Contribution from the Department of Chemistry,
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Manganese Schiff Base Complexes. 7. Synthesis and Circular Dichroism of Optically Active Tetradentate Chelates of Manganese(III) and of μ-Oxo-μ-hydroxo-dimanganese(III,IV) Dimers

L. J. BOUCHER* and C. G. COE

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The synthesis and characterization of several new optically active complexes of Mn(III) [Mn(SB)H_2O]ClO_4 and [Mn(SB)Cl] and of the Mn(III)–Mn(IV) dimers [Mn_2(SB)$_2$(OH)O]·$n$$H_2O$ where SB is the dianion of the optically active tetradentate Schiff base derived from (–)-1,2-diaminopropane and 4-*sec*-butylsalicylaldehyde or 4-*sec*-butyl-2-acetylphenol has been carried out. The electronic absorption and circular dichroism spectra of the complexes in chloroform and methanol solution have been measured. Tentative assignments are made for the absorptions in the three regions: 14–21-kK ligand field transition, 21–30-kK charge transfer, and 30–45-kK ligand transitions. The mixed-valence dimers show transitions arising from both the Mn(III) and Mn(IV) sites in the ligand field and charge-transfer regions. A prominent absorption at ~22 kK ($\epsilon \sim 5 \times 10^3$) can be assigned to an intervalence metal transition. Thus the mixed-valence dimer can be designated as a class II system with integral oxidation states and with a substantial interaction parameter, $\alpha \approx 0.17$. The chloroform solution CD spectra are consistent with a preferred δ conformation of the central ethylenediamine chelate ring with the methyl group on the *R* chiral carbon in a pseudoaxial position in all of the complexes. In methanol, solvent interactions with the salicylaldehyde derivative give rise to a shift in the chelate ring conformational equilibrium toward the λ conformation. No evidence is obtained for stereospecific binding of the tetradentate Schiff base in the β configuration for the pseudooctahedral dimers with respect to the disposition of the chelate rings.

The oxidation of Mn(III) tetradentate Schiff base complexes at pH >12 gives rise to a series of compounds originally formulated as μ-dioxo-dimanganese(IV) dimers, [Mn_2(SB)$_2$$O_2$]·$n$$H_2O$.[1] However recent low-temperature magnetic susceptibility measurements indicate that the materials are best formulated as mixed oxidation state dimers of Mn(III)–Mn(IV), [Mn_2(SB)$_2$(OH)O]·$n$$H_2O$.[2] The electronic structure and the extent of delocalization in these materials are then of some interest.[3]

The absorption spectra show many broad overlapping bands and ill-defined shoulders and are thus difficult to analyze. CD spectra of complexes generally allow a more detailed examination of electronic spectra. A straightforward way of producing optically active tetradentate Schiff base complexes, even for labile systems (vide infra), is to use a ligand derived from the optically active amines like (–)-1,2-diaminopropane.[4] We have thus synthesized two new dimers which are optically active, [Mn_2(SB)$_2$(OH)O]·H_2O, and studied their CD spectra. Structural representations and abbreviations for the ligands are shown in Figure 1. The 4-*sec*-butyl derivatives were used to ensure sufficient solubility in polar and nonpolar solvents.

Optically active tetradentate Schiff base complexes of Mn(III) have been synthesized and CD spectra measured.[5] Due to the low magnitude of the rotatory strengths of the Cotton effects and the high absorption of the solutions, accurate measurements were only possible for the Acet (acetylphenol) complexes. Increased instrumental capabilities have allowed us to measure the CD spectra for both the Sal and Acet derivatives of the Mn(III) Schiff base complexes, in this case with the 4-*sec*-butyl substituent. Thus we have also synthesized, characterized and measured the CD spectra of the Mn(III) complexes [Mn(SB)Cl] and [Mn(SB)H_2O]ClO_4. Close comparison of the electronic and CD spectra of the Mn(III) complexes with those of the dimers is of considerable interest not only from the point of view of the stereochemistry of the ligand and metal coordination sphere but also with relation to the problem of determining the extent of delocalization[6] in the mixed-valence dimers.

Experimental Section

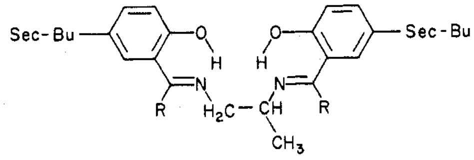
Materials. The ligands H_2BuSal((–)pn) and H_2BuAcet((–)pn) were prepared by condensation in methanol of optically active (–)-1,2-diaminopropane, resolved by the method of Dwyer,[7] with 4-*sec*-butylsalicylaldehyde prepared previously[8] or 4-*sec*-butyl-2-acetylphenol obtained from the Fries reaction with 4-*sec*-butylphenyl acetate.[9] All other materials were reagent grade and used without further purification. All of the following synthetic reactions were carried out at room temperature.

Preparation of Complexes. [Mn(BuSal((–)pn))Cl]·H_2O. The ligand H_2BuSal((–)pn), 0.50 g (0.0013 mol), was dissolved in 100 ml of methanol, and 1.0 ml of 1 M NaOH (0.001 mol) was added. Immediately upon dissolution of 1.0 g of $MnCl_2$·$4H_2O$ (0.005 mol), this solution became dark brown. The brown solution was stirred for 1 h and then evaporated to dryness in an air stream. The resulting residue was dissolved in 30 ml of chloroform, dried with Drierite, and isolated by addition of 200 ml of petroleum ether. The crude complex was recrystallized from chloroform–petroleum ether. The yield of the tan solid was 0.30 g (46% based on the amount of ligand used); R_f 0.58, $\mu_{\rm eff}$(solution) = 5.00 BM. Anal. Calcd for [$C_{25}H_{32}N_2O_2MnCl$]·H_2O: C, 59.88; H, 6.79; N, 5.59. Found: C, 60.23; H, 6.64; N, 5.58.

[Mn(BuSal((–)pn))H_2O]ClO_4·H_2O. The ligand H_2BuSal((–)pn), 4.1 g (0.01 mol), was dissolved in 100 ml of methanol and combined with 2.5 ml of 4 M NaOH (0.01 mol) in a three-neck flask. The reaction mixture was kept under a nitrogen atmosphere and all solutions were thoroughly deaerated. Addition of 6.2 g of Mn(ClO_4)$_2$·$6H_2O$ (0.017 mol) dissolved in 50 ml of methanol caused little color change in the yellow reaction solution. Then 1.3 ml of 30% hydrogen peroxide (0.011 mol) was diluted with 25 ml of methanol and added dropwise to the reaction mixture, causing the solution to darken. After 30 min the solvent was removed on a rotary evaporator and the resulting residue was dissolved in 50 ml of chloroform. The filtered solution produced a large crop of brown solid when 200 ml of petroleum ether was added and the solution was cooled at 0 °C. The compound was recrystallized from chloroform–petroleum ether and air-dried; yield 3.1 g (55% based on the amount of ligand used); R_f 0.55; $\mu_{\rm eff}$(solution) = 4.91 BM. Anal. Calcd for [$C_{25}H_{34}N_2O_7MnCl$]·H_2O: C, 51.50; H, 6.18; N, 4.81. Found: C, 51.85; H, 5.79; N, 4.73.

[Mn_2(BuSal((–)pn))$_2$(O)OH]·H_2O. The complex [Mn(BuSal((–)pn))H_2O]ClO_4·H_2O, 1.0 g (0.0018 mol), dissolved in 100 ml of chloroform was added to a modified three-neck flask with a stopcock at the bottom. A pressure-equalized dropping funnel was charged with 35.5 ml of 0.05 M NaOH (0.0018 mol) containing 0.8 ml of 30% hydrogen peroxide (0.007 mol). Both solutions were thoroughly saturated with nitrogen and then the aqueous phase was added over a 20-min period. After the addition, shaking the flask vigorously under an N_2 atmosphere for 10 min resulted in the formation of a deep red chloroform phase.

The chloroform phase was separated from the aqueous phase, filtered through paper, and concentrated to 20 ml. Addition of 300 ml of petroleum ether caused precipitation of the crude complex. The red-brown compound was recrystallized from chloroform–petroleum ether producing 0.52 g for a yield of 60% based on the amount of



SB	R
Sal	H
Acet	CH_3

Figure 1. Structural representation of the Schiff base, H_2SB.

perchlorate complex used; R_f 0.75; μ_{eff}(solution) = 2.30 BM. Anal. Calcd for $[C_{50}H_{65}N_4O_6Mn_2]\cdot H_2O$: C, 63.43; H, 7.19; N, 5.92. Found: C, 63.59; H, 7.07; N, 6.02. Molecular weight: calcd, 944; found, 976 ± 33.

[Mn(BuAcet((−)pn))Cl]·H₂O. The ligand H_2BuAcet((−)pn), 1.1 g (0.0026 mol), was dissolved in 100 ml of methanol and 0.65 ml of 4 M NaOH (0.0026 mol) was then added. The metal salt $MnCl_2\cdot 4H_2O$, 0.62 g (0.0031 mol), was dissolved in 100 ml of methanol. After bubbling of nitrogen through both solutions, they were combined and 0.3 ml of 30% hydrogen peroxide (0.0026 mol) diluted in 10 ml of methanol was added dropwise. The resulting dark solution was evaporated to dryness and the residue was extracted into 50 ml of chloroform. Addition of a tenfold excess of petroleum ether to the filtered chloroform solution caused pecipitation of the crude product. The crude product was washed with water and air-dried. Recrystallizing from chloroform–petroleum ether produced 0.8 g of complex; yield 58%. R_f 0.57; μ_{eff}(solution) = 4.94 BM. Anal. Calcd for $[C_{27}H_{36}N_2O_2MnCl]\cdot H_2O$: C, 61.26; H, 7.18; N, 5.29. Found: C, 61.64; H, 6.84; N, 5.09.

[Mn(BuAcet((−)pn))H₂O]ClO₄. The ligand H_2BuAcet((−)pn), 2.1 g (0.005 mol), dissolved in 75 ml of methanol, was placed in a three-neck flask to which was added 1.3 ml of 4 M NaOH (0.005 mol). The reaction was kept under a nitrogen atomosphere. Addition of 100 ml of a methanolic solution containing 3.0 g of $Mn(ClO_4)_2\cdot 6H_2O$ (0.008 mol) caused little change in the color of the reaction mixture. When 0.6 ml of 30% hydrogen peroxide (0.005 mol) diluted with 10 ml of methanol was added dropwise, the solution darkened. The resulting dark brown solution was taken to dryness with a rotary evaporator and the residue was washed with 20 ml of benzene to remove a significant amount of unreacted ligand. The residue was then extracted into 100 ml of acetone. The brown acetone solution was filtered and concentrated to 20 ml. Addition of diethyl ether to the acetone solution followed by cooling produced a large crop of a brown compound. The crude compound was recrystallized from acetone–diethyl ether and the resulting product washed with 50 ml of water and air-dried. The product was still tacky and therefore washed with two 30-ml portions of benzene and air-dried. The dried brown complex weighed 2.0 g for a yield of 68%; R_f 0.54; μ_{eff}(solution) = 5.03 BM. Anal. Calcd for $[C_{27}H_{38}N_2O_7MnCl]$: C, 54.86; H, 6.41; N, 4.73. Found: C, 54.97; H, 6.36; N, 4.74.

[Mn₂(BuAcet((−)pn))₂(O)OH]·2H₂O. The complex [Mn(BuAcet((−)pn))H$_2$O]ClO$_4$, 0.5 g (0.000 84 mol), dissolved in 250 ml of chloroform was added to the modified three-neck flask. An aqueous solution containing 25.3 ml of 0.05 N NaOH (0.0012 mol) and 2.0 ml of 30% hydrogen peroxide (0.018 mol), diluted with 30 ml of water, was placed in a dropping funnel. After deaeration of both solutions with nitrogen, the aqueous phase was added dropwise. Two additional 2.0-ml portions of 30% hydrogen peroxide diluted with 20 ml of water were added at 20-min intervals. After each addition the flask was shaken vigorously while being continually purged with nitrogen. The resulting dark chloroform solution was drawn off from the aqueous phase after 2 hr, filtered, and concentrated to 10 ml. Addition of 200 ml of petroleum ether followed by cooling produced 0.21 g of red-brown solid. The crude complex was recrystallized from chloroform–petroleum ether to yield 0.17 g of the desired complex; yield 40%; R_f 0.80; μ_{eff}(solution) = 2.64 BM. Anal. Calcd for $[C_{54}H_{73}N_4O_6Mn_2]\cdot 2H_2O$: C, 63.60; H, 7.19; N, 5.50. Found: C, 63.98; H, 7.15; N, 5.59.

All elemental analyses were performed by Chemalytics, Tempe, Ariz.

Physical Measurements. Absorption spectra of the complexes in chloroform and methanol were measured from the near-infrared region to the ultraviolet using a Cary 14 spectrophotometer. The circular dichroism curves were recorded with a Cary 61 CD spectrophotometer; ir spectra were obtained with a PE-337B grating spectrometer using CsI disks and Fluorolube mulls. Solution magnetic moments were determined by the NMR method using 10% TMS–$CHCl_3$ solutions of the complex, 2 mg/ml (~0.002 M), with a 250-MHz spectrometer at ambient temperature.[8] Diamagnetic corrections were calculated from the relevant Pascal constants. Molecular weights of the dimeric compounds were determined with a Perkin-Elmer vapor pressure osmometer with ~0.002 M solutions in choroform. An Industrial Instruments Model RC16B2 conductivity bridge was used for the conductivity measurements which were determined in methanol, nitromethane, and acetonitrile solutions, 10^{-3} M, at room temperature. R_f values were obtained by development on a 15-cm, 250 μ thick silica gel G plate (Analtech) with 25% methanol–benzene elution.

Results and Discussion

Synthesis and Characterization of Complexes. The infrared spectral characteristics, elemental analyses, magnetic moments, and conductivity of the Mn(III) optically active complexes synthesized here indicate that they are completely analogous to those previously reported Mn(III) Schiff base compounds.[1,5,8] The optically active dimers were synthesized by a modification of the previously reported procedure.[1] Their reduced magnetic moments, 2.3 BM for Sal and 2.64 BM for Acet, are consistent with antiferromagnetically coupled high-spin dimeric complexes with Mn(III) d^4–Mn(IV) d^3. Chloroform solution molecular weight measurements show that the compounds are dimeric. The infrared spectra of the dimeric materials show most ligand absorptions at the same frequencies as their manganese(III)–aquo and –chloride complexes of that Schiff base. As in other analogous dimeric complexes a new band due to the Mn(OH)OMn ring vibration is observed at 650 cm^{-1} for the Sal dimer and 640 cm^{-1} for the Acet compound. Using very concentrated Fluorolube mulls a weak, broad band is evident at 3620 cm^{-1} for the Acet dimer which is consistent with the presence of a bridging hydroxy group. However, no band can be detected in this region for the Sal dimer nor can a band be seen for the Mn–OH band at ~1100 cm^{-1} in the spectra of either of the dimers. Lattice water absorptions are readily seen as broad bands from 3250 to 3400 cm^{-1}. Conductivities of the dimers in acetonitrile are negligible and indicate that they are nonelectrolytes, as expected.

Spectra of Mn(III) Complexes. The absolute configuration and x-ray crystal structure of [Mn(Acet((−)pn))X], $X^- = Cl^-$, N_3^-, has been determined.[10] The complexes show square-pyramidal coordination with the metal atom above the basal plane of the four donor atoms toward the apical anion. The Schiff base ligands adopt a roughly coplanar configuration with the four donor atoms, N_2O_2, deviating from its best plane by less than 0.01 Å. As required, the absolute configuration of the chiral carbon in the molecules is *R* and the central ethylene chelate ring adopts a δ conformation with the methyl group in a pseudoaxial position pointing in the direction trans to the apical anion. In general this structure confirms the previous conclusions based on the analysis of Urbach and co-workers.[4] The chloroform and methanol solution absorption and CD spectra of [Mn(SB)Cl] have been measured and typical spectra are shown in Figures 2–5. The frequencies of the various maxima, with their extinction coefficients, are collected in Table I. The spectra of the complexes [Mn(SB)H$_2$O]ClO$_4$ are similar to those of the chloride complexes in chloroform while the methanol solution spectra are identical for both types of Mn(III) complexes.

In the ligand field region, 15–20 kK, two CD bands, II and III, of opposite sign are seen which can be assigned to d_{xy} and d_{xz}, d_{yz} to $d_{x^2-y^2}$ transitions.[5] As expected the increased donor strength of the Schiff base in going from Sal to Acet leads to a destabilization of the $d_{x^2-y^2}$ level and a blue shift of the ligand field bands. The charge-transfer region of the spectra, 21–30

Table I. Electronic Absorption and CD Spectral Data for Mn(III) Complexes

Band no.	[Mn(BuSal((–)pn))Cl]						[Mn(BuAcet((–)pn))Cl]					
	$CHCl_3$			CH_3OH			$CHCl_3$			CH_3OH		
	$\bar{\nu}$[a]	$\bar{\nu}$	$\Delta\epsilon$	$\bar{\nu}$	$\bar{\nu}$	$\Delta\epsilon$	$\bar{\nu}$	$\bar{\nu}$	$\Delta\epsilon$	$\bar{\nu}$	$\bar{\nu}$	$\Delta\epsilon$
I											16.3	−0.62
II	~15 (2.3)[b]	15.5	−0.42	~19 (2.3)	18.6	+0.16	~17 (2.6)	16.8	−1.3	~17 (2.7)	17.5	−0.80
III	~20 (3.2)	19.5	+0.28				~20 (3.1)	20.5	+0.50	~21 (2.9)	21.5	+0.60
IV	23.2 (3.65)	23.2	+2.8	~25 (3.7)	23.6	+0.88	~24 (3.6)	23.6	+5.5	~25 (3.7)	24.1	+3.6
V										26.3 (3.79)	27.6	−1.0
VI	30.7 (4.15)	30.3	+3.5	~29 (3.8)	29.4	+0.80	~32 (4.1)	32.0	+6.4	~34 (4.4)	32.5	+24
VII	34.8 (4.24)	33.4	+2.6	35.1 (4.27)	32.8	−0.86	~37 (4.2)					
VIII				41.7 (4.61)						~43.5 (4.64)	40.8	+14

[a] $\bar{\nu}$ in kK. [b] log ϵ_{max} in parentheses.

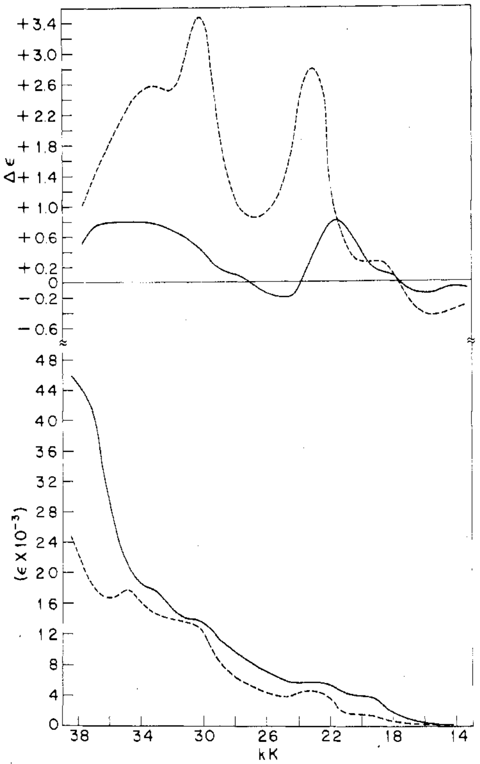


Figure 2. CD (top) and absorption (bottom) spectra of [Mn(BuSal((–)pn))Cl] (- - -) and $[Mn_2(BuSal((-))pn)_2(O)OH]$ (——) in chloroform.

kK, shows bands IV and V which can be assigned to d → π* (azomethine) transitions.[11] The ligand π → π* (azomethine) transition, band VI, is seen in the higher energy region 30–44 kK.[11] The shift of both the charge-transfer and ligand transitions with azomethine substituent is consistent with the effect of the change of substituent H to CH_3 on the ligand π levels.[12] A band on the high-energy shoulder of band VI which is clearly seen only in the [Mn(BuSal((–)pn))Cl] complex may be associated with a ligand to metal charge transfer.[13] The sign of the π → π* Cotton effect is positive for both complexes. Previous work with these Schiff base ligands complexed to a variety of metals,[4,11] as well as the crystal structure results for [Mn(Acet((–)pn))Cl], links the observed positive Cotton effect with the presence of a preponderance of δ central chelate ring conformer in the chloroform solution. The lower steric requirement for [Mn(BuSal((–)pn)Cl] in contrast to the Acet complexes leads to a more equal population of the two ring conformers, δ and λ, while still favoring the former. This accounts for the significantly lower rotatory strength of the Cotton effects of [Mn(BuSal((–)pn))Cl] in comparison to those of [Mn(BuAcet((–)pn))Cl].

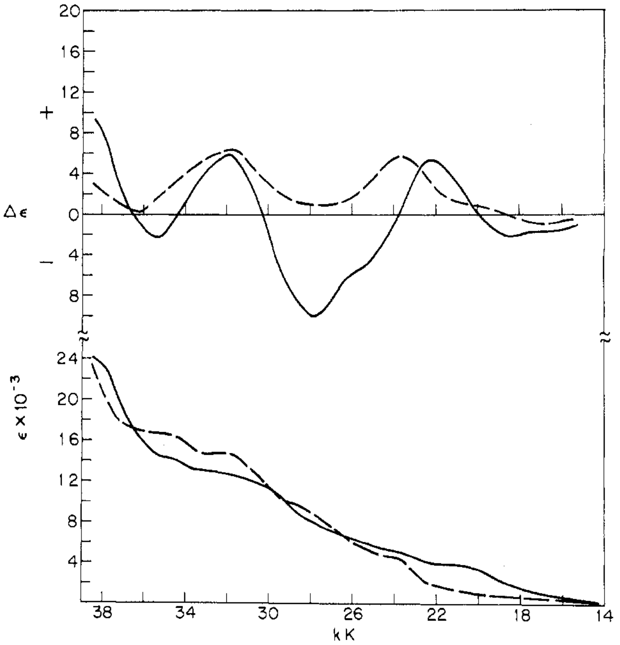


Figure 3. CD (top) and absorption (bottom) spectra of [Mn(BuAcet((–)pn))Cl] (- - -) and $[Mn_2(BuAcet((-)pn))_2(O)OH]$ (——) in chloroform.

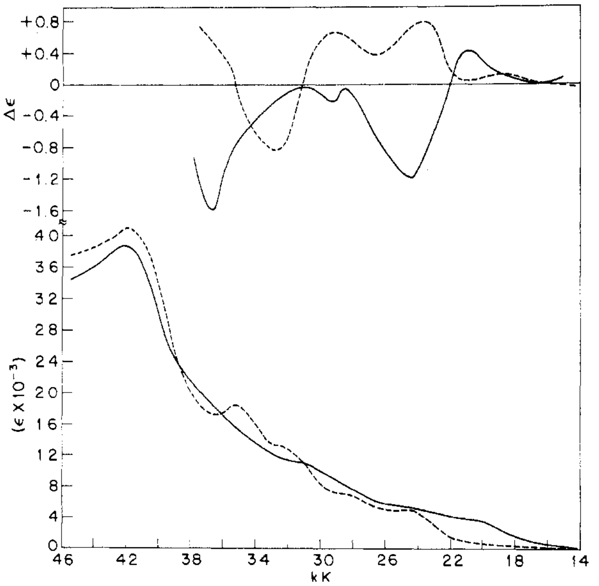


Figure 4. CD (top) and absorption (bottom) spectra of [Mn(BuSal((–)pn))Cl] (- - -) and $[Mn_2(BuSal((-)pn))_2(O)OH]$ (——) in methanol.

The methanol solution spectrum of [Mn(BuAcet((–)pn))Cl] is similar to that of this complex in chloroform. In the ligand

Table II. Electronic Absorption and CD Spectral Data for Mn(III)–Mn(IV) Dimers

Band no.	$[Mn_2(BuSal((-)pn))_2(OH)O]\cdot H_2O$						$[Mn_2(BuAcet((-)pn))_2(OH)O]\cdot 2H_2O$					
	$CHCl_3$			CH_3OH			$CHCl_3$			CH_3OH		
	$\bar{\nu}$[a]	$\bar{\nu}$	$\Delta\epsilon$	$\bar{\nu}$	$\bar{\nu}$	$\Delta\epsilon$	$\bar{\nu}$	$\bar{\nu}$	$\Delta\epsilon$	$\bar{\nu}$	$\bar{\nu}$	$\Delta\epsilon$
II	~16 (2.3)[b]	15.9	−0.12				~17 (2.7)	~16.5	−1.4			
Ia[c]	~18 (2.6)	18.5	+0.12	~18.5 (3.11)	~19	+0.10	~19 (3.3)	18.5	−2.0	~18 (3.0)	18.0	−1.6
											18.0	−1.6
	~20.5 (3.6)	21.5	+0.82	~21 (3.6)	21.0	+0.46	~21 (3.6)	22.2	+5.4	~22 (3.6)	22.2	+4.1
IIIa	~23 (3.8)	25.0	−0.18	~25 (3.7)	24.4	−1.20	~28 (3.9)	27.9	−10	~28 (3.7)	28.1	−8.1
VI	~30.5 (4.1)	~30	+0.5	~31 (4.0)	29.4	−0.20	32.0 (4.11)	31.9	+5.8		32.3	+7.7
VII	~33.5 (4.2)	33.8	+0.80									
VIIa		36.5	+0.78	~36 (4.2)	36.6	−1.6	~35 (4.2)	35.4	−2.2	~32 (4.0)	35.7	−0.6
VIII				42.2 (4.60)						43.5 (4.63)	40.0	+18

[a] $\bar{\nu}$ in kK. [b] log ϵ_{max} in parentheses. [c] Ia, IIIa, and VIIa identified as Mn(IV) Schiff base absorptions.

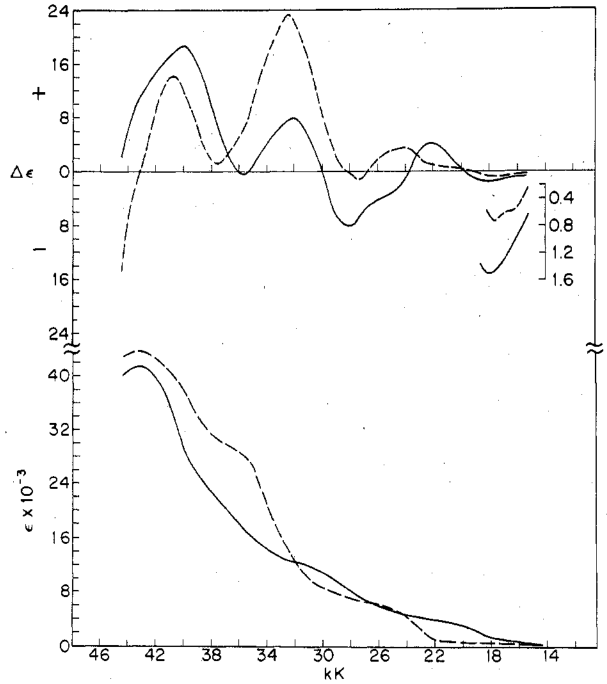


Figure 5. CD (top) and absorption (bottom) spectra of [Mn(BuAcet((−)pn))Cl] (- - -) and $[Mn_2(BuAcet((-)pn))_2(O)OH]$ (——) in methanol.

field region a prominent shoulder appears at 16.3 kK in the methanol solution spectrum in addition to bands at 17.5 and 21.0 kK. Again the three bands probably arise from a low-symmetry splitting of the d → d transitions d_{xz}, d_{yz}, and d_{xy} levels to the $d_{x^2-y^2}$ level. Further the ligand field bands are shifted to higher energy in going from the chloroform spectrum to the methanol solution spectrum. Conductivity measurements are consistent with the displacement of the coordinated chloride ion in methanol solution. Presumably the complex shows axial coordination of methanol molecules with the metal now in the plane of the Schiff base ligand.[14] This tetragonal structure gives rise to a destabilization of the $d_{x^2-y^2}$ level in comparison to the square-pyramidal structure. Thus the blue shift of the ligand field bands in going from chloroform to methanol solution can be rationalized. The increased wavelength range available in methanol solution allows the observation of an additional positive ligand $\pi \rightarrow \pi^*$ band at 40.8 kK.

The methanol solution spectrum is quite different for [Mn(BuSal((−)pn))Cl] from its chloroform solution spectrum as well as from the solution spectra of [Mn(BuAcet((−)-pn))Cl]. For example, the ligand field region only shows one broad positive band which is most likely composed of several overlapping components of the same or different signs. In addition to showing an inversion of sign, the visible "band" is blue shifted in going from the chloroform to the methanol solution spectrum. The charge-transfer band and the first $\pi \rightarrow \pi^*$ band are both shifted with change in solvent but the sign of the Cotton effect remains positive. On the other hand the presumed charge transfer, ligand to metal, at 32.8 kK has shown an apparent inversion of sign in going from chloroform to methanol solution. Finally, the second ligand $\pi \rightarrow \pi^*$ band is seen as a positive Cotton effect at ~41.7 kK. It is interesting to note that the rotatory strength of the Cotton effects decreases to one-third in going from chloroform to methanol.

The change in the CD spectra detailed here may be ascribed to specific solvation effects in the methanol solution. The formation of the disolvated complexes increases steric interactions of the axial ligands with the axial methyl group on the central chelate ring. Thus the δ conformer is further destabilized with respect to the λ conformer (with an equatorial methyl substituent).[15] Again the more nearly equal populations of the δ and λ conformer lead to a general diminution of the rotatory strengths of all the Cotton effects. However the $\pi \rightarrow \pi^*$ ligand band maintains a positive sign so that the δ conformer still predominates. In addition to the changes in conformational equilibrium with solvent, other changes must take place since at least one of the d–d bands and one of the charge-transfer bands show inversion with solvent. There has been much discussion as to the origin of the optical activity in conformationally dissymmetric molecules like those discussed here. It appears that a number of effects contribute to the overall observed CD spectrum. These include central chelate ring conformation, distortion of the donor atoms from a coplanar structure, and as yet unspecified effects related to changes in overall ligand configuration via solvation effects, maybe even in the second coordination sphere.[16] The changes in circular dichroism with solvent noted here for the Mn(III) complexes indicate that the ligand field, charge-transfer, and ligand transitions may each be differently affected by the several sources of molecular dissymmetry. In the case of the complexes like [Mn(BuAcet((−)pn))Cl] the molecular dissymmetry contributed by the large preponderance of the δ ring conformer overwhelms any other contribution. On the other hand, the small observed rotation for the complexes like [Mn(BuSal((−)pn))Cl], which primarily arises because of the nearly mutual cancelation of CD bands with almost equal concentrations of both δ and λ conformers, is most susceptible to environmental changes which affect the other small contributions to molecular dissymmetry. Thus a cancelation of opposing rotatory strengths holds for some transitions while for others the effects are additive.

Dimer Spectra. The CD and uv–visible absorption spectra of the complexes $[Mn_2(SB)_2(O)OH]$ in chloroform and methanol solutions have been measured and typical spectra are shown in Figures 2–5. The frequencies and extinction coefficients of the various maxima are collected in Table II.

The electronic absorption spectrum of mixed-valence dimers can be interpreted in a number of ways.[6] If the interaction between the two metals in different oxidation states, Mn(III)–Mn(IV), is not large (class II), then the absorption spectrum will contain the summation of absorptions typical of the two oxidation state metal complexes plus new bands which correspond to intervalence (mixed-valence) transitions, i.e., electron transfer from the Mn(III) to the Mn(IV) site. The frequency and intensity of the intervalence transition can be related to the degree of metal–metal interaction, α. Applying the standard relationship[3] and assuming that the prominent band at ~21–22 kK, which gives rise to the characteristic cherry red color of the dimers, is an intervalence band (vide infra) α is approximately 0.17. This places the dimers discussed here in class II with integral oxidation states. Since the electronic spectra of the Mn(III) Schiff base complexes have already been analyzed, it is relatively straightforward to pick out absorptions corresponding to this valence state in the dimer. Unfortunately, no monomeric Mn(IV) Schiff base complexes have been reported. Thus its bands in the dimer spectra can only be tentatively identified.

The chloroform solution CD spectra of the dimers in the ligand field region show a low-energy negative Cotton effect at 15.9 and at 16.5 kK for the Sal and Acet derivatives, respectively. The CD spectra of the analogous Mn(III) complexes show negative CD bands at 15.5 and 16.8 kK. In addition to the comparable frequencies, the bands show similar rotatory strengths. Thus it is possible that this band arises from the same Mn(III) transition: $d_{xy} \rightarrow d_{x^2-y^2}$. The d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ positive Cotton effect (~21 kK) is presumably obscured by more intense bands. The Acet dimer also shows a negative CD band at 18.5 kK which appears to be absent from the spectrum of the Mn(III) complexes. The new ligand field band may be assigned to a Mn(IV) transition. Although the actual symmetry is lower, considering only the donor atoms, cis N_2O_4, the effective symmetry at the Mn(IV) in the dimer would be C_{2v}. Under low symmetry the Mn(IV) two octahedral bands $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ would be split into several components. The rich array of visible absorptions here makes resolution of these components unlikely and bands at 18.5 kK in the dimers may be assigned to the first pseudooctahedral band. The second pseudooctahedral band would occur at higher energy and most likely be obscured by the more intense charge-transfer absorptions. The Mn(IV) ligand field transitions (components of the first pseudooctahedral band) for the dimer $[Mn_2L_4O_2]$, L = picolinate, have been observed at 15.4 and 18.7 kK.[17] The picolinate complex which has a similar array of donor atoms (N_2O_4) would be expected to show a ligand field spectrum similar to that of the Schiff base complexes. Thus the tentative assignment of the 18.5-kK band to the first pseudooctahedral band of the Mn(IV) site in the dimer is reasonable.

The $d\pi \rightarrow \pi^*$ charge transfers which appear at 23.2 and 23.6 kK in the Mn(III) complexes are only seen as shoulders at ~24–25 kK in the chloroform solution spectra of the dimers. It is likely that the analogous transition for the Mn(IV) complex would be in the same energy region. For example this charge-transfer band is seen at ~25–26 kK in the Cr(III)[18] and Fe(III)[15] Schiff base complexes. The dimer spectra show a negative band at 25.0 and 27.9 kK for the Sal and Acet derivatives which is absent from the spectra of the Mn(III) complexes. These bands may be assigned to the Mn(IV) $d\pi \rightarrow \pi^*$ charge transfer. They are expected to be at higher energy than the analogous band in the Mn(III) derivative since the $d\pi$ level of the higher oxidation should be stabilized in comparison to the lower oxidation state. The Schiff base ligand $\pi \rightarrow \pi^*$ transition is seen as a positive Cotton effect at 31.9 kK for the Acet derivative of the dimer which is at the same frequency as for the Mn(III) complexes. It is likely that this essentially ligand transition would occur at approximately the same frequency for the Mn(IV) complex. At any rate no new CD band that can be attributed to the $\pi \rightarrow \pi^*$ transition of the Mn(IV) complex is resolved. Interestingly enough the $\pi \rightarrow \pi^*$ band in the CD spectrum of the Sal derivative dimer is only seen as a shoulder at ~30 kK. It is obvious that the broad flat positive CD band observed in the uv CD spectrum of this dimer arises from the overlap of several bands. These probably arise from $\pi \rightarrow \pi^*$ transitions for the Mn(III) and Mn(IV) sites as well as charge transfers for the Mn(III) and Mn(IV) complexes.

The CD spectrum of the Acet derivative in methanol is similar to that in chloroform solution. The ligand field bands due to Mn(III) and Mn(IV) d–d transitions are not resolved and only one broad negative band is seen at 18.0 kK. In addition the Mn(III) and Mn(IV) charge transfers are at the same frequency as for the chloroform solution. The Schiff base $\pi \rightarrow \pi^*$ transition at 32 kK also shows a prominent positive Cotton effect of approximately the same frequency and rotatory strength as for the chloroform solution. An additional high-energy positive Cotton effect is seen at 40.0 kK in methanol. This intense absorption can be assigned to a Schiff base ligand $\pi \rightarrow \pi^*$ transition. As expected it shows approximately the same frequency and magnitude in the dimer as in the Mn(III) complex. Finally a relatively weak negative Cotton effect is seen in the CD spectrum of the Acet derivative at ~35.6 kK in both chloroform and methanol solution. This absorption is apparently absent in the spectrum of the Mn(III) complex and may be associated with a ligand to metal transfer of the Mn(IV) site.

The methanol solution spectrum of the Sal derivative of the dimer shows a broad positive shoulder at ~19 kK in the ligand field region. The inversion in the sign of the Mn(III) d $\rightarrow$ d band Cotton effect of the dimer with change of solvent from chloroform to methanol is also seen for the Mn(III) complexes. The Mn(IV) d–d transition must therefore either show the same solvent dependence or be obscured by the Mn(III) Cotton effect of opposite sign. Mn(III) and Mn(IV) charge transfer of the dimer appears in the methanol solution spectrum red shifted by ~0.5 kK but with the same sign as for the chloroform solution spectrum. On the other hand the ligand $\pi \rightarrow \pi^*$ band at 29.4 kK shows a weak negative Cotton effect in the methanol solution spectrum of the dimer. It appears as though the ligand to d charge transfer at ~33 kK in the Mn(III) complex is absent from the dimer spectrum. Of course the severe overlap of several weak CD bands of opposite sign in this region can give rise to a net cancelation of rotatory strength in the spectrum. Finally, a relatively strong negative Cotton effect at ~36.6 kK is seen at the high-energy end of the spectrum. This band which appears at lower energy in the spectrum of the Acet derivative may be associated with a ligand to metal charge transfer involving the Mn(IV) site of the dimer. It appears that this charge-transfer band shows an inversion of sign in going from chloroform to methanol solution. This phenomenon may be associated with the subtle solvation effect that appears to be important in the CD spectra of the Sal complexes. Equally likely, the positive Cotton effect in the chloroform solution spectrum may be a result of the fortuitous overlap of several Cotton effects of opposite sign. It must be pointed out that due to the low observed rotation and high solution absorbances accurate spectra are difficult to obtain at higher energies.

A major difference in the CD spectra of the mixed-valence dimers and the Mn(III) complexes is the presence of an intense positive Cotton effect in the chloroform dimer spectra at 21.5 and 22.2 kK. This band in the electronic absorption spectrum largely accounts for the characteristic cherry red color of the

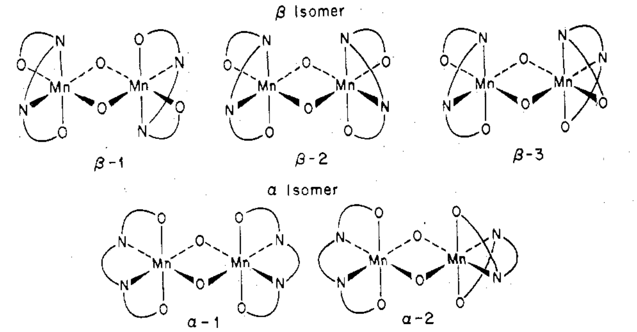


Figure 6. Structural representation of the various geometrical isomers of the μ-dioxo-bis(tetradentate ligand)dimanganese dimers.

dimers. It is reasonable to assign tentatively this band to an intervalence electron-transfer transition, e.g., Mn(III) $t_{2g} \rightarrow$ Mn(IV) e_g. The increase in energy in going from the Sal to the Acet derivative is consistent with the destabilization of the pseudooctahedral e_g orbitals with increase in Schiff base ligand field strength. A low-energy intervalence band Mn(III) $e_g \rightarrow$ Mn(IV) e_g might also be expected in the spectrum in the 5–15-kK region. A search of this region of the near-ir spectra with methanol solutions and Nujol mulls of the complexes shows no observable absorption of medium intensity ($\epsilon > 25$). The mechanism by which an intervalence absorption band of appreciable intensity arises could involve the interaction of this transition with the nonorthogonal ligand $\pi \rightarrow$ Mn(IV) $d\pi$ and Mn(III) $d\pi \rightarrow \pi^*$ ligand charge transfers.[19] Prominent absorptions of the second type at ~23 kK are well-known, while the Mn(IV) charge-transfer band has been assigned to a new band in the ultraviolet spectrum of $Mn_2(BuSal((-)\text{-}pn))_2(OH)O$ in methanol or chloroform at 36.5 kK. Since the charge-transfer bands do not involve the metal e_g orbitals for either Mn(III) or Mn(IV), an intervalence band involving only these orbitals might not have appreciable intensity. Several mixed-valence Mn(III)–Mn(II) complexes have been reported.[20] More to the point, a Mn(III)–Mn(IV) complex of bipyridyl, $[Mn_2(bpy)_4O_2]^{3+}$, has been prepared[21] and its x-ray structure determined.[22] Although this compound is reported to have a diffuse absorption in the 14–20-kK region, no detailed spectrum for it has been published. Thus no previous precedence has been set for the assignment of a Mn(III) → Mn(IV) intervalence band.

Stereochemistry of Dimers. Stereochemical considerations dictate that the tetradentate Schiff base ligand adopts a noncoplanar "cis" configuration in the dimers, i.e., either of the α or β forms as drawn in Figure 6. Molecular models indicate that, while the β isomer is somewhat strained, the α isomer would be so severely strained as to prelude existence. In support of this hypothesis, the β configuration has been found for octhedral complexes of Co(III)[23] and Mn(III)[24] with a cis configuration of a tetradentate Schiff base. No examples of the α isomer are known. Figure 6 displays the structural representation of the most likely geometrical isomers β-1, β-2, and β-3. The three isomers differ in the relative placement of the Schiff base donor atoms in the halves of the dimer. For the sake of clarity the OH^- and O^{2-} bridging groups and Mn(III) and Mn(IV) are not distinguished. Taking into account these distinguishing features as well as the presence of the optically active unsymmetrical pn chelate ring there are obviously many optical and geometrical isomers possible.

The feasibility of isomer separation is based on the assumption that the dimers would be kinetically inert, like the isoelectronic d^3 complexes of Cr(III). However, the mixed-valence system with the kinetically labile Mn(III) ion[25] and the expected rapid electron exchange between Mn(III) and Mn(IV) ions[3] would lead to a labilization of the coordination sphere of both metal ions. Preliminary NMR measurements on the dimers in chloroform solution indicate that the nonequivalent azomethine H or CH_3 groups are interconverting at a rapid rate which is commensurate with the NMR time scale.[26] Consideration of the various mechanisms, such as chelate ring opening with trigonal bipyramid formation or a pseudotrigonal twist, show that the interconversion of the nonequivalent groups could also lead to geometrical isomerization and racemization at the metal centers. No physical separation of the various geometrical and optical isomers of the dimer seems possible. Consistent with this postulate is the observation of only one spot on the thin-layer chomatograms of the various dimers.

Since we have no a priori way of selecting which of the many possible isomers is expected to be most stable and since the isomers are stereochemically nonrigid, the CD spectra have to be interpreted as the superposition of those of at least several of the isomers.

The $\pi \rightarrow \pi^*$ ligand band in the chloroform and methanol solution spectra of the Acet dimer is of the same sign and roughly the same magnitude as for the Mn(III) complex. In light of the stereochemical lability of the dimers the predominant source of molecular dissymmetry that gives rise to the rotatory strength of the dimer electronic transitions is most likely the same as for the square-pyramidal Mn(III) complex, i.e., the preferred δ (axial methyl) conformation of the central conformationally dissymmetric chelate ring. Apparently this stereochemical arrangement still holds in the β Schiff base configuration of the dimer. The signs of the ligand field Cotton effects also reflect the predominant presence of the δ ring conformer in the dimer. The similar rotatory strength of the Schiff base $\pi \rightarrow \pi^*$ transition Cotton effect for the dimer and Mn(III)–Acet complex is consistent with (but does not prove) little if any stereospecificity of the optically active Schiff base ligand, when bound in the β configuration, with respect to the disposition of the end chelate rings. The fact that the CD spectra of the Acet dimer are quite comparable in methanol and chloroform, two solvents of differing solvation properties, supports the notion that any contribution to the observed optical activity by small configurational effects (optical isomers) are swamped out here by the contribution from the central chelate ring dissymmetry.

The Sal dimers show very low rotatory strength for all of the Cotton effects, i.e., for the ligand field, charge-transfer, and ligand bands. This may arise from the fortuitous cancelation of a large number of Cotton effects of opposite sign. This appears to be an attractive hypothesis for the mixed-valence dimers which are expected to show a rich display of electronic transitions of varying energy. It is also likely that the lack of stereospecificity of the ligand results in the existence of a large number of isomers which leads to the observed result. A final point relates to the observation that the Sal dimer ligand field Cotton effect responds to the change in solvent from chloroform to methanol in the same way as the Mn(III) complex. Thus a subtle change in solvent gives rise to an observable change in the CD spectrum, indicating all other sources of molecular dissymmetry like chelate ring disposition in the various β isomers are canceling each other. This implies that a mixture of various geometrical and optical isomers must be present in solution.

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Registry No. [Mn(BuSal((−)pn))Cl], 58846-87-0; [Mn(BuSal((−)pn))H_2O]ClO_4, 58846-89-2; [Mn_2(BuSal((−)pn))$_2$(O)OH], 58933-75-8; [Mn(BuAcet((−)pn))Cl], 58846-90-5; [Mn(BuAcet((−)pn))H_2O]ClO_4, 58846-92-7; [Mn_2(BuAcet((−)pn))$_2$(O)OH], 58933-76-9.

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Contribution from the Physics Department,
Nuclear Research Center Democritos, Athens, Greece

Solvation Effects in Intermediate-Spin Ferric Complexes

ANGELOS MALLIARIS* and D. NIARCHOS[1]

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The formation of a highly covalent six-coordinate complex when bis(*N*,*N*-dialkyldithiocarbamato)iron(III) halide is dissolved in tetrahydrofuran is proved by Mössbauer studies in the temperature range between 4.2 and 300 K. Both infrared and Mössbauer studies have shown that THF is only weakly bonded to the paramagnetic center of the five-coordinate original complex. Analysis of quadrupole splitting, isomer shift, and hyperfine interactions shows that in the solvated complex the Fe^{3+} ion has $S = {}^5/_2$. The crystal field parameter D is negative, the $|\pm{}^5/_2\rangle$ Kramers doublet is the lowest spin state of the six-coordinate complex, and $|D| \geq 1.4°\ \mathrm{cm}^{-1}$.

I. Introduction

Most common trivalent iron complexes are six-coordinate, with octahedral symmetry around the paramagnetic center. Strong fields of O_h symmetry stabilize the "low-spin" ${}^2T_2(t_{2g}{}^5)$ term which originates from the free-ion ${}^2I$ state. The "high-spin" ${}^6A_1(t_{2g}{}^3\,e_g{}^2)$ term is found with weak ligand fields. In octahedral coordination no other term, except ${}^6A_1$ and ${}^2T_2$, can become the molecular ground state.[2a] By lowering the ligand field symmetry however, the ${}^4T_1(t_{2g}{}^4\,e_g)$ term (derived from ${}^4G$ in the free ion) can become the lowest lying state. The structural requirement for intermediate spin is met in the class of five-coordinate bis(*N*,*N*-dialkyldithiocarbamato)iron(III) halide complexes [hereafter denoted simply as Fe(dtc)$_2$X] which have nearly square-pyramidal symmetry around the ferric ion[2b] (Figure 1a). Considerable attention has been focused on these low-symmetry complexes with the unusual, for Fe^{3+}, coordination number 5 and total spin $S = {}^3/_2$.[3] Despite extensive studies in the solid state, there is only limited knowledge of solvation effects in Fe(dtc)$_2$X. de Vries et al.[4] have published some preliminary results which indicate that six-coordination occurs when Fe(dtc)$_2$X is dissolved in a solvent with good coordination properties. These authors observed, in the 77 K Mössbauer spectra, the appearence of a species with a small quadrupole splitting (QS = 0.7 mm/s) when Fe(dtc)$_2$Cl was dissolved in DMF, acetonitrile, etc. Since this value is characteristic of six-coordinate Fe^{3+}, they concluded that a solvent molecule was bound to the sixth vacant coordination site of the Fe^{3+}, giving rise to a complex with octahedral structure around the paramagnetic center. However it is not possible to make any safe predictions concerning the spin state of the six-coordinate complex from the QS magnitude alone. Magnetic susceptibility measurements, on the other hand, are very ambiguous, since these unstable complexes cannot be isolated from the solution where they exist in equilibrium with the five-coordinate parent compound of intermediate spin.

In this paper we report on studies of paramagnetic hyperfine structure and temperature dependence of IS and QS, measured by Mössbauer spectroscopy, which conclusively prove the formation of a highly covalent six-coordinate complex with $S = {}^5/_2$, when Fe(dtc)$_2$X is dissolved in tetrahydrofuran (THF).

II. Experimental Section

Fe(dtc)$_2$Br and Fe(dtc)$_2$Cl were prepared according to the method described by Martin and White,[5] which involves the reaction of Fe(dtc)$_3$ with a concentrated aqueous solution of the corresponding hydrohalide. The purity of the product, after recrystallization from $CHCl_3$–CCl_4, was confirmed by C, N, and H elemental analysis, as well as infrared and Mössbauer spectroscopy. The compounds used for preparation of solutions for the Mössbauer studies were synthesized with iron isotopically enriched in ${}^{57}Fe$. All solutions were prepared shortly before each measurement and immediately frozen to 77 K to prevent hydrolysis. The solid mixtures of five- and six-coordinate complexes (Figure 2) were obtained by recrystallizing solutions of Fe(dtc)$_2$X in THF under a continuous flux of nitrogen. The material used to record the spectra of Figure 2b was obtained by heating the product of the previous recrystallization for 48 h at 50 °C, to remove