morosin and Brathovde.[3]

Results

Table II summarizes the results obtained in this study for the visible and near-infrared spectra of a wide variety of manganese(III) complexes. As indicated here and elsewhere,[8–14,34] two prominent bands generally are observed between 5000 and 25,000 cm^{-1} with molar extinctions under 500 M^{-1} cm^{-1} for complexes having six similar ligand atoms surrounding the metal ion. Examples are the tris-β-diketone complexes, the alums, the tris acetate, the tris tropolonate, etc. In bis(chelate)diaquo complexes and in complexes

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TABLE I

INTERATOMIC DISTANCES AND ISOTROPIC TEMPERATURE FACTORS FOR THE REFINED STRUCTURE OF MANGANESE(III) ACETYLACETONATE

Bond	Dist,[a] Å	Temp factors, Å²	Bond	Dist,[a] Å	Temp factors, Å²
Mn–O_1	1.897	Mn 2.906 O_1 4.746	C_{12}–C_1	1.394	C_{12} 6.896
Mn–O_2	1.866	O_2 4.458	C_{12}–C_2	1.354	
Mn–O_3	1.904	O_3 4.060	C_{36}–C_3	1.421	C_{36} 5.463
Mn–O_4	1.897	O_4 4.455	C_{36}–C_6	1.407	
Mn–O_5	1.902	O_5 4.617	C_{45}–C_4	1.366	
Mn–O_6	1.897	O_6 4.315	C_{44}–C_5	1.337	C_{45} 4.533
C_1–O_1	1.239	C_1 5.314	C_1–C_{x1}	1.532	C_{x1} 6.391
C_2–O_2	1.303	C_2 4.717	C_2–C_{x2}	1.527	C_{x2} 6.844
C_3–O_3	1.253	C_3 3.630	C_3–C_{x3}	1.547	C_{x3} 5.400
C_4–O_4	1.277	C_4 4.909	C_4–C_{x4}	1.565	C_{x4} 4.775
C_5–O_5	1.287	C_5 3.530	C_5–C_{x5}	1.511	C_{x5} 5.864
C_6–O_6	1.277	C_6 3.735	C_6–C_{x6}	1.552	C_{x6} 6.086

[a] A final value of $R = 0.088$ was obtained.

TABLE II

SPECTROSCOPIC DATA FOR SOME HIGH-SPIN MANGANESE(III) COMPLEXES. NUMBERS IN PARENTHESES ARE EXTINCTION COEFFICIENTS, ϵ (L. MOL^{-1} CM^{-1})

Medium[f]	Bands, cm^{-1}	Excited state (in D_{4h})
	$Mn(acac)_2(H_2O)_2Cl \cdot 2H_2O$[e] (see Figure 1)	
Reflt	~17,230 sh	$^5B_{2g}$[a]
CH_3OH	~17,600 sh (55)	$^5B_{2g}$[a]
py	~8,500 b (34)	$^5A_{1g}$
	18,180 sh (81)	$^5B_{2g}$
	$NH_4[Mn(5\text{-}Cl\text{–}Sal)_2(H_2O)_2] \cdot 2H_2O$[e]	
Reflt	~17,000 b	$^5B_{2g}$[a]
i-C_3H_7OH	~18,900 sh (339)	$^5B_{2g}$[a]
	~21,900 w, sh	. . .
py	~13,500 sh (73)	$^5A_{1g}$
	~18,900 b, sh (89)	$^5B_{2g}$
	~21,400 w, peak (263)	. . .
	~22,700 sh (330)	^5E_g(?)
	Manganese(III) Acetate[e]	
Reflt	~11,400 b	$^5A_{1g}$
	~22,000 vb	^5E_g[b]
C_2H_5OH	~14,000 w, vb (33)	$^5A_{1g}$
	21,600 sh (137)[b,c]	$^5B_{2g}$
	$[(1,2\text{-pn})_3Co][MnCl_6]$[e]	
Reflt	~8,300 b, w	$^5A_{1g}$
	~17,540 sh	$^5B_{2g}$
	~22,400	^5E_g
	K_2MnCl_5[e]	
Reflt	~12,000 b, sh	$^5A_{1g}$
	~18,500 b	$^5B_{2g}$
	$K_3Mn(Ox)_3 \cdot 3H_2O$	
Reflt	~9,100 vb	$^5A_{1g}$
	~19,050 sh	$^5B_{2g}$
	~20,400 peak	^5E_g
C_4Cl_6[d] mull	~9,500 vb	$^5A_{1g}$
	~19,700	$^5B_{2g}$[b]
	$CsMn(SO_4)_2 \cdot 12H_2O$	
Reflt (RT) and (77°K)	~9,500 b	$^5A_{1g}$
	~20,400 sh	$^5B_{2g}$[b]
Nujol mull or C_4Cl_6 mull	~9,000 b, sh	$^5A_{1g}$[e]
	~20,400 sh	$^5B_{2g}$[b]
	Mixed Mn–Al Alum[e] $NH_4Al[Mn](SO_4)_2 \cdot 12H_2O$	
Reflt	~11,500 b	$^5A_{1g}$
	~21,050 sh	$^5B_{2g}$[b]
Nujol mull or C_4Cl_6 mull	~21,050 sh	$^5B_{2g}$[b,e]
	$Mn(tp)_3$[e] (see Figure 2)	
Reflt	~10,600 b	$^5A_{1g}$
	~16,700 sh	$^5B_{2g}$
	~20,800 peak	^5E_g
$CHCl_3$	9,090 (89)	$^5A_{1g}$
	15,875 (248)	$^5B_{2g}$
	17,545 (318)	^5E_g
	Mn^{3+}	
6 N H_2SO_4	~12,500	$^5A_{1g}$
	20,800 peak	$^5B_{2g}$
6 N HCl	11,400	$^5A_{1g}$
	~17,400 sh	$^5B_{2g}$

[a] The $^5B_{1g} \rightarrow {}^5A_{1g}$ band is under the envelope of this transition. [b] This band is broad and/or asymmetric and may contain two or more bands. [c] Extinction coefficient subject to uncertainty due to decomposition of sample. [d] Mull protected from uv-induced photodecomposition. [e] See Table III and ref 34 for additional spectral data. [f] RT is room temperature, reflt is reflectance spectrum.

which dissociate in solution, *e.g.*, $[(1,2\text{-pn})_3Co][MnCl_6]$, the low-energy ($^5B_{1g} \rightarrow {}^5A_{1g}$) band is not evident. However, the low-energy band of the bis(chelate)-diaquo species can be seen in pyridine where the coordinated water presumably is replaced by the amine (Figure 1). In a few cases, such as the tris(tropolonato)manganese(III) solution spectra, an additional band ($^5B_{1g} \rightarrow {}^5E_g$) was resolved (see Figure 2). This band probably is present in all of the spectra but may appear either under the envelope of the $10Dq$ ($^5B_{1g} \rightarrow {}^5B_{2g}$) band[12] or as an indistinct shoulder on the side of a rapidly rising charge-transfer band. It many cases it is possible to estimate or calculate the position of this third band (*vide infra*).

The spectra of the manganese(III) complexes generally appear to be unusually sensitive to the conditions under which the absorptions are observed. Solvent choice is particularly important since the position of the low-energy band ($^5B_{1g} \rightarrow {}^5A_{1g}$) in many of the complexes is very sensitive to solvent interaction.[10] Solvent perturbations usually can be recognized by comparing solution spectra with solid-state reflectance spectra.

Conversely, the results of solid-state spectra must be correlated with those of solution spectra with some care. Reflectance spectra usually show the $^5B_{1g} \rightarrow {}^5A_{1g}$ band at lower energies than any other mode used to obtain the spectrum. Transition mull spectra, on the other hand, often show the $^5B_{1g} \rightarrow {}^5A_{1g}$ band broadened and shifted to higher energies. Single-crystal spectra of dilute manganese alum crystals obtained by the pinhole method in this laboratory[34] do not show a defined low-energy band at all. In other single-crystal spectra[13] the $^5B_{1g} \rightarrow {}^5A_{1g}$ band is shifted 600–1000 cm^{-1} from the position found in reflectance spectra.

Discussion

Assignment of the Low-Energy Band.—Four reasonable assignments of the low-energy band appearing in manganese(III) complexes (Table II) have been suggested. (1) The transition arises owing to a *static* or *dynamic splitting* of the ^5E_g ground state.[5,18] (2) The

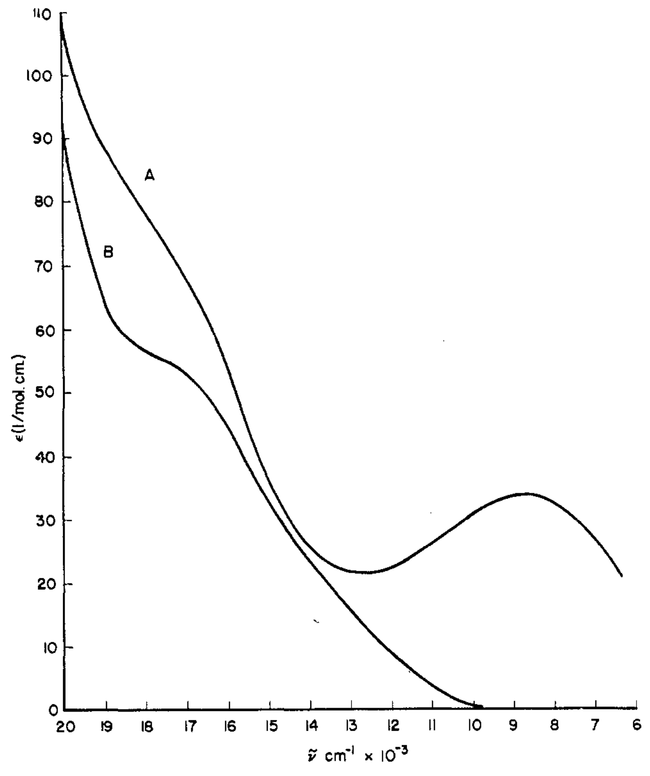

Figure 1.—Visible spectrum of $Mn(acac)_2(H_2O)_2Cl \cdot 2H_2O$ in (A) pyridine and (B) methanol.

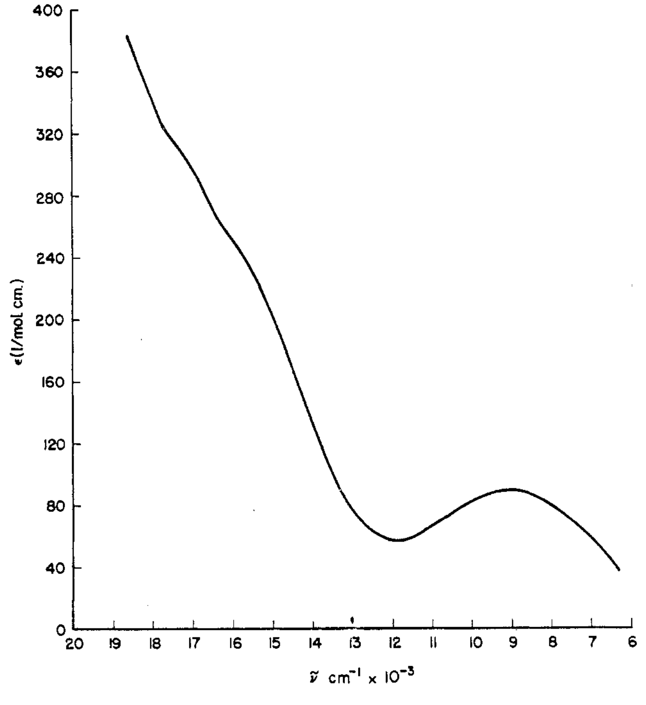

Figure 2.—Visible spectrum of manganese(III) tropolonate in chloroform.

excited state is split (by distortions); hence transitions from the ^5E_g ground state are doubled.[17] (3) Since a Tanabe–Sugano diagram[35] predicts the presence of a low-lying triplet state, the low-energy transition could be *spin-forbidden*.[15,16] (4) The transition could arise from ligand to metal "*charge transfer*."[10,14] We shall consider each of these possibilities separately.

(1) **Splitting of the E_g Ground State.**—The electronic configurations [core]$3d^9$ and (spin-free) [core]$3d^4$ produce E_g ground states in fields of octahedral symmetry. Such states are susceptible to Jahn–Teller forces which cause the removal of the orbital degeneracy. However, other phenomena such as spin–orbit coupling, lattice distortions, solvent interactions, etc., also may cause the removal of the degeneracy. Assuming these other effects are not energetically significant[36] when compared with the energy of the observed transitions in Cu^{2+}, Cr^{2+}, and Mn^{3+} complexes,[6,37–40] a splitting of the E_g ground state by 9000–15,000 cm^{-1} is required to account for the low-energy transition. An electronic splitting of this magnitude can occur only if sizable effective distortions[41] of the nuclear geometry from a regular octahedron about the central ion also occur. For an ML_6 system, distortion to D_{4h} symmetry removes the degeneracy of E_g. However, this may be either tetragonal elongation or compression, both equally probable for any one pair of *trans* M–L bonds; hence three degenerate minima in the potential surface must occur. Exchange among these minima produces the phenomenon labeled "minima exchange" or "pseudorotation."[42]

The Jahn–Teller problem with E_g ground states[43–47] has been treated thoroughly elsewhere (see Appendix). For purposes of the present discussion we will neglect any barrier which might exist to prevent "pseudorotation" and will discuss the result in terms of the energy level diagram given in Figure 3 (see Appendix). Here we assume that nuclear motion along the q_2 coordinate gives a pair of minima which are symmetric with respect to rotation about the threefold axis of the octahedron. Thus transitions may occur between components of the E_g (in O_h) ground state and from the ground state to the components of T_{2g}, which is less seriously split.[43] Should the molecule be statically distorted, as is apparent from X-ray crystal structures[44] of many chromium(II), manganese(III), and copper(II) complexes, it would be appropriate to label the states according to the symmetry observed for the molecule. Thus in the limit of an infinitely large tetragonal distortion in which the axial ligands are removed from the

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[35] F. A. Cotton, *Chemical Applications of Group Theory*, Interscience Publishers, New York, N. Y., 1963, p 210.

[36] Spin–orbit coupling splits the ^2D state in Cu^{2+} by about 2000 cm^{-1} and the ^5D states in Cr^{2+} and Mn^{3+} by smaller amounts. Lattice effects, however, may be very large.

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[38] D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.*, **4**, 1112 (1965).

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[41] Dissimilar ligands may produce an effectively distorted geometry.

[42] The exchange has the effect of a rotation about the threefold axis of the octahedron.

[43] The excited state for Mn^{3+} would arise from the configuration [core]$t_{2g}{}^2e_g{}^2$. It is less susceptible to strong Jahn–Teller perturbations with its octahedrally symmetrical distribution of antibonding electrons than is the [core]$t_{2g}{}^3e_g$ configuration.

[44] Both axial compression and elongation have been observed in the crystalline state (see ref 45–47).

[45] K. Knox, *J. Chem. Phys.*, **30**, 991 (1959).

[46] E. C. Lingafelter and H. Montgomery, private communication, found a compressed octahedron about chromium(II) in the Tutton salt.

[47] J. W. Tracy, N. W. Gregory, J. M. Stewart, and E. C. Lingafelter, *Acta Cryst.*, **15**, 460 (1962), and references therein.

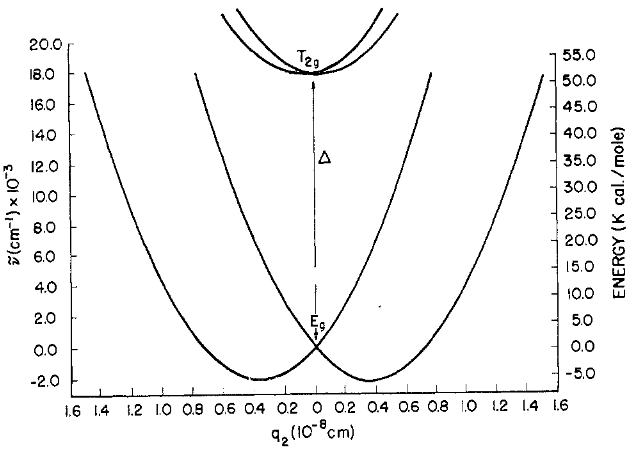

Figure 3.—Potential energy surfaces for Jahn–Teller split E_g and T_{2g} States. Only E_g states are drawn to scale (see Appendix).

metal the assignments become that of the square-planar complex (see Figure 4). Recent assignments[48] of this type for the CuO_4 square-planar geometry show that all of the "d–d" transitions may appear at energies larger than 16,000 cm^{-1}.

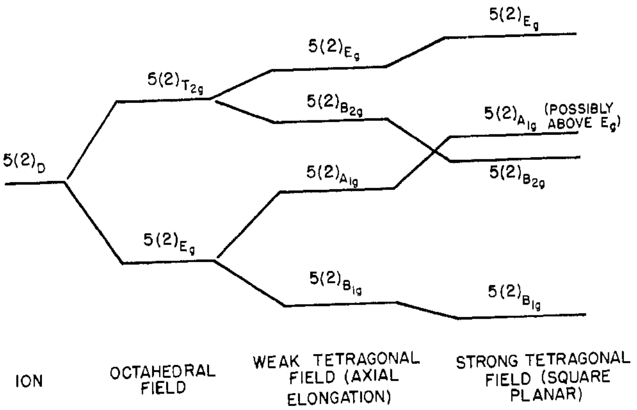

Figure 4.—Tetragonal spliting diagram.

The above assignment allows the low-energy transition between components of the E_g (in O_h) ground state in a weak tetragonal field to occur anywhere between zero and ~16,000 cm^{-1}. Since the transition is "spin-allowed," the intensity observed (Table II) should be similar to the intensity of other spin-allowed d–d bands. Also, since the minima of the components of E_g are widely separated (distortions from octahedra of 0.2–0.5 Å are commonly found), the band corresponding to a transition between components of E_g should be exceptionally broad. In cases where a low-energy band is found, its width is certainly very large (see Figure 2).

In a recent electron paramagnetic resonance study of Sc^{2+} doped into the cubic cation sites of CaF_2, Höchli[49] showed experimentally that for a 10*Dq* of ~6000 cm^{-1} in this system, a splitting of the ^2E ground state by ~2500 cm^{-1} is consistent with the data. With octahedral manganese(III), chromium(II), and copper(II) complexes, in which the e_g orbitals are clearly antibonding in character, larger splittings of the ground state appear quite reasonable.

The only apparent objection to assignment (1) for manganese(III) complexes arises from an evaluation of the X-ray structure of the acetylacetonate complex. As Morosin and Brathovde[3] showed, and as we have reproduced here, the metal–oxygen bond lengths all appear to be within experimental error of the same value. The complex clearly is not statically distorted to the extent needed to produce a low-energy electronic band at ~9000 cm^{-1}. Before considering this molecule further to show that a consistent assignment can be made within the framework of a split ^5E_g ground state, the other possible assignments will be discussed.

(2) **Split Excited State.**—If the low-energy transitions arise from components of $^5T_{2g}$ (or $^2T_{2g}$ in Cu^{2+}), the splitting is enormous (8000–20,000 cm^{-1}). For example, with $MnCl_6^{3-}$ (Table II), the $^5T_{2g}$ level would be split by 8300–10,500 cm^{-1} to be consistent with such an assignment. Since this state arises from the strong-field [core]$t_{2g}^2e_g^2$ excited-state configuration, distortions from octahedral geometry are not expected to be large as the electronic octahedral anisotropy is in the nonbonding t_{2g} orbitals.[50] As the large splittings required of the T_{2g} states would certainly be accompanied by even larger splittings of the E_g state, no consistency of assignment has been achieved with this model. Trigonal splittings of only 500–1000 cm^{-1} have been observed with some tris-chelate complexes.[16]

(3) **Spin-Forbidden Transition.**—The assignment of the low-energy band to the $^5E_g \rightarrow {}^3T_{1g}$ transition, expected on the basis of a Tanabe–Sugano diagram for a d^4 system, is ruled out by three distinct observations. First, the integrated intensity of the low-energy band often is as great as and sometimes is greater than the high-energy d–d transition. In no case is it "weak" compared with the principal visible band. Spin-forbidden transitions generally have intensities 2–3 orders of magnitude less than observed here.[51]

As predicted from a Tanabe–Sugano diagram, an increase in the ligand field should cause a decrease in the energy of the $^5E_g \rightarrow {}^3T_{1g}$ transition. Dingle[18] first showed that this result is not consistent with the observed spectra of manganese(III) complexes. Several additional exceptions are noted in Table II. The low-energy band in chromium(II) complexes also does not shift consistently[6,38] to lower energies with increasing crystal field. Finally, the spectra of copper(II) and chromium(II) complexes[6,38] suggest similar electronic transitions are found in both of these systems. However, no "spin-forbidden d–d" transitions can be achieved with copper(II); hence the assignment as a spin-forbidden transition would be specific to manganese(III) and chromium(II).

(4) **Charge Transfer.**—The low-energy band in

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(48) F. A. Cotton, J. J. Wise, and C. B. Harris, *Inorg. Chem.*, **6**, 909, 915, 917 (1967).

(49) U. T. Höchli, *Phys. Rev.*, **162**, 262 (1967). See, however, F. S. Ham, *ibid.*, **166**, 307 (1968).

(50) L. E. Orgel, "Transition-Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p 59 ff.

(51) T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

manganese(III) β-ketoenolates was assigned initially[10] to a "charge transfer" because the observed solvent shifts appeared to be inconsistent with expected shifts for "d–d" transitions. Photoreduction of manganese(III) complexes also suggested the presence of low-lying "charge-transfer" bands.

We are led to reject the charge-transfer assignment for several reasons. Certainly such an assignment for the low-energy band would have to be specific to manganese(III) complexes since chromium(II) and copper(II) complexes would show such a transition at a vastly different energy. The fact that the particular ligand atom bonded to the manganese(III) has relatively little influence on the position of the low-energy band also contradicts expectation for the charge-transfer assignment. While the manganese(III) β-ketoenolates, as a class, might have been considered unique, the presence of a low-energy band in the tris-tropolonate, tris-oxalate, and tris-acetate complexes at similar energies (Table II) shows this assumption to be incorrect.

While photoreduction of manganese(III) complexes does occur, no appreciable decomposition was found for the sensitive tris-oxalato species when light at energies greater than 20,000 cm^{-1} was removed by an appropriate filter. The photodecomposition does not appear to result from absorbance in the 8000–12,000-cm^{-1} region.

While Dingle[14] has suggested that ligands containing nonbonded electron pairs show the low-energy charge transfer, changing the bonded atom from O to F to Cl certainly would be expected to produce much more striking shifts than are actually observed. The lack of previous observation of the low-energy band for Mn(III) in Al_2O_3[52] and for Mn(III) in the sulfate alum[53] cannot be correlated with lack of charge transfer as Dingle suggests, since this band is clearly present in the alum (see Table II) and undoubtedly also would be found in Al_2O_3 under the appropriate experimental conditions (only 0.2 mol % was doped into the lattice in the sample reported in the literature[52]).

As we show (*vide infra*) the spectra of the manganese(III) β-ketoenolates also are best interpreted by an alternate assignment for the low-energy band.

General Electronic Spectral Relationships.—On attempting to systematize the electronic spectral data for manganese(III) complexes, the similarity of the data with data for chromium(II) and copper(II) complexes is readily recognized. The only assignment generally acceptable appears to be the one which assumes a rather large static or dynamic splitting of the E_g ground state. Assuming that the effective field about the metal is D_{4h}, the ground electronic state becomes A_{1g} or B_{1g} (static distortion). In the tetragonally elongated configuration which appears to predominate for complexes of known crystal structure, the electronic d–d states for the manganese(III) (and chromium(II)) complexes can be ordered energetically as $^5B_{1g} < {}^5A_{1g} < {}^5B_{2g} < {}^5E_g$ and an analysis can be carried out in terms of three parameters,[54] Dq, Ds, and Dt, where $E(^5B_{1g} \rightarrow {}^5A_{1g}) = 4Ds + 5Dt$; $E(^5B_{1g} \rightarrow {}^5B_{2g}) = 10Dq$; and $E(^5B_{1g} \rightarrow {}^5E_g) = 3Ds - 5Dt + 10Dq$. The consistency of such an analysis is obvious from the data of Table III.[5,6,9–14,55,56]

As indicated in a previous paper,[6] the apparent stabilization of the tetragonal structure over that of the hypothetical regular octahedral one is given by $-2Ds + Dt$. No obvious trends in this parameter are observed, but complexes of manganese(III), chromium(II), and copper(II) all show rather similar values (Table III). If the structures are assumed to be tetragonally compressed octahedra, unrealistic values for the various parameters are obtained.

Dynamic Effects.—As Höchli showed rather elegantly by epr studies,[49] the barrier to "pseudorotation" about Sc^{2+} in CaF_2 is sufficiently small to allow isotropic spectra to be observed to temperatures near 6°K. Below this temperature anisotropic spectra appear, consistent with static Jahn–Teller splitting of the ground state. Höchli suggests, "conservation of symmetry is the main feature which distinguishes a dynamical Jahn–Teller effect from the static Jahn–Teller effect." As in the dynamical ammonia problem where the symmetry is D_{3h}, the dynamical octahedral problem utilizes the point symmetry O_h. For Mn(III) in the sulfate alum or water or with $Mn^{III}X_6$, $Cr^{II}X_6$, and $Cu^{II}X_6$ complexes generally, the dynamical Jahn–Teller phenomenon must be considered when discussing high-temperature (room temperature may be sufficiently high) physical data. Hathaway, *et al.*,[57,58] have pointed out the relevance of dynamical effect to the epr spectra of some cobalt(II) and copper(II) complexes.

Since the Franck–Condon principle holds providing the splitting of E_g is large, it is possible to describe electronic d–d transitions in terms of the static symmetry of one potential minimum (Figure 4). However, polarization properties of electronic transitions as described by a static symmetry are useless. No polarization can occur if the crystal is cubic. In accord with this, manganese(III) in the "cubic" aluminum alum does not show spectral polarizations. At high manganese(III) concentrations, however, noncubic lines appear in the X-ray powder spectrum.[34]

The electronic spectra of the manganese(III) β-ketoenolates clearly conform to interpretation in terms of a tetragonal distortion. Assuming reasonable force constants for Mn–O vibrations, semiquantitative estimates may be made (Appendix) of the separation between potential surfaces associated with the ^5E ground state (Figure 3). The results are indeed satisfying and suggest that the potential energy barrier in the angular

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[52] D. S. McClure, *J. Chem. Phys.*, **36**, 2757 (1962).

[53] H. Hartman and H. L. Schläfer, *Z. Naturforsch.*, **6a**, 760 (1951).

[54] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 101.

[55] D. Oelkrug, *Angew. Chem. Intern. Ed. Engl.*, **5**, 744 (1966).

[56] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

[57] H. Elliot, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, **5**, 669 (1966).

[58] H. Elliot and B. J. Hathaway, *ibid.*, **5**, 885 (1966). See also M. Sturge, *Solid State Phys.*, **20**, 92 (1968).

TABLE III

TETRAGONAL PARAMETERS OF MANGANESE(III), CHROMIUM(II), AND COPPER(II) COMPLEXES[a]

Complex	Ref	Medium	$^5B_{1g} \rightarrow$ $^5A_{1g}$, cm^{-1}	$^5B_{1g} \rightarrow$ $^5B_{2g}$, cm^{-1}	$^5B_{1g} \rightarrow$ ^5E_g, cm^{-1}	*Ds*, cm^{-1}	*Dq*, cm^{-1}	*Dt*, cm^{-1}	Stabiln, cm^{-1}	Stabiln, kcal/mol
K_2MnF_5	This work	Reflt	12,100	18,750	21,400	2110	1875	735	−3485	−9.96
Na_2MnF_5	55	Reflt	12,500	18,000	21,000	2210	1800	730	−3690	−10.55
$(NH_4)_2MnF_5$	13	Single crystal	12,750	18,200	21,000	2220	1820	775	−3665	−10.47
MnF_3	9	Reflt	12,000	19,000	23,000[b]	2285	1900	570	−4000	−11.43
K_3MnF_6	55	Reflt	9,000	17,400	19,600	1600	1740	520	−2680	−7.66
K_3MnF_6	12	Reflt	9,000	17,500[b]	21,000[b]	1785	1750	370	−3200	−9.15
$[(C_2H_5)_4N]_2MnCl_5$	This work	Reflt (77°K)	11,300	16,200	23,530	2660	1620	135	−5185	−14.82
$[(bipy)H_2]MnCl_5$	11	Reflt	11,500	17,240	24,400	2665	1724	170	−5160	−14.75
$[(phen)H_2]MnCl_5$	11	Reflt	12,500	17,400	~25,000	2870	1740	205	−5535	−15.82
$[(1,2\text{-pn})_3Co][MnCl_6]$	This work	Reflt	8,333	17,540	22,400	1885	1754	160	−3610	−10.32
$Mn(acac)_3$	10	Cyclohexane	9,520	17,900	21,500	1875	1790	405	−3345	−9.56
$Mn(F_6acac)_3$	10	Cyclohexane	11,600	18,700	23,800?	2385	1870	410	−4360	−12.46
$Mn(F_6acac)_3$	...	...	11,600	18,700	21,100[b]	2000	1870	720	−3280	−9.36
$Mn(\gamma\text{-CNacac})_3$	10	Benzene	8,060	17,500	21,300	1695	1750	255	−3135	−8.96
$Mn(benzoylacac)_3$	14	CCl_4	8,600	17,900	22,500	1885	1790	210	−3560	−10.17
$Mn(DIBM)_3$	10	Cyclohexane	8,850	17,900	21,300	1750	1790	370	−3130	−8.95
$Mn(DPM)_3$	10, 5	Cyclohexane	8,700	17,900	21,300	1730	1790	355	−3105	−8.87
$Mn(tp)_3$	This work	Chloroform	9,090	15,875	17,545	1535	1587	590	−2480	−7.09
$K_3Mn(Ox)_3$	This work	Reflt	9,100	19,050	20,400	1495	1905	625	−2365	−6.76
$K_3Mn(Mal)_3$	14	Malonate buffer	9,600	19,600	20,400	1485	1960	730	−2240	−6.40
$CrCl_2 \cdot 4H_2O$	6	Reflt (77°K)	10,000	16,000	18,900	1845	1600	525	−3165	−9.05
$Cu(acac)_2$	56	*p*-Dioxane	13,500	15,100	17,500	2270	1510	885	−3655	−10.45
$Cu(acac)_2$	56	1-Pentanol	13,000	15,200	17,100	2130	1520	895	−3365	−9.62
$Cu(acac)_2$	56	Pyridine	12,100	14,800	15,900	1885	1480	910	−2860	−8.17
$Cu(acac)_2$	56	Piperidine	11,300	14,800	15,100	1655	1480	935	−2375	−6.78
$Cu(\gamma\text{-}C_2H_6acac)_2$	56	Acetone	14,300	15,600	18,700	2485	1560	870	−4100	−11.72
$Cu(\gamma\text{-}C_2H_5acac)_2$	56	*p*-Dioxane	14,100	15,450	18,250	2415	1545	890	−3490	−11.26
$Cu(\gamma\text{-}C_2H_5acac)_2$	56	Methanol	13,150	15,000	17,250	2200	1500	870	−3530	−10.09
$Cu(\gamma\text{-}C_2H_5acac)_2$	56	Pyridine	12,500	14,650	16,600	2065	1465	850	−3280	−9.37

[a] See ref 34 for tetragonal parameters of other manganese(III), chromium(II), and copper(II) complexes. [b] Band estimated.

potential expression $V(\phi) = (B/2)[1 - \cos(3\phi)]$ (where ϕ is the angular component of a polar-coordinate representation of the e_g mode and B is the barrier potential) is sufficiently small to allow pseudorotation at room temperature. Alternatively, as suggested previously,[59] a small static distortion may exist which remains undetected through a molecular disordering in the crystal. However, the isotropic temperature factors (Table I) do not allow the presence of distortions comparable in magnitude with $3d^4$ systems known by X-ray technique to be distorted.

The solution optical spectra of the manganese(III) β-ketoenolates also are acceptably interpeted by recognizing that "pseudorotation" can occur. However, when hydrogen-bonding solvents such as $CHCl_3$, CH_3OH, or acetic acid interact with the complex, the six metal–oxygen bonds are no longer equivalent. In such cases it becomes reasonable to assume the presence of a "static" tetragonal splitting of the ^5E_g ground state, a splitting related to the hydrogen-bonding strength of the solvent which leads to the nonequivalence of metal–oxygen bonds,[60] or a major shift in the relative energies of the potential energy minima.[61]

An interesting argument for the assignment of the low-energy band in manganese(III) halides to $^5B_{1g} \rightarrow {}^5A_{1g}$ can be formulated. The reflectance spectra of K_3MnF_6[12] and $MnCl_6^{3-}$ [34] show the presence of a low-energy band at ~9000 and ~8300 cm^{-1}, respectively. The single-crystal spectrum of $(NH_4)_2MnF_5$ shows a similar low-energy band at 12,750 cm^{-1} (~12,000 cm^{-1} in reflectance) which can be assigned to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition on the basis of the polarization of the bands.[13] All other halide complexes for which there are sufficient data also show a low-energy band. These include Na_2MnF_5 (12,500 cm^{-1}),[55] K_2MnCl_5 (~12,000 cm^{-1}),[34] K_2MnF_5 (12,100 cm^{-1}),[34] $[(C_2H_5)_4N]_2MnCl_5$ (~11,300 cm^{-1}),[11,34] N,N′-dihydrobipyridinium pentachloromanganese(III), $[(bipy)H_2][MnCl_5]$ (~11,500 cm^{-1}),[11] N,N′-dihydrophenanthrolinium pentachloromanganese(III), $[(phen)H_2][MnCl_5]$ (~12,500 cm^{-1}),[11] and MnF_3 (12,000 cm^{-1}).[9] In the pentahalide species, generally, the atom probably attains six-coordination by sharing of axial ligands as in $(NH_4)_2MnF_5$.[13,62] In MnF_3 all fluorines are shared to complete the distorted octahedron about each manganese(III) ion.[63]

The shift in position of the low-energy band in going from the hexahalides to the pentahalides and MnF_3 is best understood on the basis of the Jahn–Teller effect. In the hexahalides none of the ligand ions is shared; hence dynamic motion (minima exchange) of the tetragonally displaced ligands about the manganese may occur. In the pentahalides and in MnF_3, with ligand ions shared between manganese(III) ions, the minima exchange should be decreased as stabilization of the molecule in one tetragonally distorted form occurs. A shift in the low-energy ($^5B_{1g} \rightarrow {}^5A_{1g}$) band to higher wave numbers consistent with a statically distorted structure follows. A similar argument[5] was presented for aqueous MnF^{2+}.

A convenient way to describe the spectra of manganese(III), chromium(II), and copper(II) complexes is

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(59) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 401 (1966).

(60) We hope to test this description by designing experiments which effectively influence the form of the potential energy surfaces. For example, the low-energy transition should be much more sensitive to changes in pressure than the $^5E_g \rightarrow {}^5T_{2g}$ transition because the nuclear positions at equilibria are much more different for each component of ^5E_g than they are for ^5E_g and T_{2g} separately (Figure 3).

(61) L. Lohr, *Inorg. Chem.*, **6**, 1890 (1967).

(62) D. R. Sears, Ph.D. Thesis, Cornell University, 1958; *Dissertation Abstr.*, **19**, 1225 (1958).

(63) M. A. Hepworth and K. H. Jack, *Acta Cryst.*, **10**, 345 (1957).

found by constructing tetragonality diagrams assuming static distortions.[34] The energy of the B_{1g} ground state is set equal to zero and the energies of the A_{1g}, B_{2g}, and E_g states are calculated in units of Dq and plotted against the ratio Ds/Dq. The energy of B_{2g} will always be $10Dq$ but the energies of A_{1g} and E_g are calculated for various Ds/Dt ratios. Similar calculations using the experimental Ds/Dq and Ds/Dt ratios are performed for each complex. Alternatively,[34] the energy levels for a complex may be obtained from the ratios of the $B_{1g} \rightarrow A_{1g}$ and the $B_{1g} \rightarrow E_g$ band energies to the $B_{1g} \rightarrow B_{2g}$ $(10Dq)$ transition.

Tetragonality diagrams for manganese(III) complexes with bidentate ligands (Figure 5) and for some copper(II) complexes in various solvents (Figure 6) illustrate the general features of this type of diagram. Complexes with similar ligands (Figure 5) correlate well. The *decrease* in apparent tetragonal distortion that occurs when solvents of *increasing* ligand strength coordinate to planar copper(II) complexes is graphically demonstrated (Figure 6).

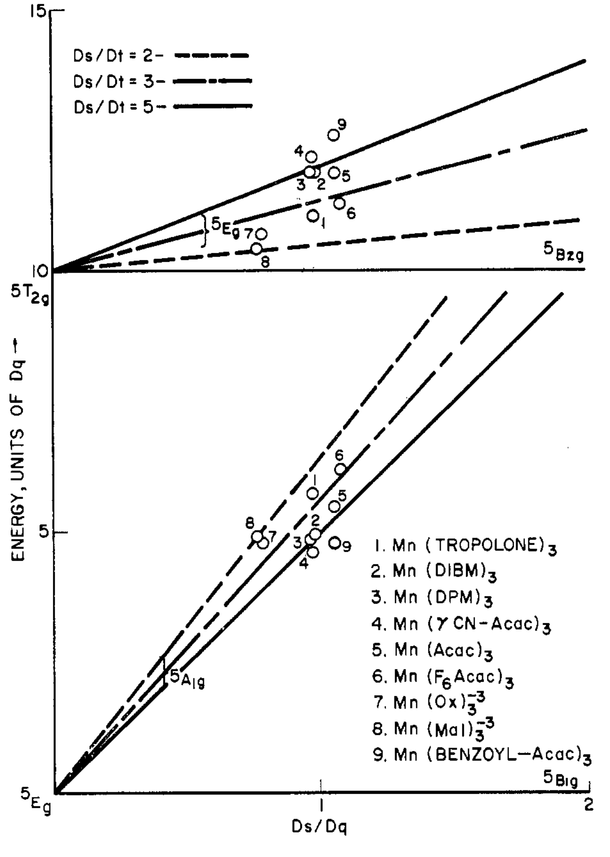

Figure 5.—Energy level diagram for mangnese(III) chelate complexes.

Conclusions

The electronic spectra of manganese(III) complexes (as well as those of copper(II) and chromium(II)) in the visible and near-infrared regions are best described in terms of E_g ground states, split significantly by static or dynamic distortions. The magnitude of the tetragonal splitting appears to be 5000–20,000 cm^{-1}, the upper limit occurring with complexes better described as planar. With aqueous complexes of these metal ions, all of the d–d transitions appear in the same spectral region. The transitions between components of the E_g state appear to be at energies comparable with $10Dq$ implying the existence of sizable distortions from octahedral symmetries. Yet the aqueous complexes are probably dynamically isotropic by pseudorotation. In the case of manganese(III) acetylacetonate, there appears to be no acceptable way to interpret the spectra in view of the X-ray structure unless pseudorotation is assumed, even in the crystalline solid.

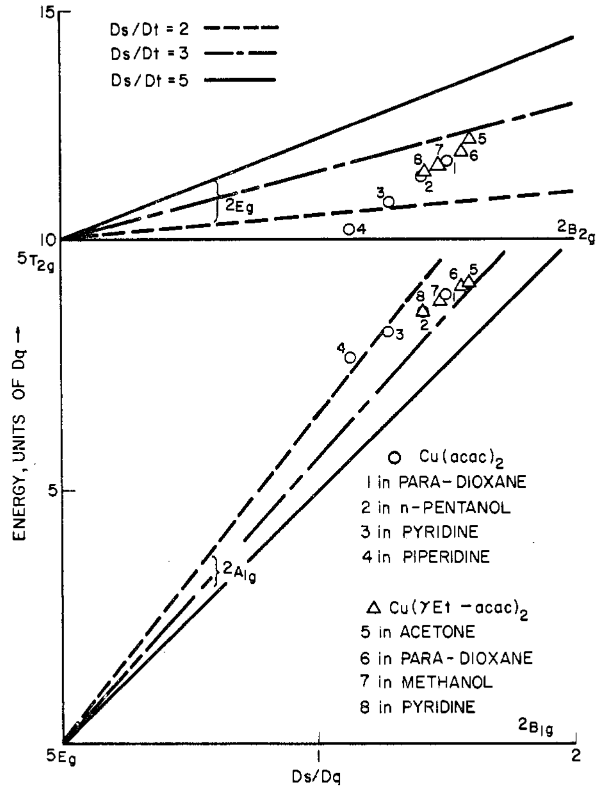

Figure 6.—Energy level diagram for copper(II) β-diketone complexes in various solvents.

Acknowledgments.—This work was supported by the National Science Foundation, GP-7889. A grant from Ferro Corp. through the Olin Center for the Study of Materials has contributed to some of the work described. Dr. I. D. Chawla prepared some of the complexes.

Appendix

As indicated in the main text, for a molecule with an E_g ground state the regular octahedral configuration may not represent a minimum of energy with respect to nuclear displacements. This leads to a consideration of the static aspects of the Jahn–Teller theorem, which has been treated in a number of papers.[4,61,64] The purpose of this Appendix is to obtain an order of magnitude of the energy for the transition between the two potential energy sheets that arise from the ground state owing to nuclear displacements in the

(64) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **3**, 304 (1958), and references therein.

symmetry of the vibrational modes. It can be seen that the a_{1g} and e_g displacements will contribute linearly to the potential energy changes, other vibrations only being effective in second order.[4] Using then the result and nomenclature of the pure crystal field calculations of Liehr and Ballhausen,[64] for the approximation that there is no barrier to pseudorotation, we have for the potential energy surface

$$E = \frac{1}{2}k_1q_1^2 + \frac{1}{\sqrt{6}}B_4q_1 + \frac{1}{2}k_2q_2^2 + \frac{1}{2}q_2\alpha \qquad (1)$$

$$\alpha = (4\sqrt{3})\left[\frac{1}{7}B_2 + \frac{5}{84}B_4\right]$$

where q_1 and q_2 are normal coordinates associated with the a_{1g} and e_g vibrational modes, k_1 and k_2 are force constants associated with the a_{1g} and e_g modes, respectively, and B_2 and B_4 are radial integrals.

While interactions involving the totally symmetric vibration can lead to a general increase or decrease in the metal–ligand bond lengths, they will not contribute to the raising of the degeneracy of the electronic E_g level. Thus the first two terms in the above expression need not be considered at this point.

Hence at this level of simplification, on minimizing with respect to the energy, $q_2 = 7\alpha/2k_2$ and $\Delta E = \alpha^2/2k_2$, where ΔE is the energy of a transition from the lower to the upper potential energy sheets. (Note: this energy does not include the a_{1g} energy contribution.) It thus remains to find suitable values for k_2 and α.

Nakamoto has assigned what is predominantly an M–O stretch in the infrared spectra of metal acetylacetonate complexes to a band occurring between 400 and 500 cm^{-1}.[65] For Cu(acac)$_2$, ν_{M-O} is ~455 cm^{-1},[65] which is very similar to that found for Mn(acac)$_3$,[66] so the k_{M-O} calculated for the former of ~2.2 × 10^5 dyn/cm is probably a reasonable value for the manganese complexes. The ν_{M-O} for the acetylacetonate complexes is rather similar to that found for $\nu_{a_{1g}}$ (394 cm^{-1}) in Raman studies on Zn(H$_2$O)$_6^{2+}$,[65] and for which ν_{e_g} was found at 200 cm^{-1}. Thus one might estimate a value for an e_g mode of $k_{M-O} \sim 0.65 \times 10^5$ dyn/cm in manganese(III) acetylacetonate.

Ballhausen and Ancmon[67] have given tabulated values of ligand field integrals. Assuming an effective nuclear charge of ~5.6 with an effective metal–oxygen bond length of 2.10 Å, α is calculated to be 0.455 × 10^{-3} dyn. This effective bond length is significantly greater than the mean observed bond length (1.894 Å) and is an essentially empirical adjustment to give a reasonable transition energy. It might, however, be viewed as allowing for electron delocalization. Using these values of α and k_2, q_2 = 0.36 Å and ΔE = 8500 cm^{-1}. The use of shorter metal–ligand bond lengths raises the value of ΔE. Thus this model would suggest that transitions of 8000 cm^{-1} or more are reasonable. The assumption of zero barrier is acceptable within the requirement that there be free rotation in the coordinate ϕ,[61] the zero-point energy of th e_g vibration being ~100 cm^{-1}. The nuclear motion is confined to the lower potential energy surface, the coordinate q_2 remaining static. The value of this latter parameter at minimum energy, ~0.35 Å, would require a nuclear motion of ~0.2 Å, with which the observed temperature factors (Table I) would be consistent.

The general form of the equation given above is independent of the bonding scheme used. While the crystal field approximation has not been very successful in the more sensitive calculation of the barrier potential,[61,68] it may be that it yields a correct order of magnitude for the transition energy.[64] It is perhaps worth noting that the stabilizations calculated in Table III are based on radial integrals that are of the same form as those used in the calculation above. The former stabilizations are then of similar value to those found from eq 1 in the absence of the terms in the harmonic potential.

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