

however, the relative intensity of the band near 30 kK in $\text{Ta}(\text{NCS})_5(\text{py})$ and $\text{Ta}(\text{NCS})_5(\text{bipy})$ is much greater than the band near 40 kK. The combination of the intraligand and charge-transfer transitions would be expected to increase the intensity of this band with respect to the other intraligand band. It was not possible to resolve this band into its component parts.

Magnetic Susceptibilities.—The magnetic data for the

nitrogen donor complexes of niobium(IV) are shown in Table IV. It can be seen that the magnetic moments of the 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine complexes range from *ca.* 1.6 to 1.7 BM, which is very close to the spin-only value of 1.73 BM. This agrees quite well with other recently reported magnetic moments for eight-coordinate complexes of niobium(IV). McCarley and Hamilton¹⁴ have reported magnetic moments of *ca.* 1.6–1.7 BM for complexes of the general formula $\text{NbX}_4(\text{dth})_2$ (where X is Cl or Br and dth is 1,2-dimethylthioethane). Similar moments have also been reported by Kepert and Deutscher¹⁵ for eight-coordinate complexes of the type $\text{NbX}_4(\text{diars})_2$ (where X is Cl, Br, or I and diars is *o*-phenylenebis(dimethylarsine)).

The moment of 0.97 BM observed for $\text{Nb}(\text{NCS})_4(\text{py})_2$ is lower than the spin-only value, but moments as low as 0.90 have previously been reported. McCarley, *et al.*,⁵ found that the moments of $\text{NbX}_4(\text{py})_2$ (where X is Cl, Br, or I) obey a Curie law with values of 1.37 (Cl), 1.26 (Br), and 1.05 (I) BM. The low moments for these complexes were accounted for on the basis of distortion from octahedral symmetry and electron delocalization. It is quite reasonable that similar effects are present in $\text{Nb}(\text{NCS})_4(\text{py})_2$ and are responsible for the observed moment.

TABLE IV

MAGNETIC PROPERTIES OF NITROGEN DONOR COMPLEXES ^a					
$\text{Nb}(\text{NCS})_4(\text{C}_{10}\text{H}_8\text{N}_2)_2$	<i>T</i>	298	190	161	84
	χ_m'	1245	1934	2252	4589
	μ_{eff}	1.72	1.71	1.70	1.75
$\text{Nb}(\text{NCSe})_4(\text{C}_{10}\text{H}_8\text{N}_2)_2$	<i>T</i>	298	205	148	86
	χ_m'	1223	1753	2563	4508
	μ_{eff}	1.72	1.70	1.74	1.76
$\text{Nb}(\text{NCS})_4(\text{C}_{12}\text{H}_{12}\text{N}_2)_2$	<i>T</i>	301	221	152	86
	χ_m'	1224	1649	2451	4361
	μ_{eff}	1.72	1.71	1.73	1.73
$\text{Nb}(\text{NCSe})_4(\text{C}_{12}\text{H}_{12}\text{N}_2)_2$	<i>T</i>	296	220	164	84
	χ_m'	1460	1839	2368	4349
	μ_{eff}	1.86	1.80	1.76	1.71
$\text{Nb}(\text{NCS})_4(\text{C}_6\text{H}_5\text{N})_2$	<i>T</i>	301	218	156	84
	χ_m'	387	498	721	1308
	μ_{eff}	0.97	0.94	0.97	0.94

^a *T* in degrees Kelvin; $\chi_m' = \chi_m^{\text{cor}} \times 10^6$ emu/mol; μ_{eff} in Bohr magnetons.

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Water-Exchange Studies on Manganese(II) Nitrilotriacetate and Ethylenediaminetetraacetate Complexes by Oxygen-17 Nuclear Magnetic Resonance

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Oxygen-17 nmr studies have been made on manganese(II) complexes with the ligands NTA, EGTA, and EDTA. From consideration of paramagnetic shifts in the ¹⁷OH₂ nmr line and infrared studies, it is concluded that the following species are present in aqueous solution: $\text{Mn}(\text{NTA})(\text{H}_2\text{O})_2^-$, $\text{Mn}(\text{EGTA})^{2-}$ (hexadentate), and $\text{Mn}(\text{EDTA})(\text{H}_2\text{O})_2^{2-}$ (seven-coordinate Mn(II)). The kinetic parameters for water exchange are the following (*k*₁ is per H₂O): $\text{Mn}(\text{NTA})(\text{H}_2\text{O})_2^-$, *k*₁(25°) = $(1.50 \pm 0.8) \times 10^8 \text{ sec}^{-1}$, $\Delta H^* = 6.6 \text{ kcal mol}^{-1}$, $\Delta S^* = 6 \text{ cal mol}^{-1} \text{ deg}^{-1}$; $\text{Mn}(\text{EDTA})(\text{H}_2\text{O})_2^{2-}$, *k*₁(25°) = $4.4 \times 10^8 \text{ sec}^{-1}$, $\Delta H^* = 7.7 \text{ kcal mol}^{-1}$, $\Delta S^* = 7 \text{ cal mol}^{-1} \text{ deg}^{-1}$. Comparison of substitution on $\text{Mn}(\text{NTA})(\text{H}_2\text{O})_2^-$ with water exchange is made. The relations of the ¹⁷O nmr data to epr and proton nmr data are discussed.

Introduction

Most of the relatively few water exchange studies reported on manganese(II) species in aqueous solution have involved Mn(II)-enzyme complexes. In these complexes increased¹ and decreased² labilities of the coordinated water, relative to $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, have been observed. To help understand these results it is advantageous to know more about how particular chemical groups affect the lability of coordinated water.

For manganese complexes containing ligands less complicated than enzymes, for example those of 1,10-phenanthroline³ and adenosine-5'-triphosphoric acid,⁴ only slightly increased water lability has been found.

Similarly, the presence of nitrogen donor ligands in the inner sphere of cobalt(II) and nickel(II) produces only increased lability of the remaining waters, the magnitude of the effect being dependent on the net electron donating capability of the nitrogen.⁵

Water-exchange studies on transition metal complexes with ligands containing carboxylate groups have received scant attention, presumably because of the general lack of precise stability constant and thermodynamic data, and the relative instability of the complexes. However, results reported for nickel(II) complexes of ethylenediaminetetraacetic acid⁶ (EDTA) and cobalt(II) complexes of malonic acid⁷ show that

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TABLE I
SOLUTION STATISTICS

A. NTA Solutions									
Soln	pH (25°)	pH (85°)	Total [Mn] × 10 ² , M	Total [NTA] × 10 ² , M	—10 ² [Mn ²⁺], ^a M—		—10 ² [MnNTA], ^a M—		μ, M
					25°	85°	25°	85°	
A ^b	7.79	6.81	1.00	1.10	404	703	9.91	9.92	0.10
B	8.52	8.57	2.00	4.00	7.95	1.66	14.8	14.1	0.16
C	7.87	7.97	2.00	4.00	33.8	5.54	18.2	17.4	0.14
D	8.75	8.79	1.00	2.00	4.88	1.14	7.71	7.56	0.10

B. EDTA Solutions						
Soln	pH (25°)	Total [Mn] × 10 ² , M	Total [EDTA] × 10 ² , M	μ	[Buffer] × 10 ² , M	
					KHP ^c	phosphate
E	5.7	10.0	10.6	~0.053		
F	5.3	0.500	0.530	~0.03	0.500 (KHP) ^c	
G	5.3	2.00	2.12	~0.12	2.00 (KHP)	
H	4.0	0.78	0.83	~0.15	10 (KHP)	
I	4.0	10.0	10.6	~0.6	10 (KHP)	
J	6.0	0.78	0.83	~0.25	10 (phosphate)	

^a Calculated from K_H and ΔH_H in ref 13 and from $\log K_1$ (82.5°) = 7.30, ΔH_1 = 1.14 kcal/mol, $\log K_2$ (25°) = 2.58, ΔH_2 = -3.6 kcal/mol. ^b [Triethanolamine] = 1.79×10^{-2} M. ^c KHP is potassium hydrogen phthalate buffer.

ligands containing carboxylate groups are capable of enhancing the water exchange rate in metal complexes.

In this paper we report the results of ¹⁷O nmr studies on Mn(II)-EDTA and Mn(II)-nitrilotriacetate (NTA) complexes. The EDTA case is particularly interesting because the structure of $Mn_3(H_2EDTA)_2 \cdot 10H_2O$ contains a seven-coordinate Mn(II) ion⁸ and the nmr studies may give information concerning the solution species.⁶ Furthermore, previous kinetic results on the substitution reactions of the $MnNTA^-$ complex with 8-hydroxyquinoline (oxine)^{9,10} may be compared with the water exchange rate of $MnNTA^-$ to test the applicability of a generally considered mechanism for metal complex formation.¹¹ The question of whether or not the waters presumed present in the inner sphere are kinetically equivalent is also of considerable interest. Nonequivalent waters have been found (by D. P. Rablen) in the nickel(II)-2,2',2''-triaminotriethylamine complex.⁵

Experimental Section

The nmr spectrometer and technique have been described previously.¹² Lorentzian shaped absorption curves were observed by using a locked frequency of 11.5 MHz and a field of ca. 20 kG (or, in some instances, 5.75 MHz and ca. 10 kG).

Currently, temperature control of the sample is achieved by surrounding the probe with a small constant-temperature bath containing silicone oil. Temperatures are known to $\pm 0.1^\circ$. Thermostatting of the Hall probe, used in field regulation, has reduced static field drift to a negligible factor.

pH measurements were made on a Beckman Zeromatic II meter. Before each pH determination, the meter was calibrated with standard buffer solutions of ~0.05 M potassium hydrogen phthalate and 0.01 M sodium tetraborate at the same temperature as the sample solution.

The ¹⁷O water was obtained from YEDA R and D Co., Ltd., Rehovoth, Israel, and contained 7 atom % ¹⁷O (normal H content). For the shift measurements, a blank of 18% ¹⁷O was used. The water was redistilled *in vacuo* before each use.

Manganese and zinc perchlorates were prepared by the action of perchloric acid on the metal carbonate. The salts were recrystallized from water and satisfactory analyses were obtained by EDTA complexometric titration. Standard nitrilotriacetic acid solutions were prepared by dissolving a known weight of the

pure acid in a known volume of dilute potassium hydroxide, the molarity of the base being such that the final manganese-NTA solutions used in the nmr measurements had the desired pH. The excess NTA in solutions B, C, and D was sufficient to buffer them; in solution A triethanolamine buffer was added.

The EDTA used was "Baker's Analyzed" disodium salt. The stock solutions were prepared by mixing about 1:1 ratios of metal ion and ligand, adjusting the pH with NaOH or KOH or with buffers. The buffers used were 0.1 M potassium hydrogen phthalate at pH 4 and 0.1 M phosphate mixtures at pH 6. The epr spectrum of $Mn(H_2O)_6^{2+}$ was checked in the Mn-EDTA solutions and excess EDTA added (ca. 6%) until the free aquo manganese ion concentration was less than 10^{-6} M where it does not appreciably contribute to the ¹⁷O line widths or shifts.

Solutions for the nmr measurements were prepared by room temperature evaporation, *in vacuo*, of known volumes of manganese-ligand stock solutions in ordinary water, addition of solid potassium nitrate (in solutions A and D only), and addition of a known volume (ca. 2 ml) of 7% ¹⁷O water. In solution A, this was followed by the addition of triethanolamine buffer. Finally, the nmr tubes were purged with nitrogen gas and stoppered. The composition of each solution is given in Table I.

Blank solutions for the line-broadening measurements contained zinc in place of manganese. Otherwise, these solutions were identical in composition with the manganese solutions. In the temperature range studied, the difference in pH between the sample and the corresponding blank solution was never greater than 0.1. (pH's were measured on "dummy" solutions containing normal water. These were prepared in an identical manner with the ¹⁷O₂ solutions.)

Shift measurements were made on solutions C and E. At least four measurements were made for each line broadening or shift used in the calculations (an equal number of upfield and downfield sweeps). The precision of the line-broadening and shift data is ca ± 4 and $\pm 1\%$, respectively. The line-broadening data for Mn-NTA are given in Figure 1.

Treatment of Data

I. NTA System. A. Equilibrium Considerations.

—Before kinetic information can be extracted from the line-broadening and shift data, it is necessary to know the composition of the solutions. For the pH's used in the NTA study, the following equilibrium constants are relevant: $K_H = [HNTA^{2-}]/[H^+][NTA^{3-}]$, $K_1 = [MnNTA^-]/[Mn^{2+}][NTA^{3-}]$, and $K_2 = [Mn(NTA)_2^{4-}]/[MnNTA^-][NTA^{3-}]$. The literature values for these constants are $\log K_H(25^\circ, \mu = 0.1) = 9.75$,¹³ $\log K_1(20^\circ, \mu = 0.1) = 7.44$,¹⁴ and $\log K_2(20^\circ, \mu = 0.1) = 3.4$.¹⁵ The corresponding enthalpies for

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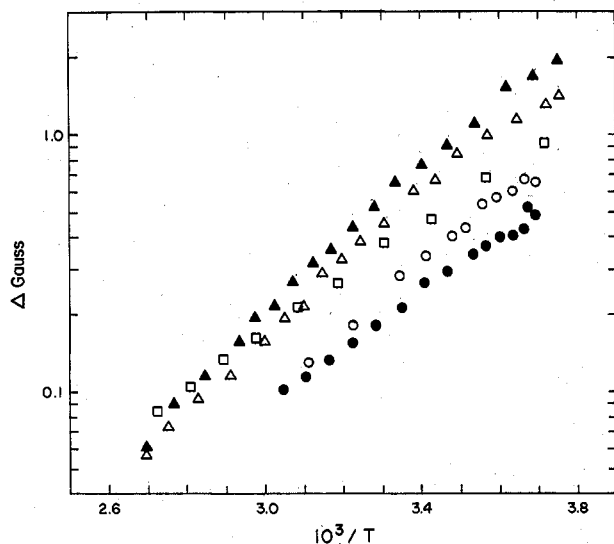


Figure 1.—Semilogarithmic plot of the line broadening (Δ) vs. $1/T$ for Mn-NTA: solution A, \square ; solution B, Δ ; solution C, \blacktriangle ; solution D, \circ , all at 11.5 MHz; solution D, \bullet , at 5.75 MHz.

K_H and K_1 , ΔH_H and ΔH_1 , are -4.68^{13} and 1.14^{16} kcal/mol, respectively.

A preliminary effort to treat the NTA line-broadening data with the above constants indicated that K_2 was too large. However, an independent evaluation of K_2 can be made with the data from solutions B and C. In these the free $[Mn^{2+}]$ is very small ($<10^{-6} M$) and does not contribute to the line broadening. If it is assumed that the only significant species in solution are $MnNTA^-$, $Mn(NTA)_2^{4-}$, $HNTA^{2-}$, and NTA^{3-} , and that only $MnNTA^-$ gives rise to the ^{17}O line broadening, then K_2 may be calculated from K_1 , K_H , and pH, and the total metal and ligand concentrations. At each temperature for each solution, the observed line broadening is proportional to $[MnNTA^-]$. Taking the proportionality constant, C , to be the same for both solutions B and C (*i.e.*, independent of pH), two simultaneous equations can be solved for K_2 and C . From the smoothed line-broadening data, $\log K_2$ at 25° is found to be 2.58 and the corresponding ΔH_2 to be -3.6 kcal/mol.

The assumptions made in the above treatment are consistent with the literature. There is no evidence to suggest that any other species are present in significant quantities under the conditions used. Furthermore, the absence of line broadening arising from completely substituted species (in this case $Mn(NTA)_2^{4-}$) and a C essentially independent of pH have always been observed in similar studies on Ni(II)¹⁷ and Mn(II)⁸ systems. (In the Mn-NTA system the stability constants are such that it is not easy to convert all the manganese species to $Mn(NTA)_2^{4-}$ to show directly that no line broadening is produced.)

However, the validity of our treatment can be tested by using the data from solutions A and D. In solution A, $[Mn(NTA)_2^{4-}]$ is very low and the $[Mn^{2+}]$ is sufficiently large to produce observable line broadening at temperatures above 30° . The line broadening arising from $MnNTA^-$ in this solution, at any temperature,

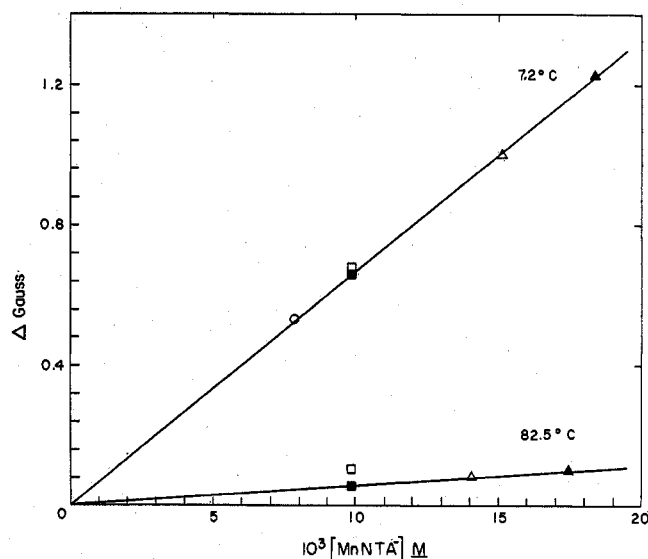


Figure 2.—Plot of $[MnNTA(H_2O_2^-)]$ vs. the line broadening (Δ) at 11.5 MHz: solution A, \square ; solution B, Δ ; solution C, \blacktriangle ; solution D, \circ ; the contribution that $MnNTA^-$ makes to Δ of solution A, \blacksquare .

may be calculated from C and $[MnNTA^-]$ which, in this case only, may be taken as being equal to the $[Mn]_{total}$. The difference between the calculated and observed broadening may be attributed to free Mn^{2+} . From previous work,³ this difference may be used to calculate the free $[Mn^{2+}]$. Thus, from $[Mn^{2+}]$, $[Mn]_{total}$, $[NTA]_{total}$, the pH, and K_H , K_1 may be calculated. At 82.5° , $\log K_1$ was evaluated as 7.44. From the literature value of ΔH_1 ,¹⁶ $\log K_1$ at 25° is 7.30, which compares favorably with the literature value of 7.44.¹⁴

In Figure 2 the line broadening is plotted against $[MnNTA^-]$ for each solution at two temperatures. The nature of the above treatment requires that, at 82.5° , the straight line passes through all the points and the origin. However, on the 72° line, the point for solution A is relatively independent of the above treatment since the broadening produced by free Mn^{2+} is very small. The fact that this straight line passes through the origin and all the points shows the validity of our treatment and justifies the assumptions made in it. The calculated compositions of the four solutions are given in Table I.

B. Kinetic Results from the Nmr Measurements.—

The line-broadening and shift data may be treated with the Swift and Connick approach.¹⁸ The shift aspects will be discussed first. At high temperatures (100 – 120°) and high complex concentration ($\sim 0.1 M$), a paramagnetic shift in the bulk water signal was observed relative to an 18% $^{17}OH_2$ sample contained in a small enclosed sample tube. However, at this concentration, the stability constants derived in the previous section will not be applicable, and therefore the concentration of $MnNTA^-$ was uncertain. Due to the availability of an analog computer or curve synthesizer (constructed by H. W. Dodgen) it became possible to generate Lorentzian curves for the sample and reference and to measure very small shifts precisely. Thus, shifts were measured on solution C between 80 and 95° . These were *ca.* 6 ppm in magnitude. A 0.5

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ppm correction was added for bulk susceptibility effects. At these temperatures, a limiting shift has been reached and the function $Q_{\text{limit}} = TS[\text{H}_2\text{O}]/[\text{MnNTA}] = nT \Delta\omega_m/\omega_0$; where T is the absolute temperature, S is the fractional observed shift $(\omega_{\text{obsd}} - \omega_0)/\omega_0$, n is the number of bound water molecules in MnNTA^- , $\Delta\omega_m = \omega_m - \omega_0$ where ω_m is the resonant frequency (radians/sec) for the bound water, ω_0 the same for bulk water, and ω_{obsd} is the observed frequency ($2\pi\nu_{\text{obsd}}$). Q_{limit} was constant at $7.24 \pm 0.1^\circ\text{K}$.

The scalar coupling constant, $A/h = T(\Delta\omega_m/\omega_0) \cdot (3k/2\pi)(\gamma_N/(S(S+1)g_{\text{eff}}\beta))$, can then be calculated taking $n = 2$, $\gamma_N = 3628 \text{ G}^{-1} \text{ sec}^{-1}$, $S = 5/2$, $g_{\text{eff}} = 2.00$, β (Bohr magneton) = $9.273 \times 10^{-21} \text{ erg G}^{-1}$, and k (Boltzmann's constant) = $1.380 \times 10^{-16} \text{ erg K}^{-1}$. It is found to be $(5.32 \pm 0.08) \times 10^6 \text{ Hz}$.

The line broadening may be expressed in terms of $T_{2p}'' = 2[\text{MnNTA}]/(\gamma_N\Delta)$ where Δ is the line broadening at half peak height (in gauss) produced by MnNTA^- . In the present case, as in the earlier Mn(II) studies,^{3,18} the complete Swift and Connick equation may be simplified to treat the T_{2p}'' data. The relatively long T_{1e} for Mn(II)¹⁹ and its complexes make the T_{2m} contributions swamp those due to $\Delta\omega_m$ in the complete equation. The simplified equation is $T_{2p}'' = (55.5/n)(\tau_m + T_{2m})$ where τ_m is the mean lifetime for exchange of a bound water molecule and $T_{2m} = (1/C)(1/T_{1e} + 1/\tau_m)$. Here, C is $(1/3)(S(S+1)) \cdot (A/h)^2$. Thus, the equation to describe the data is $T_{2p}'' = (55.5/n)(\tau_m + (1/C)(1/\tau_m + 1/T_{1e}))$. The temperature dependence of $1/\tau_m$, the water exchange rate constant, may be expressed in terms of the transition-state theory equation, *i.e.*, $1/\tau_m = (kT/h) \exp(-\Delta H^*/RT + \Delta S^*/R)$. For T_{1e} both magnetic field and temperature dependence must be considered. Recent work on proton nmr²⁰ and Mn esr¹⁹ provides the appropriate approach to T_{1e} . The basic equation²¹ used is

$$\frac{1}{T_{1e}} = \frac{32}{25} \Delta^2 \left[\frac{\tau}{1 + \omega_S^2 \tau^2} + \frac{4\tau}{1 + 4\omega_S^2 \tau^2} \right]$$

where $1/T_{1e}$ is the weighted average of the three $1/T_{1e}$ values needed to completely describe the Mn(II) ($S = 5/2$) electron spin relaxation at high fields ($\omega_S \tau > 1$), Δ is a parameter measuring the modulation of the zero-field splitting produced by solvent impacts at a mean rate of $1/\tau$, and ω_S is the esr frequency (radians/sec). One can obtain the T_{1e} values by noting that at the temperature where T_{2p}'' reaches a minimum, $\tau_m = 1/C^{1/2}$ to a good approximation. Since $C^{1/2}$ is known from the shift measurements, T_{1e} can be calculated at the two fields and with the ω_S 's values of τ and Δ can be calculated from the above T_{1e} equation. The value of τ thus found applies at the temperature of the minimum. The temperature dependence was taken in the usual way to be given by $\tau = \tau_0 \exp[E_A(1/T - 1/T_0)/R]$ where the subscript zero refers to the minimum. The value 3.6 kcal/mol was assigned to E_A somewhat arbitrarily. It is consistent with previous treatments and the temperature dependence of the viscosity of water. The kinetic parameters are insensitive to E_A which could range at least from 2 to 5 kcal/mol.

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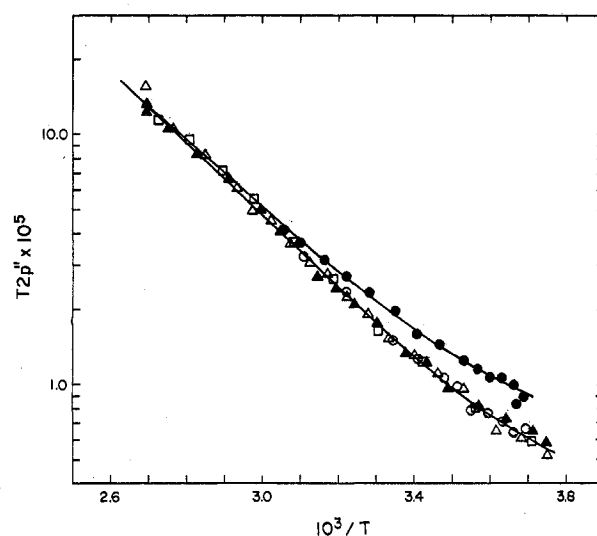


Figure 3.—Semilogarithmic plot of T_{2p}'' for Mn-NTA vs. $1/T$ at 11.5 MHz: solution A, \square ; solution B, \blacktriangle ; solution C, \triangle ; solution D, \circ ; solution D at 5.75 MHz, \bullet . The lines are calculated from the fitted parameters.

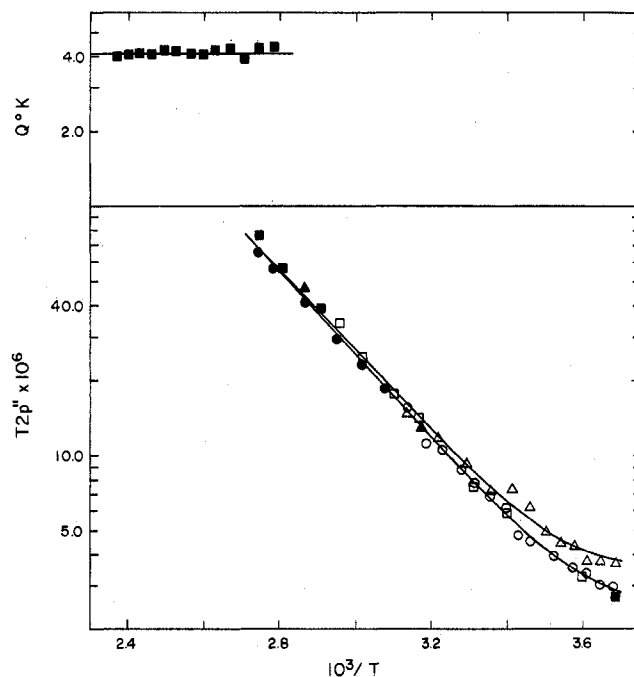


Figure 4.—Kinetic results for Mn-EDTA. Top: the shift function Q vs. $1/T$, solution E. Bottom: T_{2p}'' vs. $1/T$; higher curve (7.0 MHz): solution F, \triangle ; solution G, \blacktriangle ; lower curve (11.5 MHz): solution F, \circ ; solution G, \bullet ; solution J, \square ; solutions H and I, \blacksquare . The lines are calculated from the fitted parameters.

Having values of τ , Δ , and E_A a nonlinear least-squares program due to Dye and Nicely²² was used to find the best values of ΔH^* and ΔS^* . The T_{2p}'' fit is shown in Figure 3.

II. EDTA System. A. Equilibrium Considerations.—Above pH 4 the concentration of free Mn^{2+} can be made negligible by addition of excess (*ca.* 6%) EDTA as evidenced by the epr spectra. We have assumed that only a mono complex forms under these conditions. The line broadening and shift data are consistent with this assumption.

B. Kinetic Results from the Nmr Measurements.—

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The treatment is similar to that for NTA. As seen in Figure 4, a limiting shift region is again found so that an accurate value for A/h is obtained. It is $6.05 \pm 0.15 \times 10^6$ Hz (for one H_2O/Mn).

III. ESR Parameters.—In Table II are listed the τ

TABLE II

ESR PARAMETERS

System	Δ , gauss	$\tau(25^\circ)$, sec	Ref	Method
Mn(H_2O) $_6^{2+}$	162	3.17×10^{-12}	a	^{17}O nmr
	135 ± 15	3.3×10^{-12}	b	Esr
	150	3.2×10^{-12}	c	1H nmr
	147	2.4×10^{-12}	d	1H nmr
Mn(NTA)(H_2O) $_2^-$	442	1.80×10^{-12}	This work	^{17}O nmr
	375 ± 20	9×10^{-12}	b	Esr
Mn(EDTA)(H_2O) $_2^-$	207	1.42×10^{-12}	This work	^{17}O nmr
Mn(ATP)(H_2O) $_3^-$	226	1.55×10^{-12}	e	^{17}O nmr
	195	8.5×10^{-12}	b	Esr

^a Submitted to *J. Chem. Phys.* ^b Reference 19. ^c Reference 20. ^d N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961). ^e Unpublished work from our laboratories.

and Δ parameters for four manganese systems as obtained from our work and the literature. The significance of the comparisons lies in the fact that three different methods were used to obtain the parameters and give reasonable agreement. The derived Δ values are remarkably close. The esr results were based on a rather difficult analysis of line shapes and give rather long τ values. It seems likely that in fact the nmr results give more realistic τ values. Since the τ value is related to the impact time of molecules (most likely solvent) on the complex, one would expect them not to vary much from complex to complex and to be $<10^{-11}$ sec.²⁰ The esr spectrum of Mn-EDTA is complex and suggests considerable zero-field splitting.¹⁹ No values for τ and Δ were derived for this species in the esr study.

Results and Discussion

The kinetic and nmr parameters found are given in Table III, along with those for Mn(H_2O) $_6^{2+}$. It is

TABLE III
KINETIC AND NMR PARAMETERS

	Mn(H_2O) $_6^{2+}$		Mn(NTA)(H_2O) $_2^-$		Mn(EDTA)(H_2O) $_2^-$	
	HF ^a	LF	HF	LF	HF	LF
$k_1(25^\circ)$, sec $^{-1}$ ($\times 10^{-7}$)	2.31 ± 0.12	2.24 ± 0.39	150 ± 8	160 ± 9	43.8 ± 3	46.1 ± 3
ΔH^* , kcal/mol ^c	7.82 ± 0.02	7.87 ± 0.05	6.60 ± 0.06	6.66 ± 0.14	7.68 ± 0.10	7.60 ± 0.30
ΔS^* , cal mol $^{-1}$ deg $^{-1}$ ^c	1.38 ± 0.07	1.49 ± 0.18	5.58 ± 0.20	5.91 ± 0.50	6.76 ± 0.29	6.66 ± 0.94
A/h , Hz ($\times 10^{-6}$)		5.62 ± 0.15		5.32 ± 0.15		6.04 ± 0.15

^a HF refers to 11.5 MHz; LF to 5.75 MHz data. ^b k_1 is the rate constant per water. The errors are estimates based on precision of data. ^c The errors are standard deviations given by the computer program.

difficult to make a realistic estimate of the errors in the derived parameters. The standard deviations given by the computer are unrealistically small as indicators of reliability. Based on past experience, we would suppose that ± 0.7 kcal/mol for ΔH^* and ± 2 cal mol $^{-1}$ deg $^{-1}$ for ΔS^* might be reasonable estimates for the NTA and EDTA systems and ± 0.3 and ± 1.0 for ΔH^* and ΔS^* in the Mn(H_2O) $_6^{2+}$ case.

Both NTA and EDTA significantly labilize the remaining water molecules with NTA being quite effective. The magnitude of the effect of EDTA in $k_1(25^\circ)$ is roughly the same as found for the nickel complexes.⁶ In the nickel case there appears to be a significant decrease in ΔH^* while the Mn results suggest that the ΔS^* is mainly affected. The NTA ligand has a larger labilizing effect than EDTA, which might be ascribed to the tertiary nitrogen present in the former.

The NTA results have to be considered in the light of the possibility that the water molecules are not kinetically equivalent. The constancy of the A/h values ($av = 5.66 \pm 0.25 \times 10^6$ Hz) suggests that the proper number of water molecules has been assigned to each species. For Ni-NTA two water exchange rates are found²³ and this is also the case²⁴ for Ni-tren(H_2O) $_2^{2+}$ and Ni(dien)(H_2O) $_3^{2+}$. A hint that this may also be so for Mn-NTA comes from the low ΔH^* value. A similar low apparent ΔH^* value is found if the waters are treated as equivalent in the tren and dien nickel species. In the Mn-NTA system, however, we can find no other experimental reasons to support the idea of nonequivalent exchange rates, so the question remains unsettled. Rates differing because ΔH^* differs by greater than 2–3 kcal/mol would be expected to produce fairly obvious anomalies in the data.

The substitution of 8-hydroxyquinoline (HOx) and its anion (Ox $^-$) on MnNTA(H_2O) $_2^-$ proceeds with the following kinetic parameters:^{9,10} for HOx, $k_{25^\circ} = 1.7 \times 10^6$ M $^{-1}$ sec $^{-1}$, $\Delta H^* = 5.5$ kcal/mol, $\Delta S^* = -12$ cal mol $^{-1}$ deg $^{-1}$; for Ox $^-$, $k_{25^\circ} = 2.3 \times 10^7$ M $^{-1}$ sec $^{-1}$, $\Delta H^* = 6.6$ kcal/mol, $\Delta S^* = -3$ cal mol $^{-1}$ deg $^{-1}$. If one uses the usual treatment¹¹ that $k_t = K_{os}k_{H_2O}$, where k_t is the bimolecular substitution rate constant, K_{os} an outer-sphere complex constant, and k_{H_2O} the water exchange rate constant of the species being substituted, one sees that K_{os} is *ca.* 0.01 for Ox $^-$ -Mn(NTA) $^-$ and *ca.* 0.001 for HOx-Mn(NTA) $^-$ to be consistent with water loss alone being rate determining. In the Ox $^-$ substitution, one might suspect a charge effect but HOx substitutes even more slowly. The effect of charge has been discussed elsewhere.¹⁰ If ring closure with replacement of a more slowly exchanging water is rate determining for the substitutions, we might have detected this slow water exchange. It seems to us that some kind of concerted process may be implicated in the manganese systems.

The question of the structure of the Mn $^{2+}$ -EDTA complex in water solution remains somewhat puzzling. From pH 4 to pH 6 there appears to be only a single water-containing species. The ir spectrum of Na $_2$ Mn(EDTA)·2H $_2$ O was run in D $_2$ O solution and in the pH range 4–6 indicated that all the carboxylate groups were bound to Mn. At pH ~ 2 evidence for a protonated (unbound) carboxylate group was obtained. The structural work of Hoard, *et al.*,⁸ indicates that the Mn–O distance for the coordinated water (seven-coordinate Mn) in Mn $_2$ [MnEDTA(H_2O)] is larger than the normal octahedral Mn–OH $_2$ distance. One might expect that a smaller (than for octahedral) A/h value (a measure of overlap of unpaired spin density with the ^{17}O nucleus) per H $_2$ O molecule would be found. The

(23) Private communication from R. E. Connick.

(24) Private communication from D. P. Rablen.

measured A/h value appears, if anything, slightly larger than the "octahedral" value. If two $H_2O/MnEDTA$ were actually present the A/h value would be reduced to $ca. 3 \times 10^6$ Hz which seems rather a drastic change. Unlike the $Ni(II)-EDTA$ case where the anomalous temperature dependence of the shift in the $^{17}OH_2$ line indicated the presence (in part) of an unprotonated unbound carboxylate group, the $Mn(II)$ shift behavior is normal for a single species system. The esr results¹⁹ indicating large zero-field splitting also suggest a nonoctahedral structure is present. We conclude that the $Mn(II)$ $EDTA-H_2O$ species is at least seven-coordinate in solution but cannot strictly rule out a higher coordination number at this time.

Some preliminary measurements on $Mn-EGTA$ ($EGTA$ is $(O_2CCH_2)_2NCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2CO_2^-)_2$) reveal no $^{17}OH_2$ line broadening, consistent with reduced strain in the hexadentate $EGTA$ complex and a total coordination number of six in this complex. More nmr studies of Mn complexes are planned to get more evidence concerning the relations of A/h to structural changes.

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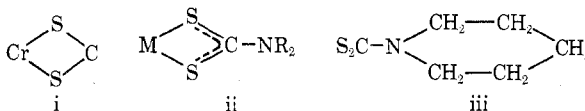
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Magnetic Circular Dichroism Spectra and Electronic Structures of Tris(dialkyldithiocarbamato)chromium(III) Molecules, $Cr(R_2tc)_3$, and Others^{1a}

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A series of tris(dialkyldithiocarbamato)chromium(III) molecules was studied in d-d regions by means of magnetic circular dichroism, ambient and 80°K electronic absorption, trigonal (D_3) crystal field theory, and ground-state semiempirical LCAO-MO calculations, and some results of the single-crystal X-ray structural analysis of the related $In(pmte)_3$, where $pmte^-$ is the pentamethylenedithiocarbamate anion, are given. MCD was found especially well suited for locating the spin forbidden transition $^4A_2 \rightarrow ^2T_2$ and was also reasonably advantageous (over the electronic absorption method) for locating $^4A_2 \rightarrow ^2T_1$. The MCD activity of 4T_2 on the other hand, is weak as in ruby and the individual trigonal components of this state were not detectable in the tc complexes. The large activity of 2T_2 permits one to conclude that the order of trigonal components of 2T_2 is $^2A_1 < ^2E$. This ordering and previous publication of the trigonal splitting of $^4T_2(t_2^2e^1)$ as $^4A_1 < ^4E$ made it possible to carry out a reliable, iterative D_3 crystal field calculation using the variable-secant analog of the Newton-Raphson method by use of an approximate Jacobian. Application of the complete configuration interaction trigonal crystal field model (absence of spin-orbit coupling) led to the conclusion that the use of zero-order theory for obtaining the primary trigonal parameter v , or $|E(^4A_1; T_2) - E(^4E; T_2)| = v_0/2$, would lead to $ca. 30\%$ underestimate of the absolute value of this parameter when it was compared to the magnitude ($|v_1|$) derived from complete theory for the molecule $Cr(detc)_3$. Interestingly the same discrepancy prevails in $Cr(detp)_3$. However, it was found that the ratio $v_1/v_0 = 1.3$ for both molecules so that the importance of the second trigonal parameter v' is perhaps the same in both compound types. Interestingly the configuration interaction parameter (K') for $Cr(detc)_3$ is numerically about equal to the splitting parameter (K). Also, semiempirical Wolfsberg-Helmholz molecular orbital calculation on the ground state of $Cr(H_2tc)_3$ leads to the conclusion that there is an unexpectedly significant antibonding, across-the-ring $Cr-C$ interaction within the four-membered rings of type i. The data of our series of tc molecules provided no new support for Nakamoto's suggestion that the variation

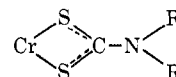


of R in ii will influence the electronic structure of the $C-N$ bond and (our anticipated) subsequent influence on the four-membered ring i. However, the initial single crystal, three-dimensional X-ray structural study of $In(pmte)_3$ indeed demonstrates such an effect, since the $C-N$ distance of S_2C-N is 0.10 Å less than the $C-N$ distance of the ring in iii. Very important, also, is that the $C-N(C)C$ group is planar, which is also consistent with $C-N$ π bonding in the S_2C-N group.

Introduction

MCD studies of D_3 tris bidentate $Cr(III)$ molecules or complex ions have been limited to date to $[Cr(en)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$.² We are in the process of studying such D_3 moieties systematically and in detail. This paper reports on the MCD study of the interesting

tris(dialkyldithiocarbamato)chromium(III) molecule types, $Cr(R_2tc)_3$, containing the groups



In review, early electronic absorption experiments were carried out on a few such dithiocarbamate (tc) complexes ($R = H, \text{ethyl}, n\text{-butyl}$) by Kida and Yoneda³ and Jorgensen,⁴ and preliminary octahedral

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