of the metal to become seven-coordinate. For example, benzylpentacarbonyltungstate anion in DME does not react perceptibly with benzyl chloride or other alkyl halides after 18 h at room temperature. In contrast, however, $RM(CO)_5^-$ complexes react rapidly with several organometallic electrophilic species including Ph_3SnCl and Ph_3PAuCl. Chlorotriphenylstannane reacts with $PhCH_2W(CO)_5^-$ rapidly to provide 70–75% yields of $PhCH_2SnPh_3$. During this process a deep red intermediate forms at −78 °C which we believe is a seven-coordinate adduct. This quickly decomposes on warming to room temperature to the observed tin species, $W(CO)_6$ and $W(CO)_5Cl^-$. Interestingly, the much less reactive $Ph_3SnW(CO)_5^-$ [3] fails to react with benzyl chloride, even at reflux, in DME.[23] By the same procedure we have also shown that $EtM(CO)_5^-$ ions provide the known $EtSnPh_3$ complexes in similar yields, thus confirming our formulation of these solvolytically unstable species.

Although our preliminary studies on the reactivities of $RM(CO)_5^-$ suggest that these species will not be useful as stoichiometric organic reagents in the same sense as are corresponding alkylcarbonylferrates,[24] we are confident that they will serve as useful precursors to novel organometallic compounds and we shall report on these studies in due course.

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Registry No. I, 62197-85-7; II, 62197-83-5; III, 62228-09-5; IV, 62197-81-3; V, 62197-79-9; VI, 62197-78-8; VII, 62197-77-7; VIII, 62197-75-5; $Na_2Cr(CO)_5$, 51233-19-3; methyl iodide, 74-88-4; benzyl chloride, 25168-05-2; $NCCH_2Cl$, 107-14-2; ethyl bromide, 74-96-4; $Na_2W(CO)_5$, 57127-91-0; $W(CO)_6$, 14040-11-0; methyl bromide, 74-83-9.

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Contribution from the Departments of Chemistry, Carnegie-Mellon University,
Pittsburgh, Pennsylvania 15213 and the University of Nebraska, Lincoln, Nebraska 68588

Manganese Schiff Base Complexes. 5. Synthesis and Spectroscopy of Some Anion Complexes of *N,N′*-Ethylenebis(acetylacetone iminato)manganese(III)

LAURENCE J. BOUCHER*[1a,2] and VICTOR W. DAY[1b]

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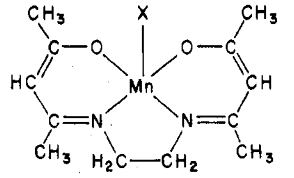
The synthesis of the series of new five-coordinate Mn(III) complexes of the type [Mn(acen)X] where acen is the dianion of the tetradentate ligand *N,N′*-ethylenebis(acetylacetone imine) and X^- = Cl^-, Br^-, NO_2^-, SCN^-, I^-, N_3^-, NCO^-, CN^-, and $C_2H_3O_2^-$ is reported. Two hydrated forms, $[Mn(acen)I]\cdot 2H_2O$ and $[Mn(acen)C_2H_3O_2]\cdot H_2O$, were also isolated. The green-brown crystalline solids show normal high-spin magnetic moments in chloroform solution at room temperature. The infrared spectra of the solids have been measured in the range 4000–100 cm^{-1} and band assignments suggested. The electronic absorption spectra of the materials in chloroform, ethanol, and pyridine have been determined and tentative band assignments made to ligand field, charge-transfer, and ligand transitions. The solid-state structure of [Mn(acen)Cl] has been determined by single-crystal x-ray diffraction techniques and is described.

Introduction

Although a large number of Mn(III) and Mn(II) complexes of a tetradentate Schiff base *N,N′*-ethylenebis(salicylaldiminato) dianion (salen), have been synthesized,[3] analogous complexes of the well-known and ubiquitous ligand *N,N′*-ethylenebis(acetylacetone imine) have not been reported. Complexes of this type of ligand have been extensively studied for the latter transition metals, especially for the oxygen-carrying cobalt system.[4] Since the two classes of ligands have different donor strengths and steric requirements, it is of interest to determine whether the coordination chemistry of their Mn(III) and Mn(II) chelates can be related to the properties of the tetradentate Schiff base. Attempts to prepare [Mn(acen)X] using the standard technique of refluxing a mixture of Mn(II) salts and the ligand in ethanol with aeration lead only to the formation of polynuclear Mn(II) complexes.[5] Another approach to the synthesis of the desired complexes was then sought and an Mn(III) salt, manganic acetate, was



[Mn(acen)X]

X = $Cl^-, Br^-, I^-, NCO^-, NO_2^-, N_3^-, SCN^-, C_2H_3O_2^-, CN^-$

Figure 1. Structural representation of [Mn(acen)X].

used as a starting material. We have thus synthesized and characterized a series of new (presumably) five-coordinate complexes [Mn(acen)X], where $X^- = Cl^-, Br^-, I^-, N_3^-, SCN^-, NCO^-, CN^-, NO_2^-$, and $C_2H_3O_2^-$ (see Figure 1 for a structural representation). [Mn(acen)Cl] has been shown by a single-crystal x-ray structural analysis to be a five-coordinate monomeric complex with the chloride anion occupying the apical site of a square-pyramidal coordination polyhedron.

Experimental Section

Materials. The Schiff base H_2acen[6] and $Mn(C_2H_3O_2)_3 \cdot 2H_2O$[7] were prepared as previously described. All other chemicals and solvents were reagent grade and used without further purification.

Synthesis of Complexes. The initial material prepared was [Mn(acen)Cl] and all other complexes were prepared from it.

[Mn(acen)Cl]. The ligand H_2acen, 10.00 g (4.46×10^{-2} mol), dissolved in 160 mL of methanol was added to a slurry of 10.00 g (3.74×10^{-2} mol) of $Mn(C_2H_3O_2)_3 \cdot 2H_2O$ in 150 mL of methanol. The resulting mixture was stirred for 12 h at room temperature and the solvent removed in an airstream. The residue was then extracted with 200 mL of distilled water and filtered. The filtrate was extracted with 200 mL of chloroform to remove unreacted excess ligand. The aqueous phase was then treated with 50 g of sodium chloride and extracted with 200 mL of chloroform. At this point the aqueous phase was light orange-brown and contained a brown insoluble solid, presumably a manganese(III) oxide.

The chloroform solution of the complex was reextracted into 100 mL of distilled water. The aqueous phase was then treated with 50 g of sodium chloride and extracted with 2 × 100 mL of chloroform. The chloroform phase was filtered, dried, and evaporated to dryness. The pure product was recrystallized from 50 mL of benzene and 500 mL of petroleum ether (bp 30–60 °C). The lustrous black crystals were isolated on a filter, washed with petroleum ether, and air-dried; yield 5.0 g, 43% based on Mn(III) used.

[Mn(acen)X]. A solution of [Mn(acen)Cl], 0.30 g (9.6×10^{-4} mol) in 50 mL of distilled water, was treated with 0.1 mol of NaX. The resulting aqueous solution was extracted with 4 × 50 mL of chloroform. The chloroform phase was then extracted into 50 mL of distilled water. The final aqueous phase was then treated with 0.1 mol of NaX and extracted, 4 × 50 mL, into chloroform. This chloroform phase was filtered, dried, and reduced in volume to 25 mL and the pure solid was crystallized by addition of 200 mL of petroleum ether. The solids were isolated on a filter, washed with petroleum ether, and air-dried; yield 0.15–0.20 g, ~50% based on [Mn(acen)Cl] used as starting material. Two hydrated materials, $[Mn(acen)I] \cdot 2H_2O$ and $[Mn(acen)C_2H_3O_2] \cdot H_2O$, were dried in vacuo over P_2O_5 at 60 °C for 16 h in a drying pistol.

Spectral Measurements. Visible–ultraviolet absorption spectra were recorded with a Cary 14 spectrophotometer using chloroform, ethanol, and pyridine solutions of the complexes. Infrared spectra of the materials, in KBr disks or fluorolube mull, were determined with a PE 337-B grating spectrophotometer for the 4000–400-cm^{-1} region while the materials in CsI disks were examined in the 650–100-cm^{-1} region with a Digilab 296-block spectrometer. Magnetic moment measurements on the solids were carried out by the Faraday method. The susceptibilities were found to be independent of field strength and the values for duplicate measurements agreed within ±2% (±0.1 μ_B). $Hg[Co(SCN)_4]$ was used as a calibrant and diamagnetic corrections were calculated from Pascal's constants.[8] Solution magnetic moments were determined by the NMR method[9] using 5% (v/v) tetramethylsilane–chloroform solutions of the complex, 5 mg/mL (~1.5×10^{-2} M), with a Perkin Elmer R-20, 60-MHz spectrometer at ambient temperature (~34 °C). Melting points of the solids were taken with a Fisher-Johns melting point apparatus and are uncorrected. NMR spectra of the paramagnetic samples in chloroform were taken with a 250-MHz spectrometer at ambient temperature.

Crystallographic Analysis of [Mn(acen)Cl].[10] Lustrous black well-shaped single crystals of [Mn(acen)Cl] obtained as described above are monoclinic, space group $P2_1/n$ (an alternate setting of $P2_1/c$-C_{2h}^5; No. 14)[11] with $a = 7.220$ (1) Å, $b = 24.350$ (3) Å, $c = 8.067$ (1) Å, $\beta = 101.37$ (1)°, and $Z = 4$. Diffracted intensities were measured for 6346 independent reflections having $2\theta_{MoK\alpha} < 71°$ (2.0 times the number of data in the limiting Cu Kα sphere) on a computer-controlled Syntex $P\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (≥2.00° wide) θ–2θ scans. The structure was solved using the "heavy-atom" technique. The resulting structural parameters have been refined (anisotropically for nonhydrogen atoms and isotropically for hydrogen atoms) to convergence [R_1 (unweighted) = 0.048 and R_2 (weighted) = 0.056 for 4620 independent reflections having $2\theta_{MoK\alpha} < 71°$ and $I > 2\sigma(I)$] in cycles of empirically weighted full-matrix least-squares refinement.

Results and Discussion

Synthesis. The formation of the complex $[Mn(acen)C_2H_3O_2]$ occurs readily at room temperature. In a few hours, a good yield (43%) is achieved. The reaction sequence is

$$Mn(C_2H_3O_2)_3 \cdot 2H_2O + H_2acen \rightarrow [Mn(acen)C_2H_3O_2] + 2HC_2H_3O_2 + 2H_2O$$

$$[Mn(acen)C_2H_3O_2] + Cl^- \rightarrow [Mn(acen)Cl] + C_2H_3O_2^-$$

presumably a complicated one since it involves reaction with manganese(III) acetate which has been shown to possess a complex basic acetate structure.[12] Thus the reactive Mn(III) species in methanol may be any of several mononuclear or polynuclear Mn(III) complexes with or without coordinated acetate anions. Nonetheless, under the same reaction conditions H_2salen gives over a 90% yield of $[Mn(salen)C_2H_3O_2]$. The substantially lower yield for H_2acen may be due to its chemical instability toward hydrolysis which is promoted by the traces of acetic acid present in the manganese(III) acetate or toward oxidation by the metal reagent which is a good oxidizing agent. More likely, the problem may lie in the inability (vide infra) of the H_2acen ligand to react with Mn(II) which is formed during the sluggish synthetic reaction by a redox decomposition of the manganese(III) acetate. In contrast to this, with H_2salen, [Mn(salen)] forms quite readily and is rapidly air oxidized to the desired Mn(III) complex.[3]

A preparative procedure which involves the air oxidation of a mixture of a Mn(II) salt and the ligand H_2acen in ethanol leads primarily to the formation of a series of polynuclear Mn(II) complexes of the free H_2acen ligand.[5] Aeration of a refluxing methanol solution of ligand dianion and excess $MnCl_2$ does however yield small amounts of [Mn(acen)Cl] in <5% yield. Excess Mn(II) salt is needed since stoichiometric amounts of Mn(II) and acen^{2-} do not yield any product except the hydrous manganese oxide and free ligand (H_2acen). The lack of formation of [Mn(acen)X] from H_2acen and MnX_2 salts is in marked contrast to the ready formation of the various [Mn(salen)X] derivatives under identical reaction conditions. In the latter case, [Mn(salen)] forms initially and then is rapidly air-oxidized to the Mn(III) complex. The difference in behavior of the two Schiff base systems cannot be related to the expected stability of their complexes nor to the ability of the ligand to stabilize the higher oxidation state, since both of these effects should tend to favor the ready formation of [Mn(acen)X]. The stability order generally ranks the acetylacetone-based Schiff base as being more stable than those derived from salicylaldehyde.[13] Furthermore, the Co(II) → Co(III) oxidation potential is more favorable for the acen complex compared to salen.[14]

Small amounts (<5%) of [Mn(acen)Cl] can be obtained from the reaction of H_2acen and Mn(III) (the Mn(III) is

Table I. Elemental Analyses[a] of [Mn(acen)X] Complexes

X^-	Color	% calcd			% found			Mp, °C	Magnetic moments, μ_B	
		C	H	N	C	H	N		Solid[b]	$CHCl_3$ soln[c]
Cl^-	Olive green	46.38	5.80	9.01	46.73	5.71	8.43	212	4.86	4.91
Br^-	Olive green	40.59	5.07	7.89	40.84	5.13	8.43	215	4.99	4.85
I^-	Brown	35.85	4.48	6.96	35.99	4.67	6.86	220	5.00	5.07
N_3^-	Mustard yellow	45.44	5.67	22.07	45.11	5.66	21.14	149	4.58	4.89
NCS^-	Mustard yellow	46.84	5.40	12.60	46.02	5.27	12.64	197	4.96	4.98
NO_2^-	Mustard yellow	44.88	5.60	13.08	44.51	5.62	12.94	145	4.68	4.77
NCO^-	Brown	49.23	5.67	13.24	48.90	5.78	13.58	198	4.90	4.96
CN^-	Rust brown	51.84	5.97	13.95	51.02	5.99	13.57	142	4.30	4.82
$C_2H_3O_2^-$	Olive green	50.32	6.02	8.38	49.32	6.31	7.74	141	5.09	4.96
$C_2H_3O_2^- \cdot H_2O$	Olive green	47.74	3.30	7.94	47.45	6.15	8.41	77	4.95	4.83
$I^- \cdot 2H_2O$	Mustard yellow	32.90	5.04	6.39	32.89	4.74	6.20	94	4.66	4.97

[a] Performed by Chemalytics, Tempe, Ariz. [b] 20 °C. [c] 34 °C.

generated in situ by the oxidation of aqueous Mn(II) chloride with stoichiometric amounts of $KMnO_4$ or MnO_2). Another synthetic method that works well for the corresponding salicylaldehyde complex was unsuccessful when applied to the acetylacetone derivative.[15] Thus, the reaction of [Mn(acac)$_3$] with excess ethylenediamine gives rise to reduction of the Mn(III) to Mn(II) by the amine with the formation of [Mn(acac)$_2$en].[16] Even though H_2acen is formed in a side reaction, no evidence is obtained for a reaction of this ligand with Mn(II) in air. Furthermore, no intramolecular ligand condensation within [Mn(acac)$_2$en] to form [Mn(acen)] is noted. Finally, the reaction of [Mn(acac)$_2$] and H_2salen in ethanol and air does not lead to exchange but yields instead the six-coordinate complex [Mn(salen)acac].[17]

The difference noted here between the coordination chemistry of H_2acen and H_2salen may be related to the ability of the ligands to form Mn(II) complexes. Thus, Mn(II) complexes of the tetradentate Schiff base ligands like H_2salen and its derivatives are well-known while similar complexes of H_2acen are unknown. This may be a consequence of steric effects. One way the two ligand systems differ is that the azomethine carbon substituent is H for H_2salen while it is CH_3 for H_2acen. Steric interaction of the methyl substituent with the ethylene hydrogens of the central chelate ring may effectively prevent formation of the tetradentate ring system needed for stability of the complex for the large and weakly binding high-spin Mn(II) ion (especially in a good coordinating solvent like methanol). Consistent with this steric argument is the synthesis of Mn(II) complexes of the type *trans*-[MnL$_2$(H$_2$O)$_2$] where L is the bidentate β-ketimine 4-amino-3-penten-2-one, 4-methylamino-3-penten-2-one, or 4-anilino-3-penten-2-one.[18] In these complexes, the intra- and interligand interactions can be minimized by adopting a *trans*-N_2O_2 arrangement. There is a report of an Mn(II) complex of the tetradentate Schiff base derived from acetylacetone and 1,3-diaminopropane-2-ol.[19] Presumably the presence of the trimethylene linkage in the central chelate ring relieves steric strain in the ligand. It is interesting to note that no Mn(III) complexes of the latter ligand or of the bidentate β-ketimine ligands have been reported.

The various anion complexes, [Mn(acen)X], can be prepared by a simple anion-exchange reaction with either the chloride or the acetate complex.

$$[\mathrm{Mn(acen)Cl}] + 2\mathrm{H_2O} \rightleftarrows [\mathrm{Mn(acen)(H_2O)_2}]^+ + \mathrm{Cl}^-$$

$$[\mathrm{Mn(acen)(H_2O)_2}]^+ + \mathrm{X}^- \xrightleftharpoons{\text{in } \mathrm{H_2O/CHCl_3}} [\mathrm{Mn(acen)X}]$$

In aqueous solution the Mn(III) complexes are most likely hydrated and the species are involved in a series of labile equilibria. Addition of a large excess of a coordinating anion should shift the equilibria to favor the formation of the desired product. However, their solubility is high and they do not generally precipitate out of aqueous solution. Fortunately, the distribution coefficient is such that the products can be conveniently extracted into chloroform. Using this method, the complexes [Mn(acen)X] where $X^- = Cl^-, Br^-, I^-, N_3^-, NCO^-, NCS^-, CN^-, NO_2^-$, and $C_2H_3O_2^-$ were prepared. However, complexes where $X = F^-, ClO_4^-$, and NO_3^- were not formed. This may be due to the lack of complex formation in aqueous solution with these poorly coordinating anions and/or to the limited solubility of the anion complex in chloroform. It is interesting to note that the CN^- complex forms for the acen system while it apparently does not for the salen or porphyrin complexes.[3] In contrast to the other anions, addition of CN^- to an aqueous solution of [Mn(acen)Cl] yields a color change, i.e., to blood red, which extracts into chloroform as a green solution. The initial color change is probably related to the rapid formation of multicyanide complexes which revert back to the monocyanide on extraction. The complexes are not allowed to reside in the aqueous phase for more than a few minutes, thus preventing the slow formation of [Mn(CN)$_6$]$^{3-}$.

Characterization of Complexes. Elemental analyses of the solids are given in Table I. Except for the iodide and acetate complexes, crystals of these materials contain no solvent molecules. Mild drying of the iodide and acetate complexes at 60 °C in vacuo yields the anhydrous materials. Since the materials are extracted from aqueous solution and are subject to at best mild drying conditions and no attempt is made to exclude water in the workup, it appears that the formation of six-coordinate structures with a coordinated water molecule is not favored. In fact, crystallization of them from pyridine does not yield the pyridinate complex. Whether six-coordinate adducts can be prepared with other Lewis bases is yet to be determined.

The new complexes are crystalline solids whose colors vary (Table I). The solids generally darken slowly and then melt with decomposition. The melting points of the complexes, which are shown in Table I, can be used to separate the solids into two groups, namely, those that melt (or decompose) in the high-temperature range (195–220 °C) and those that melt in a lower temperature range (140–150 °C). It is interesting to note that the hydrated materials [Mn(acen)I]·2H$_2$O and [Mn(acen)C$_2$H$_3$O$_2$]·H$_2$O show low melting points of 94 and 77 °C, respectively. Removal of the lattice water in vacuo at 60 °C raises the melting point of the iodide complex to above that of the high-melting solids while the melting point of the acetate complex now falls near the range for the low-melting solids. If, however, the hydrated materials are dried at ~100 °C, they melt with decomposition before they can dehydrate.

Solid-State Structure of [Mn(acen)Cl]. The results of the precise x-ray structural analysis for single crystals of [Mn(acen)Cl] reveal that the crystals are composed of discrete

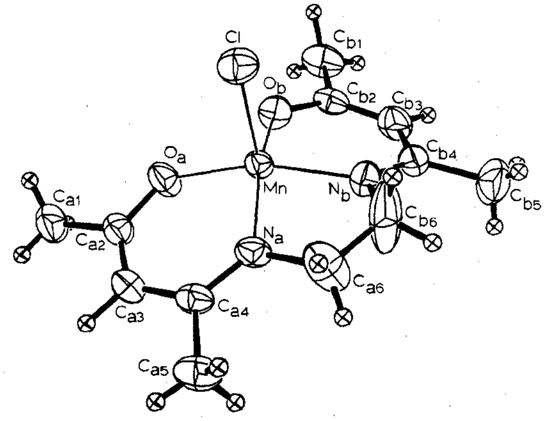


Figure 2. Perspective ORTEP drawing of the five-coordinate square-pyramidal [Mn(acen)Cl] molecule. All nonhydrogen atoms are represented by (50% probability) ellipsoids which reflect their refined anisotropic thermal parameters. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

mononuclear five-coordinate square-pyramidal molecules like that shown in Figure 2. Although the molecule possesses no rigorous crystallographic symmetry, the coordination polyhedron approximates idealized C_{4v} symmetry and the molecule as a whole approximates quite closely its maximum possible symmetry of C_s-*m*; Mn, Cl, the midpoint of the C_{a6}–C_{b6} bond, and the midpoints of the $O_a \cdots O_b$ and $Na \cdots N_b$ vectors ideally lie on this pseudomirror plane. Atoms of the two "equivalent halves" of the molecule in Figure 2 are labeled with a subscripted a or b, respectively. The four coordinated oxygen and nitrogen atoms of the acen ligand are coplanar to within 0.001 Å and comprise the "square" base of the coordination polyhedron which is normal to the pseudo-fourfold axis that ideally passes through the Mn and apical Cl atoms. The Mn atom is displaced by 0.344 Å from the least-square mean plane of the four "basal" atoms toward the Cl atom.

Averaged values for the complexing bond length are Mn–Cl = 2.381 (1) Å, Mn–N = 1.969 (2, 5, 5) Å,[20] and Mn–O = 1.901 (2, 7, 7) Å.[20] Averaged values for the chemically distinct types of bonds between nonhydrogen atoms within the acen ligand are C_2–O = 1.298 (4, 0, 0) Å,[20] C_4–N = 1.309 (4, 3, 3) Å, C_6–N = 1.467 (5, 8, 8) Å, C_1–C_2 = 1.498 (5, 3, 3) Å, C_2–C_3 = 1.363 (4, 4, 4) Å, C_3–C_4 = 1.416 (4, 1, 1) Å, C_4–C_5 = 1.511 (5, 0, 0) Å, and C_{a6}–C_{b6} = 1.395 (7) Å.

Although the atoms of each seven-atom (C_1, C_2, C_3, C_4, C_5, O, and N) acetylacetone imine skeletal grouping are coplanar to within 0.05 Å, the entire acen ligand in [Mn(acen)Cl] is quite nonplanar. Each planar acetylacetone imine grouping is folded along its O···N polyhedral edge (by 14.9° for *a* and 18.6° for *b*) out of the plane of the "square" base and away from the Cl atoms. The atoms of each six-atom (Mn, O, C_2, C_3, C_4, and N) chelate ring are coplanar to within 0.05 Å. The four-atom (N_a, C_{a6}, C_{b6}, and N_b) grouping for the remaining chelate ring is similarly folded by 9.7° along its N···N polyhedral edge out of the plane of the "square" base and toward the Cl atom.

Magnetic Susceptibilities and Melting Points. The magnetic moments of the complexes are given in Table I. The chloroform solution moments are in the range 4.8–5.1 μ_B and are consistent with the presence of monomeric high-spin d^4 Mn(III) complexes. However, on the basis of the solid-state moments, the complexes can be divided into two groups: one which shows a normal moment (4.8–5.1 μ_B) with $X^- = Cl^-$, Br^-, I^-, NCS^-, NCO^-, and $C_2H_3O_2^-$ and a second which shows moments that are lowered from the normal value (4.3–4.7 μ_B) for $X^- = NO_2^-$, N_3^-, and CN^-. Although some lowering of the magnetic moment may arise from other sources such as low-symmetry ligand fields and spin-orbit coupling, a more likely source is the presence of an intramolecular antiferromagnetic interaction in the solid between neighboring paramagnetic manganese atoms. This type of interaction could occur if the [Mn(acen)X] molecules exist as dimers or other associated species. Some of the [Fe(salen)X] complexes[21] form dimers where the two coordination polyhedra are linked at the base by having metal atoms of each one interact with a ligand oxygen atom of the other. Although this kind of structure is well-known for salen complexes[22] and has been postulated for Mn(III) derivatives as well, no examples of this form for acen complexes are known.

The infrared spectrum of [Mn(acen)NO_2] (vide infra) indicates that the anion is acting as a bridging ligand in the solid state. A type of infinite-chain structure with the anion bridging adjacent manganese atoms has been observed for [Mn(salen)$C_2H_3O_2$].[23] The low magnetic moment and infrared spectra appear to support the existence of a similar structure for [Mn(acen)NO_2]. However, the infrared spectra of [Mn(acen)X] for $X^- = N_3^-$ and CN^- indicate that the anions are not acting as bridging ligands. Thus in these cases, the low magnetic moments could arise from dimer formation in the solid involving the acen ligand.

Examination of the melting points and magnetic moments shows that there is an empirical correlation between these data. Thus, those solids that melt in the high-temperature range show normal magnetic moments. Conversely, those solids that show melting points in the low-temperature range show magnetic moments lowered from the spin-only value. Since the solid-state x-ray structure of [Mn(acen)Cl] reveals a monomeric five-coordinate square-pyramidal species, it is tempting to assign a similar structure to the other members of this (high-melting, normal magnetic moment) group. The iodide complex shows interesting behavior in that the hydrated crystalline form shows a low melting point and lowered magnetic moment while the anhydrous form has a high melting point and normal magnetic moment. Thus mild drying, at 60 °C, may transform the solid-state structure. Both the anhydrous and hydrated crystalline forms of the acetate complex have (albeit different) low melting points and normal magnetic moments.

The 5–10% lowering of the solid magnetic moments is in the same range as previously reported for manganese(III) Schiff base complexes.[3] For example, [Mn(Bu(salen))X] ($X^- = NCO^-$, N_3^-, I^-, Cl^-), [Mn(salen)X] ($X^- = Br^-$, $C_2H_3O_2^-$), [Mn(aceten)X] ($X^- = C_2H_3O_2^-$, NCS^-), and [Mn(SB)Cl] (SB^{2-} = 4-CH_3salen, 4-Br(salen), 3,4-$(CH_3)_2$aceten) all show reduced moments.[24] It should be pointed out that the other anion complexes show normal magnetic moments. Thus, the formation of antiferromagnetically coupled associated species in the solid state is a function of the particular anion and Schiff base in the complex; no simple pattern is evident which relates anion or Schiff base donor strength to the formation of dimers or to the magnitude of magnetic moment lowering. Of course, the formation of associated species and the extent of the magnetic coupling may be a complicated combination of a number of factors, including crystal packing forces and bonding effects. In fact, they may depend on the conditions which obtain during crystallization of the solid. Finally, it must be pointed out that the observation of normal solid magnetic moments at room temperature may be due to the presence of monomeric units in the crystal or due to the presence of "loose" dimers or other associated species in which there is a weak exchange interaction.[25] Detailed magnetic measurements at various temperatures as well as further crystallographic studies are obviously needed.

The solids are soluble in chloroform, benzene, acetone, ethanol, methanol, pyridine, and water. The solutions appear

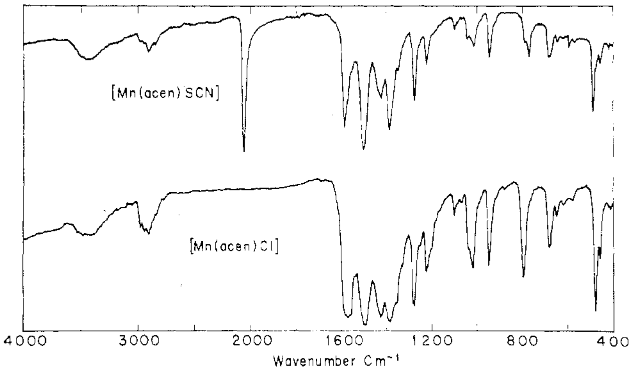


Figure 3. Infrared spectra of [Mn(acen)Cl] and [Mn(acen)NCS] in KBr disks.

unchanged at room temperature after several days and the materials can be reisolated in their original form. Similarly, refluxing of solutions of the complexes in methanol or chloroform for 24 h in air does not lead to decomposition. Conversely, refluxing pyridine solutions of the complexes for 24 h in air does lead to decomposition. Also, refluxing aqueous solutions leads to a brown, insoluble manganese(III) oxide, small amounts of the original complex, and an uncharacterized Mn(III) complex after 24 h. The major product (in 40% yield) is $C_7H_{13}N_2X$, a 2,3-dihydro-1,4-diazepenium salt which forms from the intramolecular condensation of H_2acen[26] that is liberated in the decomposition of [Mn(acen)X]. Aqueous solutions of [Mn(acen)X] at pH 11 and room temperature slowly yield H_2acen and manganese(III) oxide. Although qualitatively similar, the solution stability of [Mn(salen)X] complexes appears to be greater than that of [Mn(acen)X]. Thus, higher pH (≥12) is required to decompose an aqueous solution of [Mn(salen)X]. Neutral aqueous solutions of [Mn(salen)X] can be refluxed for 24 h with only slight decomposition (~1%). Reaction of a stoichiometric amount of the reducing agent $Na_2S_2O_4$ and [Mn(acen)X] in aqueous solution rapidly yields the free ligand and Mn(II). Presumably the initial reaction is a reduction of Mn(III) to Mn(II) which is followed by demetalation of the unstable [Mn(acen)]. Addition of H_2S to an aqueous solution of [Mn(acen)Cl] also slowly yields H_2acen with an insoluble brown manganese sulfide. Similar results are obtained for the reaction of [Mn(salen)X] with H_2S or $Na_2S_2O_4$.

Infrared Spectra. Spectra in the 4000–400-cm^{-1} region were taken of the solids in KBr disks. Figure 3 displays typical spectra. All of the complexes show prominent ligand absorptions which are insensitive to the anion. Since acen complexes show similar absorptions, bands at 2960, 2910, and 2860 cm^{-1} can be assigned to the various C–H stretching vibrations of the CH_2, C–H, and CH_3 groups.[27] The strongest absorptions in the spectra are seen at 1573–1585 and 1495–1502 cm^{-1}. These broad bands are associated with the stretching vibrations of the unsaturated C═N, C═C, and C═O linkages in the ligand. Medium-intensity absorptions at 1425 and 1387 cm^{-1} can be assigned to the CH_3 and CH_2 deformations.

Absorptions which arise from the internal vibrations of the axially coordinated anion are also seen in the NaCl region of the IR spectra. For example, the multiple-bond stretching frequencies of NCS^-, N_3^-, NCO^-, and CN^- are found at 2055, 2040, 2190, and 2105 cm^{-1}, respectively. In the case of both the SCN^- and NCO^- complexes, the frequency of the band is consistent with the presence of the N-bonded anion.[28] This result is confirmed for the former complex by the observation of ν(CS) at 770 cm^{-1}. The frequencies of the bands for all of these complexes are typical for the terminal *non*bridging anions. The acetate complex shows bands at ~1540–1550 (b), 1410, and 655 cm^{-1} which can be assigned to the carboxylate bands ν_{as}(OCO), ν_s(OCO), and δ(OCO). This and the normal magnetic moment are consistent with the presence of a terminal nonbridging acetate.[29] The nitrite complex is somewhat unusual in that it shows $\nu(NO_2^-)$ absorption at 1202 and 1045 cm^{-1} while no prominent δ(ONO) is seen at ~830 cm^{-1}. Of course, additional bands may be obscured by the many other strong ligand absorptions. However, the frequencies of the observed bands seem to indicate that the nitrite ion may be acting as a bridge between manganese atoms, thus forming an infinite chain in the solid.

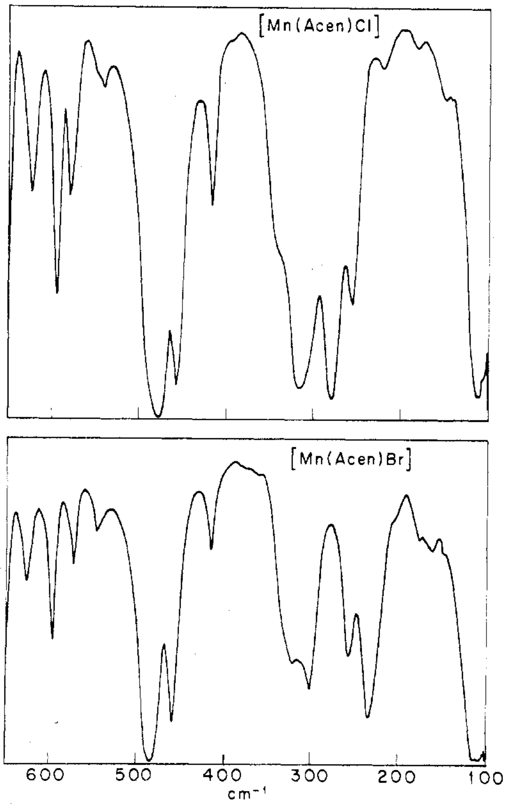


Figure 4. Infrared spectra of [Mn(acen)Cl] and [Mn(acen)Br] in CsI disks.

The far-infrared spectra (650–100 cm^{-1}) were obtained with [Mn(acen)X] in CsI disks. Typical spectra are shown in Figure 4. The spectra show a number of medium-to-strong ligand absorptions, presumably ligand deformations, which are insensitive to the anion at 622, 594, 574, 484, 458, 260, and 110 cm^{-1}. In addition, two medium-strong absorptions appear at 325 and 300 cm^{-1}, which may contain contributions from the Mn–O and Mn–N stretches. Although these bands are not regularly dependent on the anion, they do show changes in relative intensity on going from one anion to the next and in one case, Cl^-, they appear to merge into a broad strong band. There are other strong absorptions in the spectra which are related to the presence of the axially bound anion. For example, the halide complexes Cl^-, Br^-, and I^- show additional bands at 279, 234, and 218 cm^{-1}, respectively. The progression is consistent with the assignment of these bands to the ν(Mn–X) stretching frequency. An analogous assignment has been made of ν(Mn–Cl) and ν(Mn–Br) to bands at 290 and 262 cm^{-1} for $[Mn(acac)_2X]$.[30] The lower frequency of these absorptions for [Mn(acen)X] may be related to an enhanced in-plane donation in this complex which results in a weakened axial bond.

The spectrum of the N_3^- complex shows a δ(NNN) band at 634 cm^{-1} which is quite close to that of the ionic N_3^-. In addition, two broad overlapping bands are seen at 227 and 195

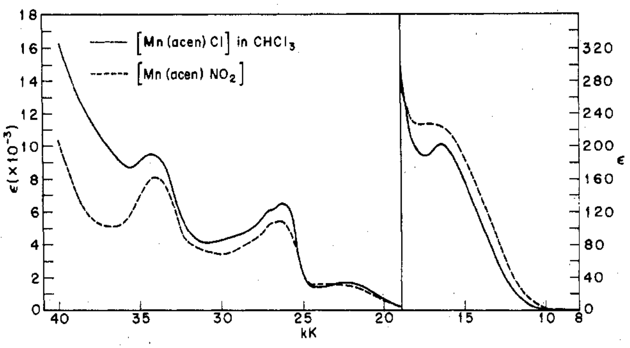


Figure 5. Electronic absorption spectra of [Mn(acen)Cl] and [Mn(acen)NO_2] in chloroform.

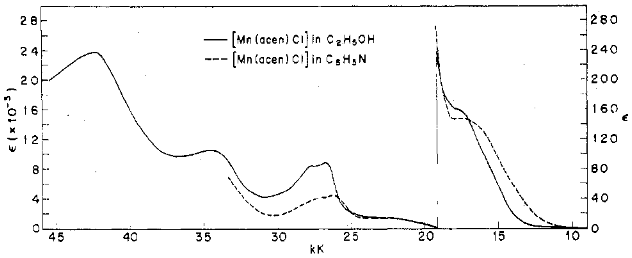


Figure 6. Electronic absorption spectra of [Mn(acen)Cl] in pyridine and ethanol.

cm^{-1}. The NO_2^- and NCO^- complexes show a similar pattern of absorptions at 211, 192, and 233, 198 cm^{-1}, respectively. The spectrum of the NCS^- complex contains a strong band at 232 cm^{-1}. The interpretation is complicated here by the fact that the solid-state spectra of the sodium or potassium salts of X^- generally show similar lattice absorptions in this region.[31] Since no other additional bands appear in the spectrum, it is quite likely that the observed bands for [Mn(acen)X] do contain a contribution from the ν(Mn–N) and δ(Mn–N) vibrations. If this is the case, then the low frequency of the ν(Mn–N) is indicative of a relatively weak axial bond to these anions. The δ(NCO) band appears at 610 cm^{-1} while the analogous band for NCS^- is obscured by acen absorptions in the 400–500-cm^{-1} region. The CN^- complex shows medium-intensity bands at 388 and 226 cm^{-1} which may be assigned to the ν(Mn–C) and δ(MCN) absorptions. Finally, the acetate complex shows a medium-intensity band at 176 cm^{-1}. It must be pointed out that interpretation of the far-infrared spectra is quite equivocal and any assignments which are made should be considered tentative.

Aside from small frequency shifts and relative intensity changes of the bands that generally follow change in anion, no obvious correlation can be made between the IR spectra of the solids and the magnetic moments. While the anhydrous solids show no absorption in the ν(OH) region, [Mn(acen)I]·$2H_2O$ shows lattice water bands at 3460, 3270, and 3180 cm^{-1} and [Mn(acen)$C_2H_3O_2$]·H_2O shows bands at 3570 and 3390 cm^{-1}. In the lower frequency region, the spectra of the hydrated and anhydrous solid for [Mn(acen)I] are different in detail. For example, the ligand bands at 1575, 625, 598, and 459 cm^{-1} are shifted to 1585, 633, 607, and 464 cm^{-1} on going from the latter to the former. Further, a sharp medium-intensity band at 776 cm^{-1} in the hydrated form is split into two bands at 774 and 763 cm^{-1} in the anhydrous form. This crystal lattice effect on the spectrum is presently difficult to interpret. Conversely, the spectra of the hydrated and anhydrous forms of [Mn(acen)$C_2H_3O_2$] are identical.

Electronic Spectra. The absorption spectra of the complexes in chloroform, ethanol, and pyridine were measured in the 1250–220-mμ region. Typical spectra are shown in Figures 5 and 6 and the frequencies of the absorption maxima are listed in Table II. The spectra of the hydrated materials for I^- and $C_2H_3O_2^-$ are identical with those of the anhydrous complexes.

Table II. Absorption Maxima (× 10^3 cm^{-1}) of [Mn(acen)X] Complexes in Chloroform

X^-	$\bar{\nu}$ (log ϵ_{max})
Cl^-	16.4 (2.31), 22.4 (3.23), 26.2 (3.81), 34.2 (3.98)
Br^-	16.4 (2.32), 22.3 (3.20), 25.9 (3.72), 33.8 (3.91)
I^-	16.5 (2.16), ~22.2, 26.6 (3.68), 33.6 (3.79)
N_3^-	~16.7, ~22.5, 26.6 (3.78), 34.2 (3.92)
NO_2^-	16.6 (2.36), ~22.7, 26.3 (3.73), 34.1 (3.91)
OCN^-	16.6 (2.26), 22.5 (3.20), 26.3 (3.68), 34.3 (3.99)
NCS^-	16.5 (2.27), 22.4 (3.22), ~26, 34.1 (4.04)
CN^-	16.6 (2.36), 23.6 (3.20), 26.6 (3.68), 33.9 (3.80)
$C_2H_3O_2^-$	~16.7, 22.7 (3.26), 26.6 (3.83), 34.0 (3.91)
Cl^- [a]	17.5 (2.20), 22.5 (3.15), 26.8 (3.95), 34.5 (4.00), 42.4 (4.38)
Cl^- [b]	17.5 (2.17), 22.8 (3.15), 26.2 (3.65)

[a] Ethanol solution. [b] Pyridine solution.

The chloroform solution spectra show three regions of absorption. In the first region, (8–20) × 10^3 cm^{-1} a moderate-to-weak (ϵ ~200) band is seen at ~16.5 × 10^3 cm^{-1}. The second region, (20–30) × 10^3 cm^{-1}, shows two moderate-intensity bands at ~22.5 and ~26.4 × 10^3 cm^{-1}. Finally in the third region, >30 × 10^3 cm^{-1}, an intense band at ~34.0 × 10^3 cm^{-1} is observed. For energy and intensity reasons, absorptions in the first region should be ligand field bands. By assuming a square-pyramidal structure for the complexes in chloroform and approximate equivalence of the basal ligand donor atoms, the ligand field about the metal could be described as pseudo-C_{4v}. Under this symmetry three d–d transitions are expected: $d_{z^2} \rightarrow d_{x^2-y^2}$ (I), $d_{xy} \rightarrow d_{x^2-y^2}$ (II) and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ (III) (from lower to higher energy).[32] The band at 16.5 × 10^3 cm^{-1} observed for [Mn(acen)X] can be assigned to transition II rather than I, since the frequency of this band is found to be insensitive to the axial anion. If the d_{z^2} orbitals were involved in the observed transition, then a measurable dependence of the visible band energy should be noted. Then transition I must occur at <8 × 10^3 cm^{-1} for no other absorptions are seen up to this limit in the near-infrared region. The separate band for transition III is not apparent. Most likely it contributes to the broad and more intense higher energy band centered at 22.5 × 10^3 cm^{-1}. The assignment of the band at 16.5 × 10^3 cm^{-1} to transition II is supported by the observation of similar bands at ~15 × 10^3 cm^{-1} for [Mn(salpn)Cl] and 16.5 × 10^3 cm^{-1} for [Mn(acetpn)Cl].[33] This agrees with the expected sensitivity of this band to the in-plane ligand field and the energy order corresponds to the observed ligand field strength of the similar tetradentate ligands: acetpn ≥ acpn > salpn.[34]

The bands at 22.5 and 26.4 × 10^3 cm^{-1} in the second region are intense enough to be considered as charge-transfer bands. Previous studies on Cu^{II}– and Ni^{II}–acpn complexes have indicated that bands in this energy region arise from d → π^* (azomethine) charge transfers.[35] Since the bands are not sensitive to the axial anion, the ~22.5 × 10^3 cm^{-1} band can be assigned to a $d_{xy} \rightarrow \pi^*$ band while the 26.4 × 10^3 cm^{-1} band can be assigned to a $d_{xz}, d_{yz} \rightarrow \pi^*$ transition. The high-energy shoulder or splitting of the latter band noted for many of the spectra may arise from a low-symmetry splitting of the d_{xz}, d_{yz} orbital under the actual symmetry of the complexes. Further, the broadness of the charge-transfer band at 22.5 × 10^3 cm^{-1} may arise because of the overlap of the $d_{xz} \rightarrow \pi^*$ with the partially split $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition (III). The energy difference between the two charge-transfer bands $d_{xy} \rightarrow \pi^*$ and $d_{xz}, d_{yz} \rightarrow \pi^*$ is ~4 × 10^3 cm^{-1}. This would place the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ band at ~20.5 × 10^3 cm^{-1}; i.e., it would appear as a low-energy shoulder on the charge-transfer band. The last band seen in the spectrum at 34.0 × 10^3 cm^{-1} is in the region of a ligand $\pi \rightarrow \pi^*$ (azomethine) absorption and has previously been assigned to this transition for acen complexes.[35]

The spectra of the complexes in donor solvents like ethanol and pyridine are qualitatively different from those in chloroform. Typical spectra are shown in Figure 6. The spectra are identical for all of the anion complexes, [Mn(acen)X], in each particular solvent. This indicates that the same absorbing species is present in that solvent, presumably the tetragonal six-coordinate complex *trans*-$[\mathrm{Mn(acen)(solvent)_2}]^+$. Conductivity measurements on [Mn(salen)X] are also consistent with extensive anion dissociation in coordinating solvents.[15] The ethanol solution spectra show the ligand field band at $\sim 17.5 \times 10^3$ cm^{-1} in contrast to $\sim 16.5 \times 10^3$ cm^{-1} for the chloroform solution spectra. This seems to indicate that the $d_{x^2-y^2}$ orbital increases in energy on going from a five-coordinate structure in which the metal is out of the plane of the acen ligand donor atoms to a six-coordinate structure in which the metal is in the plane of these four atoms. The $d \rightarrow \pi^*$ charge-transfer bands are slightly shifted on going from chloroform to ethanol. Similarly, the ligand $\pi \rightarrow \pi^*$ transitions appear at 34.5 and 42.4×10^3 cm^{-1}. The pyridine solution spectra are similar to those in ethanol and can be interpreted in the same way. Finally, the methanol solution spectra of [Mn(aceten)Cl] and [Mn(salen)Cl] show the ligand field bands at $\sim$18.2 and $\sim 16.5 \times 10^3$ cm^{-1}. This gives the expected ligand field order: aceten > acen > salen. These data tend to support the assignment of this band to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition.

It is instructive to compare the frequencies of the charge-transfer $d\pi \rightarrow \pi^*$ and ligand $\pi \rightarrow \pi^*$ transition for the Mn(III) complexes in ethanol with those of the other trivalent metal complexes $[\mathrm{Cr(acen)(H_2O)_2}]^+$ [36] and [Co(acen)-(OH)$\mathrm{H_2O}$][37] in methanol. Presumably the octahedral species present under these conditions are of the type *trans*-[M-(acen)$\mathrm{S_2}]^+$ where S = methanol or ethanol. The Cr(III) and Co(III) complexes show charge-transfer absorptions at 22.2, 27.4 and 23.0, 27.7×10^3 cm^{-1}, respectively, while the corresponding bands for Mn(III) are seen at 22.5 and 26.8×10^3 cm^{-1}. The fact that the d^3 Cr(III), d^4 high-spin Mn(III), and low-spin d^6 Co(III) complexes show this similar pattern of charge-transfer transitions tends to support their assignment to $d\pi$ (d_{xy}, d_{xz}, d_{yz}) $\rightarrow \pi^*$ transitions, since the only common property of the three metal ions is the presence of $d\pi$ electrons.

In general, the frequencies of the ligand $\pi \rightarrow \pi^*$ transitions are sensitive to the metal ion for both divalent and trivalent metal complexes and are shifted considerably from the free-ligand value. This not only indicates that the electronic state of the ligand in the metal complexes differs from that in the free ligand but that the individual metal ions are interacting with the relevant ligand orbitals. Since it is known[34] that $\mathrm{H_2}$acen exists in the β-keto amine form rather than the β-keto imine form, the electronic spectral results seem to indicate that the ligand electronic state in the metal complexes differs considerably from that of the β-keto amine. Thus, molecular orbital calculations indicate that the anionic ligand when bound to the metal has a π system which is delocalized over the chelate ring and that there is considerable metal ligand–π interaction.[38] The Cr(III), Co(III), and Mn(III) complexes show the first ligand $\pi \rightarrow \pi^*$ transition at 36.1, 33.3, and 34.5×10^3 cm^{-1}, respectively. The metal ion effect on this electronic transition of the ligand can be ascribed to a π-mixing mechanism with the metal $d\pi$ levels. The variation in energy of the charge-transfer bands and ligand band with trivalent metal ion can be rationalized by taking into account the expected stabilization of the $d\pi$ metal orbitals in going across the first transition series from Cr to Co and by assuming that the ligand π^* is destabilized in the order Cr > Mn > Co. The latter effect could arise from a metal-to-ligand back-π-bonding ($d\pi \rightarrow \pi^*$) being somewhat larger for Cr(III) than Mn(III) or Co(III).

The covalent interaction between the metal and ligand in the [Mn(acen)X] complexes that is implied in the foregoing discussion of their electronic spectra can also be related to some preliminary results on the proton magnetic resonance spectra of the paramagnetic complex [Mn(acen)Cl] in deuteriochloroform which show large contact shifts for the various nonequivalent protons in the complex. Assignments can be made based on relative intensity considerations. Thus the contact shifts (from the $\mathrm{H_2}$acen proton resonances) are as follows: $\mathrm{CH_3}$, −43 and −87 ppm; CH, +18 ppm; $\mathrm{CH_2}$, +70 ppm. The relatively narrow line widths are 2–4 ppm. Since pseudo (dipolar) contact shifts are not expected to be large for square-pyramidal high-spin complexes,[39] the large paramagnetic shifts noted for [Mn(acen)Cl] originate in a contact interaction which arises from σ and π interactions of the ligand and Mn(III). In fact, the shifts for [Mn(acen)Cl] are somewhat larger than for the structurally analogous[40] [Mn(porphyrin)Cl] complexes which show extensive metal–ligand σ and π bonding.[39] It is interesting to note that the contact shifts noted for [Co(acen)] are as follows: $\mathrm{CH_3}$, +21 and +26 ppm; CH, +79 ppm; $\mathrm{CH_2}$, −108 ppm. In this case, a predominant π-delocalization mechanism is suggested on the basis of the relative signs of the contact shifts and of molecular orbital calculations.[41] The signs of the contact shifts for [Mn(acen)Cl] are accordingly not consistent with an exclusively π delocalization of spin but a substantial σ delocalization must also contribute. Further NMR measurements on [Mn(acen)X] will be of use in sorting out the details of bonding in these interesting complexes.

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Registry No. [Mn(acen)Cl], 62126-45-8; [Mn(acen)Br], 62126-46-9; [Mn(acen)I], 62126-47-0; [Mn(acen)$\mathrm{N_3}$], 62126-48-1; [Mn(acen)NCS], 62126-49-2; [Mn(acen)$\mathrm{NO_2}$], 62125-98-8; [Mn-(acen)NCO], 62126-50-5; [Mn(acen)CN], 62126-51-6; [Mn-(acen)$\mathrm{C_2H_3O_2}$], 62126-64-1.

References and Notes

(1) (a) Carnegie-Mellon University. (b) University of Nebraska.

(2) Address correspondence to this author at the Departmento de Fisica y Quimica, Universidad Autonoma Metropolitana-Iztapalapa, Apartado postal 55-534, Mexico 13, D.F. Mexico.

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Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306

Nuclear Magnetic Resonance Studies of Diamagnetic Metal–Aminopolycarboxylate Complexes

P. A. BAISDEN, G. R. CHOPPIN, and B. B. GARRETT*

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Proton resonance spectra of EDTA, MEDTA, and HEDTA complexes of diamagnetic ions including alkali, alkaline earth, and rare earth metals are described. Quartet splittings of the methylenic protons of the acetate groups, indicative of long-lived metal–nitrogen bonds, are found for each ligand in the complexes of the cations of higher charge density. The ligand proton chemical shifts are shown to correlate with the effective charge density of the metal ion. Evidence is presented that this correlation is reflective of ordering in the solvation shell rather than a result of direct metal–ligand electrostatic or inductive effects.

Introduction

Proton resonance spectra for the complexes in aquecus solution of ethylenediaminetetraacetate, EDTA, *N*-hydroxyethylethylenediaminetriacetate, HEDTA, and *N*-methylethylenediaminetriacetate, MEDTA, with a number of diamagnetic metal ions including alkali, alkaline earth, and trivalent lanthanide ions have been obtained to learn more about the bonding and structural characteristics of these complexes. Day and Reilley[1,2] interpreted the spectra of EDTA complexes of alkaline earth and transition metals in terms of the labilities of the metal–oxygen and metal–nitrogen bonds. Kostromina et al.[3] extended these studies to the HEDTA and EDTA complexes of the diamagnetic lanthanide cations. Sawyer and co-workers[4] investigated the pH dependence of the exchange rates for the alkali, alkaline earth, and some transition metal complexes of EDTA. Ryhl[5] studied the kinetics of ligand exchange of $LaEDTA^-$ and $LuEDTA^-$ using line shape analysis. In addition to these studies of diamagnetic ions there have been a number of investigations of paramagnetic lanthanide complexes emphasizing their use as shift reagents for organic systems.[6,7] Both the theory and the practical aspects of paramagnetic shift reagents are sufficiently complex that a fuller understanding might result from a more complete interpretation of the somewhat simpler spectra of the diamagnetic lanthanide complexes.

The structures of EDTA, MEDTA, and HEDTA are shown in Figures 1, 3, and 6, respectively. EDTA is normally a hexadentate ligand although there are examples of pentachelation.[8,9] Neibohr[10] has observed an unbonded acetate group in the spectrum of $EuEDTA^-$ at low temperatures in 3 M LiCl. Elgavish and Reuben proposed that in a LiCl medium, the hexachelated $LnEDTA^-$ complexes are shifted to pentachelation;[6b] thus the low-temperature "pentadentate" species was probably EuLiEDTA. MEDTA, with a methyl group replacing one acetate of the EDTA structure, can only be five-coordinate. HEDTA, in which an ethanolic group has replaced an acetate of the EDTA structure, can fill either five- or six-coordination positions. Powell and Burkholder[11] explain the elution trends of LnHEDTA complexes from cation-exchange resins by assuming that HEDTA is pentadentate with the heavier lanthanide ions (i. e., Tb–Lu) and hexadentate with the lighter members of the series (i. e., La–Tb). From infrared and dehydration studies Moeller and Horwitz[12] inferred five coordination positions for HEDTA in lanthanide complexes. In a thermodynamic study Gritmon proposed that the trends for ΔH_{101} and ΔS_{101} with lanthanide atomic number suggested that the β-hydroxyethyl group of HEDTA interacts with the cation via an intermediate water molecule.[13] Thus the majority of opinions favor pentadentation for HEDTA with lanthanides but the evidence is rather indirect.

Experimental Section

Reagents and Solutions. Alkaline earth metal stock solutions of 0.25 M were prepared by dissolving either the chloride or nitrate salt in D_2O. Lanthanides of purity >99.99% were obtained from the American Potash and Chemical Corp. Stock solutions were prepared by dissolving a stoichiometric amount of the appropriate rare earth oxide in concentrated $HClO_4$. The concentration of metal ion in the stock solution was determined by titration with Baker "reagent" grade EDTA using xylenol orange as an indicator in an acetate (pH 5) buffer. The lanthanide perchlorates in D_2O were taken to dryness several times to eliminate H_2O. The sodium deuterioxide used for most pH adjustments was obtained from Diaprep Inc. as a 40% solution in D_2O.