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Dynamic Stereochemistry of Tris-Chelate Complexes. II.[1] Tris(dithiocarbamato) Complexes of Manganese(III), Vanadium(III), Chromium(III), Gallium(III), and Indium(III)

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The temperature-dependent pmr spectra of tris(N,N-disubstituted dithiocarbamato)metal(III) complexes, $M(dtc)_3$, where M = vanadium, manganese, chromium, gallium, and indium have been examined in noncoordinating solvents. All of the complexes are stereochemically nonrigid except for the chromium complex and kinetic parameters were determined for intramolecular metal-centered rearrangement by pmr line-broadening techniques. This rearrangement results in optical inversion and the trigonal twist mechanism has been assigned as the primary rearrangement pathway. The chromium complex is rigid up to 84° in $CDCl_3$. The overall metal ion dependence on the rate of optical inversion is In, Ga, V > Mn > Cr. Trends in the rate and mechanism of rearrangement are considered in light of solid-state structural parameters and electronic configuration

Introduction

Tris(dithiocarbamato) complexes of iron, cobalt, and ruthenium have recently been shown to be stereochemically nonrigid on the pmr time scale in noncoordinating solvents.[1-5] These complexes exhibit two distinct pmr observable kinetic processes which result in cis-trans isomerization and optical inversion, respectively. The former has been assigned to S_2C–N bond rotation[5] and the latter to intramolecular metal-centered rearrangement. The application of nmr spectroscopy to elucidating rates and mechanisms of isomerization reactions has recently been thoroughly reviewed.[6-9] Several papers have also appeared in which nmr has been successfully used to determine the mechanisms for metal-centered rearrangement reactions of tris(chelate)metal complexes.[1,3,4,10,11] The tris(dithiocarbamato) complexes, $M(dtc)_3$, of iron(III), iron(IV), and ruthenium(III) have yielded the simplest analyses because the paramagnetism, which causes large isotropic pmr shifts, permitted resolution of magnetically similar environments.[1-5,9] The pmr averaging patterns for these complexes are consistent only with one intramolecular metal-centered rearrangement permutation. The trigonal twist mechanism is considered the most reasonable pathway which gives this permutation. $M(dtc)_3$ complexes of Co(III) have not yielded mechanistic information but undergo optical inversion with a $\Delta H^{\ddagger}$ of 10 and 15 kcal/mol greater than for Fe(III) and Fe(IV) complexes, respectively.[1,4] The relative kinetic parameters for these complexes have been rationalized in terms of a ligand field stabilization energy (LFSE) argument.[1]

In the present work we report the details of a pmr study on the kinetics and mechanism of metal-centered rearrangement for $M(dtc)_3$ complexes where M = Mn(III), V(III), Cr(III), Ga(III), and In(III). This investigation was undertaken in order to extend the previous work[1] to other metals and to assess the importance of LFSE in affecting the rate of optical inversion. Kinetic parameters and some mechanistic information have been determined by pmr line-shape analyses on these complexes.

Experimental Section

Preparation of Compounds. All of the complexes used in this study with the exception of the V(III) complexes were synthesized according to literature preparations or slightly modified literature preparations (*vide infra*) and were characterized by elemental analysis, pmr and infrared spectroscopy, and magnetic susceptibility (Table I). (a) **Mn(RR′dtc)$_3$** where RR′ = BzBz and MePh[12] were prepared according to Delepine[13] but with absolute ethanol as solvent. Recrystallization was done under a nitrogen atmosphere which prevented air decomposition.[14] (b) **V(RR′dtc)$_3$** where RR′ = BzBz and MePh have not been previously reported and were prepared by mixing degassed ethanolic solutions of anhydrous vanadium trichloride and the sodium or lithium salt of the appropriate dtc ligand. A brown product precipitated which was recrystallized from CH_2Cl_2–heptane. All operations were performed under a nitrogen atmosphere. Principal infrared bands for RR′ = BzBz (KBr disk): 1492 (s), 1471 (s), 1448 (s), 1428 (m), 1414 (m), 1356 (m), 1204 (s), 1197 (m), 1076 (m), 1027 (m), 996 (m), 729 (m), 682 (s) cm^{-1}. (c) **Cr(EtEtdtc)$_3$** was prepared according to the method of Delepine.[13] (d) **Ga(RR′dtc)$_3$** and **In(RR′dtc)$_3$** where RR′ = BzBz and MePh were prepared according to the method of Delepine[15] but with absolute ethanol as solvent.

Pmr Measurements. All spectra were recorded on a Varian XL-100-15 nmr spectrometer equipped with a variable-temperature probe and deuterium lock. Temperatures were measured by a thermocouple mounted in an nmr tube and are accurate to ±1°. All spectra were recorded using CD_2Cl_2 or $CDCl_3$ solutions *ca.* 0.10 *M* in complex. Chemical shifts were measured relative to the ^2H internal lock frequency and are reported in ppm relative to either $CHDCl_2$ or $CHCl_3$. Samples of Mn and V complexes were prepared under nitrogen in selaed nmr tubes.

Magnetic Measurements. Solid magnetic moments were determined by the Faraday method using $Hg[Co(SCN)_4]$ as calibrant. Diamagnetic corrections were calculated from Pascal's constants.

Kinetic Analysis. A total line-shape analysis, TLSA, was per-

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(12) Abbreviations used throughout: Me = methyl, Et = ethyl, Bz = benzyl, Ph = phenyl, pyr = pyrrolidyl.

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(15) M. Delepine, *Ann. Chim. (Paris)*, 6, 633 (1951).

Table I. Characterization Data for Tris-Dithiocarbamato Complexes

		Elemental analysis							
		Calcd			Found				
Complex	Mp, °C	% C	% H	% N	% C	% H	% N	μ_{eff},[d] BM	Pmr data[a]
V(BzBz(dtc))$_3$	120 dec	62.34	4.85	4.84	61.86	4.88	4.77	2.74	CH$_2$: −7.45
V(MePh(dtc))$_3$	148 dec	48.20	4.02	7.03	47.78	3.94	6.93	2.79	CH$_3$: −8.17
Mn(BzBz(dtc))$_3$	151 dec	62.05	4.83		61.95	5.00		4.93	CH$_2$: −9.44
Mn(MePh(dtc))$_3$	173 dec	47.88	3.99		47.90	3.86		4.99	CH$_3$: −29.18
Ga(BzBz(dtc))$_3$	217–218	61.00	4.74		60.90	4.85		Diamag	CH$_2$: +0.31
Ga(MePh(dtc))$_3$	240–242	46.80	3.90		47.07	3.94		Diamag	CH$_3$: +1.63
In(BzBz(dtc))$_3$	203–204	58.06	4.51		57.64	4.34		Diamag	CH$_2$: +0.19
In(MePh(dtc))$_3$	294–295	43.61	3.63		43.92	3.51		Diamag	CH$_3$: +1.56
Cr(EtEt(dtc))$_3$	135 dec							3.80[c]	CH$_2$:[b] −4.80 −14.30

[a] Pmr shifts in ppm relative to CHDCl$_2$ internal standard, at 31° in CD$_2$Cl$_2$ solution. [b] Relative to CHCl$_3$ internal standard. [c] Reference 19. [d] At 23° in solid state.

Table II. Kinetic Parameters[a] for Intramolecular Metal-Centered Inversion For M(dtc)$_3$ Complexes in CD$_2$Cl$_2$ Solution

Complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol (temp, °C)	Ref
V(BzBz(dtc))$_3$	<8.2[b]		<7.7 (−103)	*e*
V(MePh(dtc))$_3$	<8.2[b]		<7.7 (−98)	*e*
Mn(BzBz(dtc))$_3$	11.0 ± 1.0	1.5 ± 5.0	10.6 ± 0.2 (−35)	*e*
Mn(MePh(dtc))$_3$	9.8 ± 1.0[b]		9.1 ± 0.5 (−50)	*e*
Ga(BzBz(dtc))$_3$	<8.6[b]		<8.1 (−85)	*e*
In(BzBz(dtc))$_3$	<8.6[b]		<8.1 (−85)	*e*
Cr(EtEt(dtc))$_3$	>17.1[b]		>16 (84)[c]	*e*
Fe(BzBz(dtc))$_3$	10.3 ± 1.0	4.1 ± 5.0	9.3 ± 0.2 (−54)	*f*
Fe(MePh(dtc))$_3$	8.7 ± 1.0	1.7 ± 5.0	8.5 ± 0.2 (−80)	*f*
Fe(pyr(dtc))$_3$	7.6 ± 1.7[b]		7.1 ± 0.3 (−103)	*f*
Co(BzBz(dtc))$_3$	25.5 ± 1.0	4.1 ± 5.0	23.6 ± 0.2 (168)[d]	*f*
Rh(BzBz(dtc))$_3$	>27		>25.3 (200)[d]	*f*

[a] See Experimental Section. [b] Values determined from $\Delta G^{\ddagger}$ and assuming $\Delta S^{\ddagger} = 3.0$ eu. [c] CDCl$_3$ solution. [d] NO$_2$C$_6$D$_5$ solution. [e] This work. [f] Reference 1.

formed on Mn(BzBz(dtc))$_3$. Optical inversion results in a two-site exchange between diastereotopic methylene environments (*vide infra*) where no coupling is observed due to paramagnetic relaxation. The exchange-broadened line shapes were computer calculated using the Gutowsky-Holm equation[16] and the best fits were visually selected. Line widths at half-height, $H_{1/2}$, and chemical shift separations, $\Delta\nu$, in the region of exchange broadening were determined by linear interpolation and extrapolation from slow-exchange values of the plots ln $H_{1/2}$ *vs.* $1/T$ and $\Delta\nu$ *vs.* $1/T$, respectively. These plots are shown in Figure 1. The rate constant for optical inversion, k (sec^{-1}), is defined as $1/\tau$, where τ is the preexchange lifetime of a proton in either environment (τ defined here equals 2τ in the Gutowsky-Holm equation[16]). $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by a least-squares fit to the ln (k/T) *vs.* $1/T$ plot.

The two-site exchange between nonequivalent N-Me environments in Mn(MePhdtc)$_3$ (*vide infra*) was computer fit at one temperature near the coalescence point. $\Delta G^{\ddagger}$ at this temperature was calculated using the equation $k = (k_BT/h) \exp(-\Delta G^{\ddagger}/RT)$. $\Delta H^{\ddagger}$ was calculated assuming $\Delta S^{\ddagger} = 3.0$ which is the average value obtained for other M(dtc)$_3$ complexes (Table II). For the V, In, and Ga complexes the slow-exchange limit could not be completely reached and $\Delta\nu$ values were estimated in calculating upper limits to $\Delta G^{\ddagger}$.

Results and Discussion

Pmr, Magnetic, and Stereochemical Properties. (a) Mn(RR'dtc)$_3$ Complexes. The manganese(III) complexes crystallize as air-sensitive burgundy needles. The complexes are high-spin d^4 with magnetic moments between 4.9 and 5.0 BM (Table I). The variable-temperature pmr spectrum shows isotopic shifts which have linear $1/T$ behavior in the temperature interval of *ca.* −80 to +31°. These results are consistent with other Mn(dtc)$_3$ complexes[17-19] and indicate a ^5E_g ground term (in O_h) with no population of the excited low-spin $^3T_{2g}$ term.[19] The solid-state structure of Mn(EtEt(dtc))$_3$ has been determined[20] and reveals the usual trigonal distortion from octahedral symmetry but with a significant tetragonal distortion superimposed which presumably results from the Jahn-Teller effect.[20] This structure differs from those of most other M(dtc)$_3$ complexes which possess only the trigonal distortion and have approximate D_3 symmetry.[21]

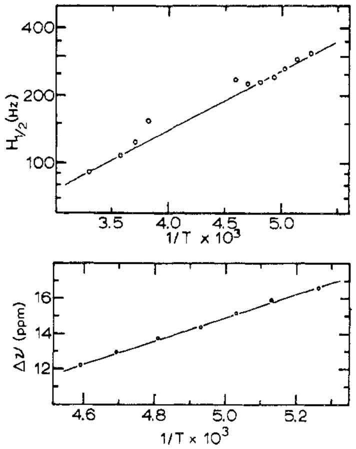

Figure 1. ln $H_{1/2}$ *vs.* $1/T$ and $\Delta\nu$ *vs.* $1/T$ plots for the N-CH$_2$ resonances of Mn(BzBz(dtc))$_3$.

Geometrical (cis-trans) and optical isomerism is possible in these compounds. The −78° pmr spectrum of Mn(MePhdtc)$_3$ is shown in Figure 2 and reveals four N-CH$_3$ resonances which are assigned to the cis (C) and trans (T$_1$,

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(17) R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, W. C. Tennant, and A. H. White, *J. Chem. Phys.*, **52**, 3105 (1970).

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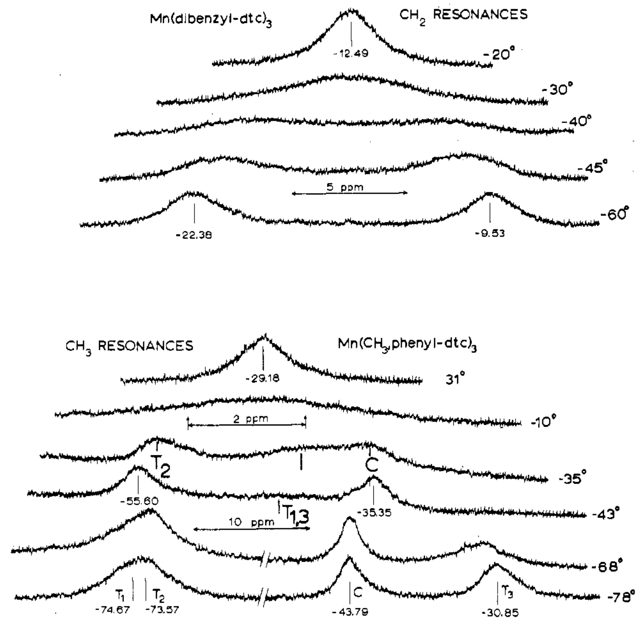

Figure 2. Pmr spectra at various temperatures for the N-CH$_2$ and N-CH$_3$ resonances of Mn(BzBz(dtc))$_3$ and Mn(MePh(dtc))$_3$, respectively, recorded in CD$_2$Cl$_2$ solution at 100 MHz. Chemical shifts are relative to CHDCl$_2$ internal standard.

T_2, T_3) isomers. Assignment of the cis isomer was made by peak integration which gave a cis:trans ratio of *ca.* 1:3.3 at −68°. The resonances T_1 and T_2 are overlapped and chemical shifts are approximate. Also shown in Figure 2 is the −60° spectrum of the N-CH$_2$ resonances in Mn(BzBz(dtc))$_3$. The N-CH$_a$H$_b$ proton environments a and b are diastereotopic[1,22] and are nonequivalent in the limit of slow metal-centered optical inversion. These spectra demonstrate that cis-trans and optical isomerization are slow on the pmr time scale below *ca.* −60° for these Mn(dtc)$_3$ complexes. It is assumed that these two compounds isomerize by the same mechanism and at similar rates.[23,24] The pmr spectra at various temperatures for these two complexes are also shown in Figure 2. Two distinct kinetic processes occur for Mn(MePh(dtc))$_3$, and are indicated by the coalescence of T_1 and T_3 (low-temperature process, coalescence at *ca.* −43°) and the simultaneous coalescence of the three remaining resonances, C, T_2, and T_{13} (high-temperature process, coalescence at *ca.* −10°). The two processes are kinetically different and result in the environmental averaging of two trans resonances and in geometrical isomerization, respectively. Mn(BzBz(dtc))$_3$ reveals only one kinetic process which results in coalescence of the diastereotopic environments. This averaging corresponds to the low-temperature process of Mn(MePh(dtc))$_3$ and demonstrates that metal-centered optical inversion is occurring.

(b) V(RR′dtc)$_3$ Complexes. M(dtc)$_3$ complexes of vanadium(III) have not previously been reported. The compounds with RR′ = MePh and BzBz are isolated under nitrogen as brown crystals which slowly turn blue on exposure to air. The magnetic moments (Table I) are characteristic of two unpaired electrons as expected for a d^2 configuration. Variable-temperature pmr data for V(BzBz(dtc))$_3$ exhibit linear $1/T$ dependence for the isotropic shifts. The ir spectrum between 900 and 1100 cm^{-1} of V(BzBz(dtc))$_3$ recorded in CS$_2$ solution is nearly superimposable on spectra of the analogous cobalt(III) and rhodium(III) complexes which have tris(bidentate chelate) coordination. The ir spectra for the vanadium complexes do not contain the extra peak near 1000 cm^{-1} which has been found for monodentate dtc complexes.[25] The V(dtc)$_3$ complexes are therefore classified as tris(bidentate chelate) complexes.

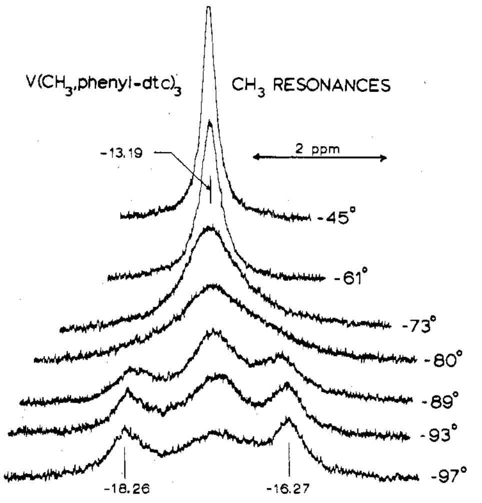

Figure 3. Pmr spectra at various temperatures for the N-CH$_3$ resonances of V(MePh(dtc))$_3$ recorded in CD$_2$Cl$_2$ solution at 100 MHz. Chemical shifts are relative to CHDCl$_2$ internal standard.

The pmr spectrum at various temperatures of the N-CH$_3$ resonances for V(MePh(dtc))$_3$ is shown in Figure 3 and reveals two kinetic processes. The high-temperature process causes line broadening between *ca.* −89 and −61° and is characterized by the coalescence of three resonances into one. This process results in cis-trans isomerization. The low-temperature process cannot be frozen out but is clearly beginning by −97°. The center resonance is broadening while the two outside peaks remain relatively narrow. Presumably the central resonance will split into two resonances in an analogous manner to T_1 and T_3 of Mn(MePh(dtc))$_3$. The cis isomer cannot be assigned in this case but clearly it is the resonance at either −18.26 or −16.27 ppm. The pmr spectrum at various temperatures of V(BzBz(dtc))$_3$ reveals a similar low-temperature process. The methylene resonance rapidly broadens at *ca.* −100° but again the slow-exchange limit could not be attained in CD$_2$Cl$_2$ solution. The coalescence patterns for the low-temperature process in these complexes are the same as observed with the analogous manganese(III) complexes (*vide supra*). This process, which is assumed to be the same for V(BzBz(dtc))$_3$ and V(MePh(dtc))$_3$, results in environmental averaging of two trans methyl environments without cis-trans isomerization but with metal-centered optical inversion.

(c) Cr(EtEtdtc)$_3$. The magnetic properties of this complex have been previously studied.[19] This compound has a $^4A_{2g}$ ground term (O_h symmetry) and its magnetic moment is essentially independent of temperature.[19] The ir spectrum indicates a tris(bidentate chelate) coordination.[26] The 30° pmr spectrum contains two broad methylene resonances (Table I) which indicates that optical inversion is slow on the pmr time scale. The resonances exhibit linear $1/T$ temperature dependence and no exchange broadening is observed up

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(22) K. Mislow and M. Rabin, *Top. Stereochem.*, 1, 1 (1965).

(23) This assumption has been proven valid for a number of other tris-chelate complexes, for example, Fe(dtc)$_3$,[1] Fe(dtc)$_3^+$,[1] Ru(dtc)$_3$,[24] and M(α-(R)-tropolonate)$_3$ where M = Co, Al, or Ga.[10]

(24) D. J. Duffy and L. H. Pignolet, in preparation.

(25) F. Bonati and R. Ugo, *J. Organometal. Chem.*, 10, 257 (1967); D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969).

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to 84°. Above this temperature the compound decomposes.

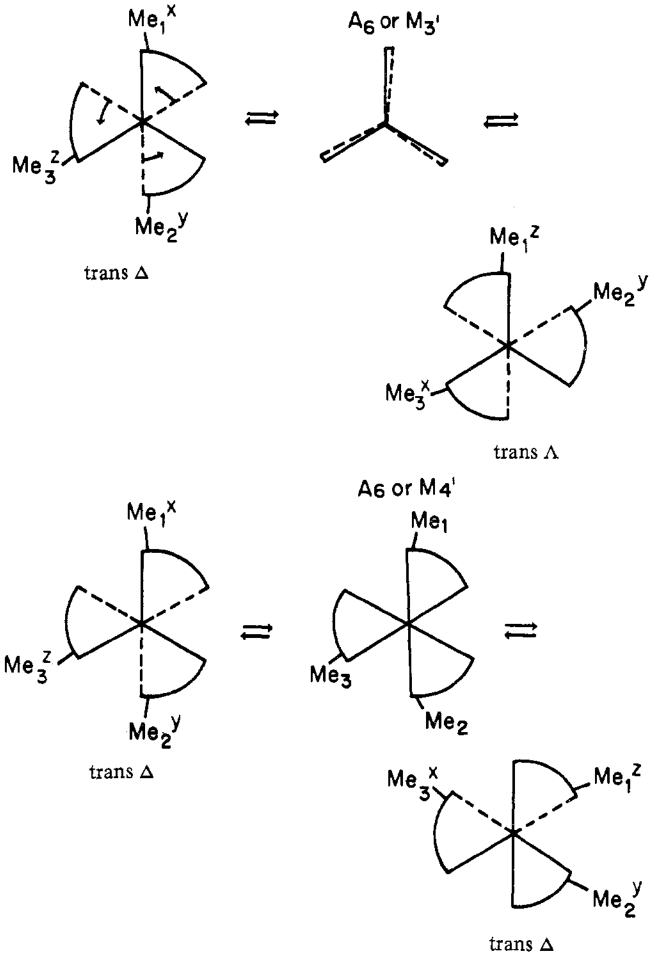
(d) $Ga(RR'dtc)_3$ and $In(RR'dtc)_3$ Complexes. Ir spectra indicate tris(bidentate chelate) coordination and the compounds are diamagnetic. The dynamic pmr spectra of the complexes where RR' = MePh and BzBz behave similarly for gallium and indium. At 30° only one $N-CH_3$ resonance is observed for the MePh complexes. As the temperature is lowered to *ca.* −50° the peak broadens and an asymmetric shoulder appears which remains down to *ca.* −85°. For the BzBz complexes only one methylene resonance is observed down to −100°. The −50° broadening and splitting in the spectra of the MePh complexes must result from slow cis-trans isomerization because optical inversion is fast on the pmr time scale. If optical inversion were slow, the benzyl methylene protons of the BzBz complexes would show an AB spectrum as has been observed for $M(BzBz(dtc))_3$ complexes of cobalt and rhodium.[1] The size of δ_{AB} in these complexes is typically 0.16 ppm at 31° and becomes larger as the temperature is lowered.[1]

Ligand Exchange. The intramolecular nature of the dynamic processes described in the previous section is proved for the vanadium, manganese, gallium, and indium complexes by ligand-exchange experiments. Equimolar amounts of $M(MePh(dtc))_3$ and $M(BzBz(dtc))_3$ were dissolved in degassed $CDCl_3$. With M = V, Ga, and In, mixed complexes formed at once and the resonances due to these complexes were not averaged with those of the pure complexes at temperatures where the previously described dynamic processes are fast. With M = Mn, mixed complexes did not form after 1 day at room temperature. The resonance positions of the pure complexes were also not altered. In all previous cases where mixed complexes formed with dtc ligands, they were easily observed by pmr. In this case it must be assumed that ligand exchange is exceedingly slow. The dynamic processes in these complexes are therefore intramolecular in nature.

Experiments were also performed by mixing the analogous thiuram disulfide with both $Mn(dtc)_3$ and $V(dtc)_3$. The pmr spectra consisted of separate resonances for each species. The thiuram disulfide had no effect on the dynamic processes.

Mechanism of the Metal-Centered Rearrangement. The high-temperature kinetic process described for the manganese and vanadium complexes results in geometrical isomerization. This same process is observed with the gallium and indium complexes. This isomerization presumably results from S_2C-N bond rotation[5] and will be the subject of a future publication.[27] The low-temperature kinetic process for the manganese and vanadium complexes results in the environmental averaging of two trans methyl environments for $M(MePh(dtc))_3$ and in the coalescence of the diastereotopic methylene environments for $M(BzBz(dtc))_3$. This rearrangement reaction therefore results in metal-centered optical inversion without cis-trans isomerization. This conclusion assumes that the MePh and BzBz analogs isomerize by the same mechanism at similar rates (*vide supra*).[23]

Detailed descriptions of the possible physically reasonable intramolecular metal-centered rearrangement mechanisms for tris-chelate complexes have been reported.[7-9,28-30] Permutational analyses on tris-chelate complexes have also been recently carried out.[31-35] The results of these analyses show that only two permutations give the site interchanges found for the methyl environments in $M(MePh(dtc))_3$ where M = Mn or V. The compatible rearrangement modes are A_6 according to Eaton[34,35] (or the identical $M_{3'}$ from Musher[33]) and A_2 (or $M_{4'}$). These modes are depicted in **1** for the trans Δ isomer along with their most reasonable physical pathways. Numbers refer to methyl groups and letters refer to environments. The permutation of the Me group environments is identical for both rearrangement modes, *i.e.*, (xz); however, only mode A_6 (or $M_{3'}$) results in optical inversion. These two pathways are best envisioned as the well-known nonbond rupture trigonal twist (A_6 or $M_{3'}$) with a trigonal-prismatic transition state and a rearrangement reaction which is best described as a simultaneous rotation of the three chelate rings 180° about their C_2 axes *via* an approximate hexagonal-planar transition state (A_2 or $M_{4'}$). The latter transition state has been suggested by Stiefel and Brown[36] for $M(dtc)_3$ complexes because of their highly compressed nature.



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The results from $M(BzBz(dtc))_3$ complexes of Mn and V

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[27] B. L. Edgar, D. J. Duffy, L. Que, Jr., and L. H. Pignolet, in preparation.

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demonstrate that this rearrangement reaction occurs with optical inversion thereby eliminating mode A_2 (or $M_{4'}$). Rearrangement mode A_6 (or $M_{3'}$) is therefore proved with a high degree of certainty and the trigonal twist mechanism is the most reasonable mechanism which gives this permutation. This proof depends on results from two similar complexes so $Mn(MeBz(dtc))_3$ was also examined. This complex can in principle provide both the (xz) Me averaging and the CH_2 diastereotopic probes. Unfortunately the broadness of the resonances prevented satisfactory resolution so an analysis was not attempted.

Dynamic pmr results for $Ga(MePh(dtc))_3$ and $In(MePh(dtc))_3$ show that geometric isomerization is slow below *ca.* −50°. The number of Me resonances cannot be determined because these diamagnetic complexes do not give well-resolved spectra. No site interchanges can be elucidated. The $M(BzBz(dtc))_3$ complexes demonstrate that optical inversion is fast above −95°. These results combined yield some mechanistic information. The metal-centered process which is occurring faster than the pmr time scale causes optical inversion but not geometric isomerization. Only two rearrangement modes are consistent with this observation: A_5 and A_6.[35] Rearrangement mode A_5 corresponds to a physical mechanism which is similar to A_2 (*vide supra*) except that the rotation of the ligands about the C_2 axes is continued only to positions approximately perpendicular to the original ones (in mode A_2, the rotations are continued the full 180° to yield the same chirality). Mode A_6 is the trigonal twist. Experimentally a choice cannot be made between these two mechanisms. However, the trigonal twist pathway is considered the most likely one because it has been found for other $M(dtc)_3$ complexes where M = Fe(III),[1] Fe(IV),[1,3] and Ru(III).[4]

It should be pointed out that rearrangement mechanisms can never be proved by the nmr experiment. Only the site-interchange pattern and hence the rearrangement mode can be determined. In the cases at hand the trigonal twist mechanism is demonstrated in the sense that it is the most reasonable motion which yields the observed mode.

$Cr(EtEt(dtc))_3$ is stereochemically rigid up to +84°. Above this temperature the complex decomposes. The two methylene enrivonments are diastereotopic and hence optical inversion is slow. No mechanistic information can be inferred.

Recently, Golding, *et al.*,[37] reported that certain $M((i\text{-}Pr)_2\text{-}dtc)_n$ complexes where $n = 2$ or 3 show a splitting of the isopropyl methyl group at low temperatures. They interpreted this in terms of hindered rotation about the $S_2CN(\text{-}CH(CH_3)_2)_2$ bonds. Steric hindrance leading to slow exchange was only observed for large bulky N substituents like isopropyl ($E_a \approx 5$ kcal/mol). They did not find such a splitting for benzyl or ethyl substituents. Smaller N substituents such as RR' = BzBz and MePh do not show pmr slow rotations about the $S_2CN\text{-}C$ bond at temperatures as low as −100°.[1] In $Co(BzBz(dtc))_3$, the AB pattern is observed at −100° with no sign of further kinetic broadening.[1] Therefore, the pmr spectra of complexes in this study are not affected by this hindered rotation.

Kinetics of the Rearrangement. A TLSA was performed on $Mn(BzBz(dtc))_3$ (see Experimental Section). The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are reported in Table II. $\Delta S^\ddagger$ is near zero which is consistent with the trigonal twist mechanism for which zero or slightly negative values have been found.[1,8,11,34,38] Bond-rupture mechanisms are characterized by positive $\Delta S^\ddagger$ values.[39,40] $\Delta G^\ddagger(-50°)$ was determined for $Mn(MePh(dtc))_3$ near the coalescence point by a computer fit of the entire exchange-broadened spectrum. Limits to $\Delta G^\ddagger$ were estimated for the other complexes. In the cases of the fast complexes (V, Ga, In) reasonable chemical shift separations between exchanging environments were estimated. For these complexes, $\Delta S^\ddagger$ equal to 3 eu was assumed[41] and values of $\Delta H^\ddagger$ were calculated. All of the kinetic results for $M(dtc)_3$ complexes are presented in Table II.

Most of the complexes listed in Table II have been shown to undergo optical inversion by the trigonal twist mechanism. Only for Co and Cr is there no real mechanistic information. The following order for the rate of optical inversion for $M(dtc)_3$ complexes is In, Ga V > Mn > Fe > Ru > Co > Rh with Cr at least <Ru. The iron(III) complexes have a further dependence on the position of the $S = {}^1/_2 \rightleftarrows S = {}^5/_2$ spin-state equilibrium.[1] This explains the rather large spread in $\Delta H^\ddagger$ values.

Relation of Electronic and Molecular Structures to Kinetic Parameters. Recently there have been several attempts to rationalize kinetic parameters for metal-centered rearrangement using solid-state structural results.[1,10,11,29,34] Complete X-ray structures have been reported for several $M(dtc)_3$ complexes where M = Co,[42] Fe,[21,43] and Mn.[20] The Co and Fe complexes have similar structures which are characterized by approximate D_3 symmetry. These complexes are distorted toward trigonal-prismatic geometry in that the twist angle and chelate pitch angle have values intermediate between trigonal-antiprismatic (TAP) and trigonal-prismatic (TIP) geometries.[21,43,44] The Mn complex possesses a similar trigonally twisted (from TAP) geometry but with a significant tetragonal distortion superimposed.[20] Structural arguments alone cannot explain the difference in rate of optical inversion for the Co and Fe complexes. The rate constants are 9×10^{-6} and 6×10^{6} sec^{-1} at 25°, respectively. Electronic arguments must be used to account for this $\sim 10^{12}$ difference in rate constant. Recent ligand field calculations[45,46] have been performed on TAP, TP, and intermediate geometries which yield good estimates of the ligand field stabilization energy for TAP and TP geometries for the various d electronic configurations. A complex which undergoes optical inversion by the trigonal twist mechanism can be assumed to proceed from a TAP geometry through a TP transition state. Ideally, the activation energy should be related to LFSE(TAP) − LFSE(TP) which is called ΔLFSE in Table III. The results in Table III show a definite trend in $\Delta H^\ddagger$ which is in general agreement with the above supposi-

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(37) R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, 11, 2435 (1972).

(38) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, 93, 360 (1971).

(39) J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, 92, 5319 (1970).

(40) A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, 92, 7061 (1970).

(41) $\Delta S^\ddagger$ = 3 eu is the average value for all $M(dtc)_3$ complexes which have been subjected to a total line-shape analysis (Table II).

(42) S. Merlino, *Acta Crystallogr., Sect. B*, 24, 1441 (1968); T. Brennan and I. Bernal, *J. Phys. Chem.*, 73, 443 (1969).

(43) P. C. Healy and A. H. White, *Chem. Commun.*, 1446 (1971); B. F. Hoskins and B. P. Kelly, *ibid.*, 1517 (1968).

(44) The twist angle 2θ and the pitch angle ϵ have been defined in ref 21. The similarity in the structures of $Co(EtEt(dtc))_3$ and $Fe(MePh(dtc))_3$ can be seen by comparing metal–ligand distance (r), 2θ, ϵ, and the distance between the parallel triangles measured along the C_3 axis (d). The values for the Co and Fe complex, respectively, are as follows (r; 2θ; ϵ; d): 2.26, 2.32 Å; 43.0, 40.4°; 29.8, 28.8°; 2.46, 2.47 Å.

(45) W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *Inorg. Chem.*, 9, 1825 (1970).

(46) E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, 11, 2652 (1972).

Table III. ΔLFSE[a] Values and $\Delta H^{\ddagger}$ Values for Optical Inversion of $M(dtc)_3$ Complexes

Metal ion	No. of d electrons	ΔLFSE (*Dq*)	$\Delta H^{\ddagger}$, kcal/mol
Ga(III)	10	0	<8.6
In(III)	10	0	<8.6
V(III)	2	3.4	<8.2
Mn(III), hs	4	3.4	9.8-11.0
Fe(III), hs	5	0	7.6-10.3[b]
Fe(III), ls	5	10.2	
Ru(III), ls	5	10.2	~13[c]
Cr(III)	3	6.8	>16
Co(III), ls	6	13.6	25.5
Rh(III), ls	6	13.6	>27[d]

[a] ΔLFSE = LFSE(TAP) − LFSE(TP) according to Gillum.[45]
[b] Values are for various positions of the ls ⇌ hs equilibrium. [c] $Ru(BzBz(dtc))_3$.[24] [d] $Rh(BzBz(dtc))_3$.[1]

tion. The Mn complexes have $\Delta H^{\ddagger}$ values which are in fair agreement with the ΔLFSE argument; however, the $\Delta H^{\ddagger}$ values are a little high. This might be expected because the tetragonal distortion which is observed in $Mn(EtEt(dtc))_3$ would make the simple twist motion more difficult. This would presumably cost more energy. The Ru complex also appears to have a slightly high $\Delta H^{\ddagger}$ compared with the Fe compounds. Second-row transition metals are expected to have higher barriers to inversion than first-row metals in the same group according to this LFSE argument because *Dq* values are higher for second-row metals with the same ligand system.[47] This can account for the slightly high $\Delta H^{\ddagger}$ of $Ru(dtc)_3$ complexes. The higher $\Delta H^{\ddagger}$ for Rh than for Co is also consistent with this argument. The most notable exception to the LFSE argument is with Cr. In this case, however, neither mechanistic nor structural data are available. Possibly a different mechanism is operative or perhaps the solid-state geometry is not typical for $M(dtc)_3$ complexes. The LFSE argument is admittedly an oversimplification, and while it appears to account for the general trend in rate, it will fail if other factors such as bond energy changes or nonbonded interactions are important.

The LFSE argument has been previously applied to optical inversion rates for some other tris-chelate complexes with similar success.[1] This argument assumes that all of these complexes isomerize by the trigonal twist mechanism. This pathway has not been proven for the Rh, Co, and Cr compounds.[48] However, all of the $M(dtc)_3$ complexes for which a mechanism has been determined do indeed utilize the trigonal twist pathway.[1-4] Also $\Delta S^{\ddagger}$ for $Co(BzBz(dtc))_3$ is very similar to $\Delta S^{\ddagger}$ of other $M(dtc)_3$ complexes of known mechanism. Therefore, it is not a bad assumption that the $M(dtc)_3$ complexes in Table III undergo optical inversion by the trigonal twist mechanism.[49-51]

Relation of Solid-State Structure to Mechanism. $M(dtc)_3$ complexes fall into the highly compressed[36] trigonally distorted (*i.e.*, twisted toward TP geometry, *vide supra*) class of tris-chelate compounds.[52] These distortions from ideal TAP geometry result in part from the small bite angle, α, of the dtc ligand which is typically *ca.* 75° but as small as 69° for $In[(CH_2)_4dtc]_3$.[51] Stiefel and Brown[36] have pointed out that the highly compressed $M(dtc)_3$ type complexes would twist through a TP transition state which is severely compressed and may be energetically unfavorable. Indeed, a distorted hexagonal transition state (rearrangement modes A_2 or A_5[35]) was suggested. Our results with $M(dtc)_3$ complexes, however, demonstrate that the trigonal twist mechanism (mode A_6) which presumably requires a TP transition state is indeed operative. Hence, these compressed complexes choose to rearrange *via* this mechanism. Kepert[53] has performed ligand-ligand repulsion calculations for a number of tris-chelate complexes and has found that the barrier to optical inversion *via* the trigonal twist mechanism is lower for small bite angle ligands than for large ones. This result may explain why the small bite angle dtc complexes choose the trigonal twist mechanism whereas the larger bite angle β-diketonate ligands ($\alpha \simeq 88°$)[54] isomerize by bond rupture pathways.[39,40] The small bite angle tris (α-(*R*)-tropolonato) complexes of Co and Al also isomerize *via* the trigonal twist pathway[10,34] (α = 82.6° for tris(tropolonato)aluminum(III)[55]). Hence, solid-state structural parameters appear to be important in their influence on mechanism. Relative rates of isomerization, on the other hand, are best rationalized by electronic arguments. A comprehensive comparison of the rates and mechanisms for optical inversion of various tris-chelate complexes will be presented in a future publication.[24]

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Registry No. $V(BzBzdtc)_3$, 42535-56-8; $V(MePhdtc)_3$ 42535-57-9; $Mn(BzBzdtc)_3$, 33291-11-1; $Mn(MePhdtc)_3$, 36869-11-1; $Ga(BzBzdtc)_3$, 42535-59-1; $Ga(MePhdtc)_3$, 42535-60-4; $In(BzBzdtc)_3$, 42535-61-5; $In(MePhdtc)_3$, 42535-62-6; $Cr(EtEtdtc)_3$, 18898-57-2.

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(47) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 242.

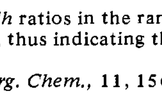
(48) The word "proven" is perhaps too strong because pmr data can never really prove a mechanism (*vide supra*). Also the arguments used for Ga and In are not as strong as for the other metals. Nonetheless, all evidence strongly suggests that this is the correct rearrangement pathway.

(49) Caution is needed here because some $M(dtc)_3$ complexes are not true tris chelates. For example, the structure of $As(EtEt(dtc))_3$ has been determined[50] and shows two types of As-S bonds; three have a distance of ~2.35 Å while three have ~2.85 Å. Clearly, this complex falls into a different class and could isomerize by a bond-rupture mechanism. Recently the structure of $In[(CH_2)_4dtc]_3$ appeared[51] which shows it to be a true tris chelate with six In-S bonds nearly identical.

(50) M. Colapietro, A. Domenicano, L. Scaramuzza, and A. Vaciago, *Chem. Commun.*, 302 (1968).

(51) P. J. Hauser, J. Bordner, and A. F. Schreiner, *Inorg. Chem.*, 12, 1347 (1973).

(52) The compression ratio is defined as *s/h* where *s* is the side of an equilateral triangle and *h* is the distance between parallel equilateral triangles defined in the figure[36]



$M(dtc)_3$ complexes have *s/h* ratios in the range 1.3-1.5.[36] An ideal octahedron has $s/h = 1.22$, thus indicating the compressed nature of $M(dtc)_3$ complexes.

(53) D. L. Kepert, *Inorg. Chem.*, 11, 1561 (1972).

(54) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, 88, 2951 (1966).

(55) E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 94, 8046 (1972).