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Preparation and Characterization of Some Aminopolycarboxylate Complexes of Manganese(III)

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Received June 15, 1966

The complexes of manganese(III) with *trans*-1,2-diaminocyclohexanetetraacetic acid (CyDTA), ethylenediaminetetraacetic acid (EDTA), and hydroxyethylethylenediaminetriacetic acid (HEDTA) were prepared in the crystalline state. The absorption spectra of these compounds and the compounds prepared from them by addition of base were run. The rates of decomposition of the complexes in acidic solution were established. The slowest decomposition was found for $Mn^{III}CyDTA^-$ complex with a first-order rate constant of 6.8×10^{-6} sec^{-1} at 25°. $Mn^{III}EDTA^-$ and $Mn^{III}HEDTA$ gave first-order rate constants for decomposition of 1.2×10^{-5} and 4.2×10^{-5} sec^{-1} at 25°. The standard potentials for the reaction $Mn^{III}Y + e^- \rightleftharpoons Mn^{II}Y$ were determined for the three complexes. These potentials showed all three complexes to be about equally good as oxidizing agents. The formation constants of the three manganese(III) complexes were calculated.

Few manganese complexes of oxidation state three have been prepared and characterized owing to the relative instability of the manganese(III) ion. The aquomanganese(III) ion is a strong oxidizing agent but is not stable primarily because of its disproportionation to manganese(II) ion and manganese(IV) oxide. The complexes of manganese(III) are generally more stable because of the fact that the formation constants of manganese(III) complexes are greater than the formation constants of the comparable manganese(II) complexes. Manganese(III) complexes are therefore much poorer oxidizing agents, but are primarily more stable because they are not subject to disproportionation.

Cartledge and Eriks[1] have prepared the trioxalato and dioxalato complexes of manganese(III). They were prepared by oxidizing the corresponding complexes of manganese(II) with potassium permanganate. The complexes were crystallized out of ethanol. When care was taken to isolate a pure product, the trioxalatomanganate(III) complex could be kept at 20° in the absence of light with little decomposition. The dioxalatomanganate(III) was less stable but kept fairly well at 0°.

The solid ethylenediaminetetraacetic acid (EDTA) complex of manganese(III) has been prepared and characterized by Yoshino, *et al.*[2] They found that it was decomposed by heat and light and was unstable at room temperature. They noted that in solution two forms existed depending on the pH of the solution. It was proposed that an equilibrium existed

$$[Mn^{III}EDTA(OH_2)]^- \rightleftharpoons [Mn^{III}EDTA(OH)]^{2-} + H^+$$

This leads to the conclusion either that the EDTA ligand is coordinated at only five sites with a water occupying the sixth position or that the manganese(III) is capable of forming seven-coordinated complexes. The idea of seven-coordinated manganese is reasonable in light of the crystallographic establishment of the EDTA complex of manganese(II) as a seven-coordinated structure.[3]

trans-1,2-Diaminocyclohexanetetraacetic acid (CyDTA) has been reported to form metal complexes which are more stable than the analogous EDTA complexes.[4] The greater stability of the *trans*-CyDTA complexes has been explained on the basis of the rigidity of the cyclohexane ring by Day and Reilley.[5] The inflexibility of the cyclohexane ring makes it more difficult to move either of the acetate arms away from the metal ion. Because of its stabilizing effect on the metal ions and the general instability of manganese(III), the CyDTA complex of manganese(III) was investigated.

Experimental Section

The HEDTA, EDTA, and CyDTA ligands were obtained from the Geigy Chemical Corp. They were recrystallized twice from hot water and air dried before use.

The potassium salt of the $Mn^{III}CyDTA^-$ complex was prepared in a manner similar to the method described by Yoshino[2] to prepare the $K[Mn^{III}EDTA]$ complex.

In the method used, a mixture of potassium hydroxide and manganese(IV) oxide was prepared by adding 10 g of powdered potassium permanganate to a mixed solution of 70 ml of water and 20 ml of 95% ethanol. The mixture was stirred and slowly warmed until the reaction began to take place with the evolution of gas. After the reaction was complete, the mixture was warmed to distil the excess ethanol and aldehyde. The mixture was then cooled in an ice bath until it reached 10°. To the mixture was added 18 g of CyDTA (H_4Y) which upon stirring caused a vigorous reaction with the evolution of carbon dioxide. When the reaction was complete, the excess manganese(IV) oxide was filtered off of a sintered-glass filter, and a dark red solution was the filtrate. To this was added an equal volume of cold ethanol and the solution was put in a Dry Ice–acetone bath until frozen. The solution was then removed and allowed to come slowly to 10°. Dark red crystals remained which were filtered on a sintered-glass filter funnel and were washed with absolute alcohol and were dried in a vacuum desiccator at room temperature. The yield was 40–45% based on the amount of CyDTA used.

An alternate method of preparation was to add the MnO_2 slurry to a slurry at 0° containing CyDTA and $Mn(NO_3)_2$ in a 2:1 molar ratio. This mixture was vigorously stirred from 0.5 to 1 hr, during which time no generation of gas was observed. The manganese(IV) oxide remaining was filtered off and the first pro-

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[1] G. H. Cartledge and W. P. Eriks, *J. Am. Chem. Soc.*, **58**, 2061 (1936).

[2] Y. Yoshino, A. Ouchi, T. Tsunoda, and M. Kojima, *Can. J. Chem.*, **40**, 775 (1962).

[3] S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).

[4] G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 936 (1954).

[5] R. J. Day and C. N. Reilley, *Anal. Chem.*, **37**, 1326 (1965).

cedure was followed. The yield was about 80%. The product was identical with that produced in the first method.

The hydroxyethylethylenediaminetriacetic acid (HEDTA) and the EDTA complexes of Mn(III) were also prepared by methods which were essentially the same as for the CyDTA complex. The lower temperature of 0° was used for the mixing of the manganese(IV) oxide–potassium hydroxide mixture with the HEDTA free acid.

Analysis.—The manganese(III) content was determined by an iodometric method in which a sample of the complex was added to an acidified solution of potassium iodide. The liberated iodine was titrated with standard thiosulfate solution. The nitrogen analysis was performed by the Kjeldahl method. *Anal.* Calcd for KMn(CyDTA)·2.5H$_2$O: Mn, 11.41; N, 5.82. Found: Mn, 11.27; N, 5.82. Calcd for KMn(EDTA)·2.5H$_2$O: Mn, 12.86; N, 6.55. Found: Mn, 12.74; N, 6.59. Calcd for Mn(HEDTA)·2.5H$_2$O: Mn, 14.65; N, 7.48. Found: Mn, 14.59; N, 7.53.

The absorption spectra were determined using a Beckman Model DU spectrophotometer.

The rate of decomposition of the complexes was measured by recording the decrease in absorbance with time at the respective absorption maxima. The first-order rate constant was equal to 2.3 times the slope of the log *A vs.* time plot.

Determination of Standard Oxidation–Reduction Potential.—Equal amounts of manganese(II) perchlorate and the disodium salt of the complexing anion were mixed in 50 ml of sodium acetate–acetic acid buffer solution. The resulting solution was 0.05 *M* in sodium acetate, and the ionic strength was maintained at 0.20 by the use of sodium perchlorate. The solution was placed in a constant-temperature bath thermostated at 25.00 ± 0.05°. Nitrogen gas was bubbled through the solution to remove the dissolved oxygen. After allowing the solution to come to temperature, a weighed amount of the solid Mn^{III}Y complex was introduced into the cell and thoroughly mixed by bubbling nitrogen gas through the solution. At this point a 5-ml portion of the solution was removed and placed in a spectrophotometer cell in the constant-temperature block of the spectrophotometer. The block was also thermostated at 25.00 ± 0.05°. The absorbance of the solution was recorded as a function of time, the addition of the Mn^{III}Y complex being counted as zero time. The potential of the solution was measured by the use of a Beckman pH meter using a platinum electrode and a saturated calomel reference electrode separated from the solution by a potassium nitrate–agar bridge. The equilibrium potential was obtained at a time when the absorbance had decreased by less than 1% in all cases.

Results

The absorption spectrum of the Mn^{III}CyDTA$^-$ complex in the pH range 2–7 shows a single broad peak with a maximum at 510 mμ. The molar absorptivity is constant in this pH range with a value of 345 M^{-1} cm^{-1}. In the pH range 7–9 the complex changes from the deep red color to a straw yellow color. The yellow species is stable up to about pH 11. The peak has now shifted to a maximum at 448 mμ, with a molar absorptivity of 329 M^{-1} cm^{-1}. Upon addition of acid to the yellow species, it immediately reverts to the red species with maximum at 510 mμ. The spectra of these species are shown in Figure 1.

Figure 2 shows a plot of the absorbancy at 510 mμ against the pH of the solution. From this data the p*K* value between the red and yellow species was evaluated to be 8.11. Solutions that are taken to a pH above about 11 decompose into manganese(II) hydroxide and manganese(IV) oxide.

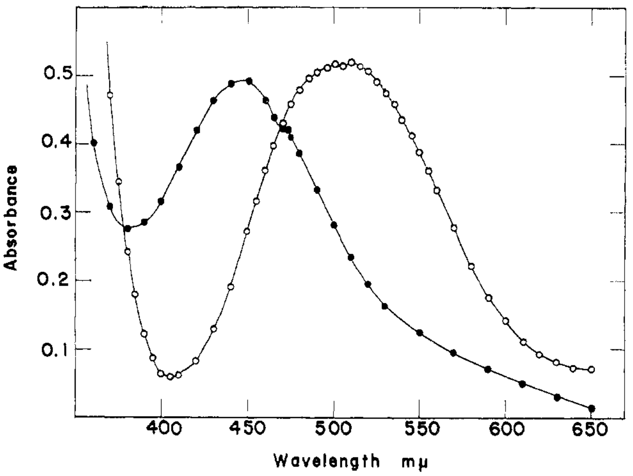

Figure 1.—Absorption spectra of Mn^{III}CyDTA species: ○, pH 2–7; ●, pH 9–11; [Mn^{III}CyDTA] = 1.51 × 10^{-3} *M*.

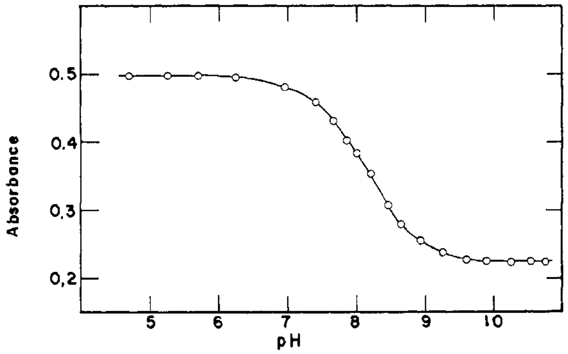

Figure 2.—Absorbance of Mn^{III}CyDTA solution as a function of pH at 510 mμ; [Mn^{III}CyDTA] = 1.51 × 10^{-3} *M*.

The Mn^{III}HEDTA spectrum is somewhat similar to that of the CyDTA complex; however, three species were found to exist at varying pH values. One species exists in the pH range 1.5–3.5, with maximum at 475 mμ and ε 312 M^{-1} cm^{-1}; the second exists in the pH range 4–7 with maximum at 467 mμ and ε 337 M^{-1} cm^{-1}; and the third exists from pH 7.5 to 9.5 with maximum at 449 mμ and ε 337 M^{-1} cm^{-1}. At pH values greater than 10, the complex decomposes rapidly to manganese(II) hydroxide and manganese(IV) oxide.

Acid–base titrations were run on the complexes to aid in determining their structures. When an aqueous solution of the potassium salt of the Mn^{III}CyDTA$^-$ complex was titrated with standard base, curve A of Figure 3 was obtained. The curve has a single inflection point at pH 9.50 corresponding to 1 mole of sodium hydroxide/mole of the complex. It can be observed that the pH of the half-neutralized solution agrees well with the p*K* value reported from spectral measurements. When the complex was passed through the hydrogen form of a cation-exchange resin, the free complex acid was obtained. The titration curve of the free acid is shown in Figure 3 as curve B. Two inflection points are observable at 1 and 2 moles of sodium hydroxide/mole of the complex.

The spectrophotometric titration and the acid–base titrations support an equilibrium for Mn^{III}CyDTA$^-$

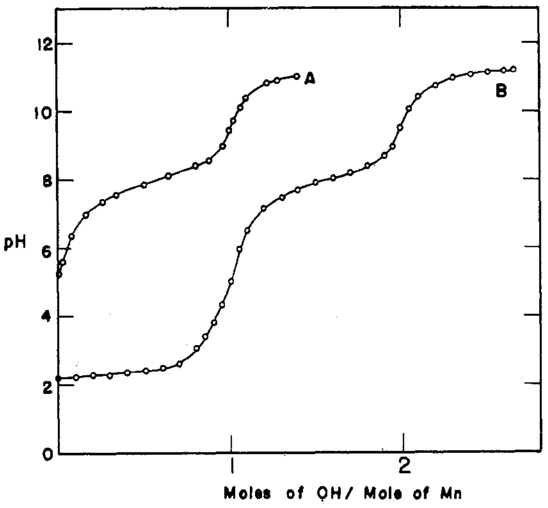

Figure 3.—Titration of $Mn^{III}CyDTA$ with sodium hydroxide: A, compound $K[Mn^{III}CyDTA(H_2O)]$; B, same compound after passage through hydrogen-form cation-exchange column.

that is similar to that proposed previously[2] for Mn^{III}-$EDTA^-$.

Decomposition Rates.—The pH of solutions of the complex was kept constant by using an acetic acid–sodium acetate buffer medium. In these solutions it was found that a tenfold increase of the buffer concentration did not noticeably affect the rate of decomposition. First-order rate constants were obtained by plotting log A_t *vs.* time where A_t is the absorbancy at time t. This is possible because the infinite-time absorbancy of the solutions is zero. In the pH range 3–6 the $Mn^{III}CyDTA^-$ complex decomposition was pH independent. The decomposition of the $Mn^{III}EDTA^-$ complex was pH independent over the same range, but the $Mn^{III}HEDTA$ complex was pH independent over the pH range 4–7. The specific rate constants for these decompositions at 25 ± 0.05° are given in Table I along with the activation parameters for the reactions.

TABLE I

Species	10^5k, sec^{-1}	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mole^{-1}
$Mn^{III}CyDTA^-$	0.65	24.3 ± 0.3	-1.5 ± 0.4
$Mn^{III}EDTA^-$	1.20	23.5 ± 0.5	-0.6 ± 1.1
$Mn^{III}HEDTA$	4.2	22.0 ± 0.4	$+0.3 \pm 0.9$

The products of the decomposition of the manganese(III) complexes of CyDTA and EDTA were Mn(II) complexes with oxidation of some of the ligand to formaldehyde, carbon dioxide, and the triacetate ligand.[6] Complete identification of the products from the decomposition of $Mn^{III}HEDTA$ has not been accomplished, because of the mixture of products.

Oxidation-Reduction Potentials.—Tanaka, *et al.*,[7] have measured the standard oxidation–reduction potential of the $Mn^{III}EDTA$–$Mn^{II}EDTA$ system and calculted the formation constant of the $Mn^{III}EDTA^-$ complex. In general for the complex $Mn^{III}Y$, where Y is CyDTA, EDTA, or HEDTA, reactions 1–4 must be considered

$$Mn^{3+} + e^- \rightleftharpoons Mn^{2+} \qquad E°_{Mn} \qquad (1)$$

$$MnY^{(n-3)-} + e^- \rightleftharpoons MnY^{(n-2)-} \qquad E°_{MnY} \qquad (2)$$

$$Mn^{2+} + Y^{n-} \rightleftharpoons MnY^{(n-2)-} \qquad K_{Mn^{II}Y} \qquad (3)$$

$$Mn^{3+} + Y^{n-} \rightleftharpoons MnY^{(n-3)-} \qquad K_{Mn^{III}Y} \qquad (4)$$

where Y^{n-} is the nonprotonated anion of the complexing ligand, $E°_{Mn}$ and $E°_{MnY}$ are the standard oxidation–reduction potentials for eq 1 and 2, and $K_{Mn^{II}Y}$ and $K_{Mn^{III}Y}$ are the formation constants of the respective complexes.

The half-cell expression for eq 2 can be written

$$E_t = E°_{MnY} - 0.0591 \log \{[Mn^{II}Y]_t/[Mn^{III}Y]_t\}$$

where E_t represents the equilibrium potential and $[Mn^{III}Y]_t$ and $[Mn^{II}Y]_t$ represent the concentrations of the respective complexes at equilibrium. The concentration of $Mn^{II}Y$ at equilibrium was known from the original amount taken, and the concentration of $Mn^{III}Y$ at equilibrium was calculated from the absorbancy at this time and the known molar absorptivity.

A plot of E_t *vs.* log $[Mn^{II}Y]_t/[Mn^{III}Y]_t$ was made for 20 or more experiments with different Mn(II) and Mn(III) concentrations for each of the ligands studied. These plots were straight lines. The intercept at the point where the log term reaches zero is $E°_{MnY}$. These values are given in Table II.

TABLE II

STANDARD POTENTIALS FOR THE REACTION $Mn^{III}Y + e^- \rightleftharpoons Mn^{II}Y$ AND THE FORMATION CONSTANTS OF THE $Mn^{III}Y$ COMPLEXES AT 25° AND $\mu = 0.20$

Y	$E°_{MnY}$, v	log $K_{Mn^{II}Y}$	log $K_{Mn^{III}Y}$
CyDTA	0.814	17.4[a]	28.9
EDTA	0.823[c]	13.6[b]	24.9[c]
	0.825		24.8
HEDTA	0.782	10.7[d]	22.7

[a] G. Anderegg, *Helv. Chim. Acta*, **46,** 1833 (1963). [b] Reference 4. [c] Reference 7. [d] S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, **77,** 1477 (1955).

The value of the formation constants were calculated by means of the equation

$$\log K_{Mn^{III}Y} = (E°_{Mn} - E°_{MnY})/0.0591 + \log K_{Mn^{II}Y}$$

The formation constants for $Mn^{II}Y$ were available from other sources, as shown in Table II. The value of $E°_{Mn} = 1.49$ was taken from Vetter and Manecke.[8]

Discussion

The absorption spectra of the $Mn^{III}CyDTA^-$ complex and the titrations of this complex with base indicate that the structure of this complex is not different in any major way from the EDTA complex. This conclusion results because of the parallel nature of the observations in this investigation to those made on the EDTA complex.[2]

The fact that there appear to be three separate

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(6) K. A. Schroeder and R. E. Hamm, *Inorg. Chem.*, **3**, 391 (1964).

(7) N. Tanaka, T. Shirakashi, and H. Ogino, *Bull. Chem. Soc. Japan*, **38**, 1515 (1965).

(8) K. J. Vetter and G. Manecke, *Z. Physik. Chem.*, **195**, 270(1950).

species upon titration of the HEDTA complex with base may be evidence for having two coordinated water molecules on the complex.

Of the three complexes studied the $Mn^{III}CyDTA^-$ potassium salt was by far the most stable in the solid state. This fact is probably due to kinetic factors as is shown by the decomposition rates of the compounds in solution. The potassium salt of $Mn^{III}CyDTA^-$ was so stable that a sample of it was kept at room temperature for several months in the dark with no experimentally observable change in its assay as an oxidizing agent.

Because of the very slow rate of decomposition of the $Mn^{III}CyDTA^-$ complex it can be used as a moderately strong one-electron oxidizing agent for studies of the kinetics of oxidation of various species. It can be used over a very wide range of pH for oxidation–reduction studies.[9] Almost all previous studies of oxidation of compounds by means of manganese(III) complexes have been in very acid solution because of the instability of the complexes (sulfate and pyrophosphate) as the pH increases.[10]

The ratio of the formation constants of the Mn(III) complex to those of the Mn(II) complex remains quite constant for the three complexes investigated. One might expect this constant ratio for CyDTA and EDTA, as they are very similar ligands. The HEDTA ligand is not greatly different.

Acknowledgment.—The authors wish to express their thanks to the Research Committee of Washington State University and to the National Science Foundation for the funds which made this investigation possible.

[9] M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, **6**, 142 (1967).

[10] W. A. Waters and J. S. Littler, "Oxidations in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, part A, pp 213, 214.

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The Mechanism of Oxidation of Oxalate with *trans*-1,2-Diaminocyclohexanetetraacetatomanganate(III) in Aqueous Solution

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Received June 15, 1966

The oxidation of oxalate with the 1,2-diaminocyclohexanetetraacetatomanganate(III) ion can be fitted by the rate equation $d[Mn^{III}CyDTA^-]/dt = -2k_1[Mn^{III}CyDTA^-][HC_2O_4^-] - 2k_2[Mn^{III}CyDTA][C_2O_4^{2-}]$, over the pH range 3.0–7.0. At 20° the specific rate constants were determined to be $k_1 = 5.4 \times 10^{-3}$ sec^{-1} M^{-1} and $k_2 = 7.08 \times 10^{-3}$ sec^{-1} M^{-1}. Experiments over a range of temperatures from 15 to 35° gave $\Delta H_1^{\ddagger} = 20.9$ kcal mole^{-1}, $\Delta S_1^{\ddagger} = 3.5$ cal deg^{-1} mole^{-1}, $\Delta H_2^{\ddagger} = 16.0$ kcal mole^{-1}, and $\Delta S_2^{\ddagger} = -13.0$ cal deg^{-1} mole^{-1}.

The oxidation of various compounds with permanganate ion in acid solution has been considered to involve the rapid formation of manganese(III) complexes which then decompose unimolecularly to the manganese(II) ion and oxidation products. The reaction of permanganate ion with oxalic acid has been extensively investigated.[1-3] Taube[3] has studied the kinetics of decomposition of the oxalate complexes of manganese(III) and has found that the rates could be accounted for by the simple mechanism in which each of the ions $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$, and $Mn(C_2O_4)_3^{3-}$ undergoes decomposition. These species are known to be in equilibrium with one another according to

$$MnC_2O_4^+ \xrightleftharpoons{+C_2O_4^{2-}} Mn(C_2O_4)_2^- \xrightleftharpoons{+C_2O_4^{2-}} Mn(C_2O_4)_3^{3-}$$

Owing to the equilibria involved between the different species of the oxalatomanganese(III) complexes and between the three forms of oxalic acid, it is kinetically impossible to distinguish between the reactions

$$Mn(C_2O_4)_2^- + HC_2O_4^- \xrightarrow{\text{fast}} H^+ + Mn(C_2O_4)_2^{3-} \xrightarrow{\text{slow}} Mn(C_2O_4)^{2-} + C_2O_4^- \quad (1)$$

$$Mn(C_2O_4)_2^- + HC_2O_4^- \xrightarrow{\text{slow}} Mn(C_2O_4)_2^{2-} + H^+ + C_2O_4^- \quad (2)$$

It is possible that a part of the reaction involves a reaction of the second type as well as the first.

The *trans*-1,2-diaminocyclohexanetetraacetic acid (CyDTA) complex of manganese(III) has been found to be a very stable solid compound that decomposes only slowly in aqueous solution.[4] It undergoes a unimolecular decomposition with a specific rate constant of 6.8×10^{-6} sec^{-1} at 25° and an ionic strength of 0.20. The composition of the complex is expressed as $Mn(CyDTA)H_2O^-$ where either the CyDTA ligand is acting as a pentadentate ligand or it is a hexadentate ligand with the manganese(III) having a water molecule in a seventh coordination position. The idea of manganese being seven coordinated is not completely unreasonable as indicated by the crystal structure investigation of the $Mn^{II}EDTA$ complex which shows it

[1] S. J. Adler and R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2036 (1955).

[2] H. F. Launer, *ibid.*, **54**, 2597 (1932).

[3] H. Taube, *ibid.*, **70**, 1216 (1948).

[4] R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, **6**, 139 (1967).