Discussion

The trigonal bipyramidal structure found for $SbCl_5$ in the gaseous state[8] persists in the crystalline state as shown in Fig. 3. This makes a seventh structural design for achieving the 1:5 stoichiometric ratio and the second one wherein the coördination number is five. Examples of each of the seven types are given in Table II.

TABLE II

STRUCTURAL TYPES HAVING A 1:5 STOICHIOMETRIC RATIO

PCl_5	PCl_4^+, PCl_6^- (CsCl type)[5]
PBr_5	PBr_4^+, Br^{-}[17]
Tl_2AlF_5	AlF_6 (infinite octahedral chains)[18]
$(NH_4)_3ZnCl_5$	$ZnCl_4^=$, Cl^{-}[19]
$(NH_4)_2InCl_5 \cdot H_2O$	$(InCl_5H_2O)$(octahedra)[2]
K_2SbF_5	SbF_5^- (octahedra)[3]
$SbCl_5$	$SbCl_5$ (trigonal bipyramid)

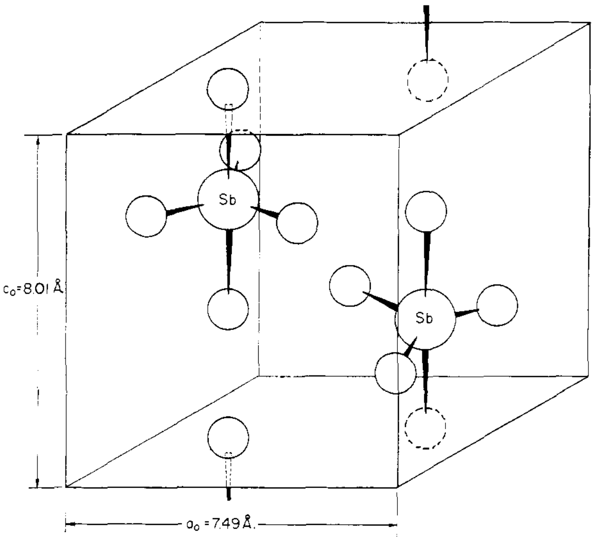

Fig. 3.—The crystal structure of $SbCl_5$.

The bond distance between the antimony and the three basal chlorine atoms, 2.29 Å., is in good agreement with that found for the gas, 2.31 Å. The distance between the antimony and the apical chlorine atoms is 2.34 Å., which is 0.09 Å. less than that found for the gas. The packing of the molecules is such that the closest intermolecular distance is 3.33 Å. between apical chlorine atoms. The next closest intermolecular approach is 4.09 Å. between a basal chlorine and an apical chlorine and hardly seems sufficient to hold the crystal together. If the space group is changed to D_{3h}^4–$P\bar{6}2c$, this permits rotation of the three basal chlorine atoms about the molecular Cl–Sb–Cl axis and thereby the van der Waals distance between basal chlorine atoms and apical chlorines could be brought within the range normally observed. However, structure factor calculations based on the space group D_{3h}^4–$P\bar{6}2c$ with a range of coördinates chosen to yield more reasonable van der Waals distances did not agree with the observed data as well as did those based on D_{6h}^4–$P6_3/mmc$. (This was taken as a further confirmation of the original choice of space group). Inspection of the Fourier projection on the (00·1) face (Fig. 1) suggests a more likely explanation for the large intermolecular Cl–Cl distance. It is seen that the chlorine atoms are somewhat elliptical with their major axes perpendicular to the Sb–Cl bond. This could indicate a torsional vibration of the three basal chlorine atoms about the Cl–Sb–Cl molecular axis. Thus, although the van der Waals distance between the basal chlorine atoms and the apical chlorines of neighboring molecules is large for the atoms at rest, the aforementioned type of thermal vibrations could bring these atoms within the normal van der Waals range.

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(17) H. M. Powell and D. Clark, *Nature*, **145**, 971 (1940).

(18) C. Brosset, *Z. anorg. allgem. Chem.*, **235**, 139 (1937).

(19) H. P. Klug and L. Alexander, THIS JOURNAL, **66**, 1056 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, TEXAS TECHNOLOGICAL COLLEGE]

The Chemistry of the Solvated Metal Chelates. I. Thermochemical and Kinetic Studies[1,2]

BY JAMES H. VAN TASSEL AND WESLEY W. WENDLANDT

RECEIVED JULY 7, 1958

The heats of solvation and the kinetics of the thermal decomposition of the thorium and uranium(VI) 8-quinolinol chelates were determined. The heats of solvation, represented by the reaction $M(C_9H_6NO)_n(s) + C_9H_6NOH(s) = M(C_9H_6NO)_n \cdot C_9H_6NOH(s)$, were found to be 6.5 ± 0.2 and 4.9 ± 0.2 kcal./mole for the thorium and uranium chelates, respectively. The thermal decomposition was found to be first order with activation energies for the thorium and uranium chelates of 42 ± 4 and 26 ± 2 kcal./mole, respectively. A new mechanism for the thermal decomposition of the thorium chelate is proposed. From the heats of solvation and kinetic studies, the nature of the interaction between the solvate molecule and the metal chelate is discussed.

Introduction

8-Quinolinol (oxine) forms five-membered ring chelates with a large number of metal ions having the general formula $M(Ox)_n$, where M is a metal ion of charge *n*, and Ox is the 8-quinolinol ion.

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(1) Taken in part from the M.S. thesis of J. H. Van Tassel, August, 1957.

(2) Presented at the 13th Southwest Regional Meeting of the American Chemical Society, Tulsa, Oklahoma, December 5–7, 1957.

However, with scandium,[2a] thorium,[3] uranium(VI)[4] and plutonium(VI),[5] metal chelates having the general formula $M(Ox)_n \cdot HO_x$ are obtained.

The nature of the interaction between the 8-quinolinol and the metal chelate has been the subject of a number of investigations.[6-9] The solvate molecule is thought to be held in the crystal lattice by weak forces of unknown magnitude.

It is the purpose of this investigation to study more fully the nature of this interaction between the solvate molecule and the metal chelate. The interaction energy, represented by the equation

$$M(C_9H_6NO)_n(s) + C_9H_6NOH(s) = M(C_9H_6NO)_n \cdot C_9H_6NOH(s) \quad \Delta H_4$$

was determined by calorimetric measurements. Since the thorium and uranium 8-quinolinol chelates readily lose 8-quinolinol when heated, the kinetics of the thermal decomposition process was also studied.

Experimental

Reagents.—8-Quinolinol, m.p. 74–76°, was obtained from the Matheson, Coleman and Bell Co., Norwood, Ohio; thorium nitrate 4-hydrate from the Lindsay Chemical Co., West Chicago, Ill.; and uranium nitrate 6-hydrate from Merck and Co., Rahway, N. J.

All other chemicals were of C.P. quality.

A solution of 3.00 ± 0.03 *N* hydrochloric acid was prepared from C.P. hydrochloric acid and standardized against carbonate-free standard sodium hydroxide.

Preparation of Metal Chelates.—The orange solvated thorium chelate was prepared and converted to the yellow normal chelate as previously described.[7]

The solvated uranium chelate was first prepared by the method of homogeneous precipitation,[10] but the method was found to produce inconsistent results. A modification of the method of Classeen and Visser[11] was adopted in that an acetone solution of 8-quinolinol, instead of an acetic acid solution, was added to the uranium solution. The solvated chelate was converted to the normal chelate by heating.[10]

The metal chelates were analyzed for metal content by ignition to metal oxide in platinum crucibles at 800°. The metal contents were within 0.2 to 0.5% of the theoretical stoichiometry.

Calorimeter.—A heat of solution calorimeter was constructed from a 500-ml. silvered, evacuated Dewar flask. The mouth of the flask was fitted with a 0.5 inch thick plastic cover shaped to fit the flask tightly and to project beyond the outer wall to form a protective flange. Through the cover projected a stirrer, cooling coil, electrical heating coil, sample tube and breaker device, and a thermistor probe. The calorimeter was stirred by a 600 r.p.m. 120 volt a.c. synchronous motor mounted above the calorimeter cover. Temperature changes inside the calorimeter were measured with an E. H. Sargent and Co., glass covered thermistor probe and a No. S-8160 thermometric bridge. The unbalance in the thermometric bridge circuit was detected by a Leeds and Northrup reflecting galvanometer of 9×10^{-5} μ amp. per mm. sensitivity at one meter. The Dewar flask was immersed in a constant temperature bath at 25.00 ± 0.03°. The electrical heating circuit was similar to that previously described.[12]

Calorimeter Calibration and Procedure.—Heats of solution were made by the method of comparative measurements. Changes in temperature caused by chemical reactions were duplicated electrically without changing the heat capacity of the calorimeter.

The calorimeter was calibrated by measuring the heat of solution of sodium nitrate in water at a mole ratio of 1:200. The average of 5 measurements was 4.94 kcal./mole; this compared favorably with the accepted value of 4.84 kcal./mole.[13] A calibration check with anhydrous sodium carbonate gave an average of 5.64 kcal./mole; the accepted value is 5.60 kcal./mole.[13]

The following procedure was used for the heat of solution measurements. The dried and powdered sample was weighed out into the sample tube and attached to the calorimeter cover. Into the Dewar flask was introduced 250 ml. of standard hydrochloric acid solution which had previously been suspended in the constant temperature bath to attain temperature equilibrium. The calorimeter was assembled and water from the constant temperature bath circulated through the cooling coil for at least 30 minutes. After the calorimeter had attained a steady state, temperature measurements were recorded at one minute intervals for about 10 minutes. The sample was introduced into the acid solution by breaking the cover glass on the sample container. Temperature measurements were again recorded at one minute intervals for a period of 10 minutes. Cold water then was circulated through the cooling coil of the calorimeter until the temperature was slightly lower than the original temperature. The calorimeter then was allowed to warm slowly to the temperature of the first readings. By use of electrical heating, the temperature of the calorimeter now was raised to the initial value caused by the dissolution of the metal chelate.

Thermobalance.—An automatic recording thermobalance as previously described[14] was used for the thermal decomposition measurements. Samples ranging in weight from 180 to 185 mg. were heated at a linear heating rate of 3.8° per min. Duplicate and, in some cases, triplicate runs were made on all samples with a resulting agreement to each other of about 1%.

Experimental Results

Heat of Solvation Studies.—The heats of solvation of the thorium and uranium(VI) 8-quinolinol chelates were determined indirectly by measuring the heats of solution of the metal chelates in acid solution. Spectrophotometric studies have shown that the metal chelates are completely dissociated in 1 *N* hydrochloric acid solution[8,9] so that these dissociation reactions are assumed to take place

$$Th(Ox)_4 \cdot HOx(s) + 9H^+(aq) + 9Cl^-(aq) = Th^{+4}(aq) + 5HOxH^+(aq) + 9Cl^-(aq) \quad \Delta H_1 \quad (1)$$

$$Th(Ox)_4(s) + 8H^+(aq) + 8Cl\ (aq) = Th^{+4}(aq) + 4HOxH^+(aq) + 8Cl^-(aq) \quad \Delta H_2 \quad (2)$$

$$UO_2(Ox)_2 \cdot HOx(s) + 5H^+(aq) + 5Cl^-(aq) = UO_2{}^{+2}(aq) + 3HOxH^+(aq) + 5Cl^-(aq) \quad \Delta H_1 \quad (3)$$

$$UO_2(Ox)_2(s) + 4H^+(aq) + 4Cl^-(aq) = UO_2{}^{+2}(aq) + 2HOxH^+(aq) + 4Cl^-(aq) \quad \Delta H_2 \quad (4)$$

$$HOx(s) + H^+(aq) + Cl^-(aq) = HOxH^+(aq) + Cl^-(aq) \quad \Delta H_3 \quad (5)$$

The heat evolved in each reaction is represented by ΔH; since the reactions were exothermic, they all had a negative sign. By use of the laws of Hess, the heat change for the formation of the solvated chelates

$$Th(Ox)_4(s) + HOx(s) = Th(Ox)_4 \cdot HOx(s) \quad \Delta H_4 \quad (6)$$

$$UO_2(Ox)_2(s) + HOx(s) = UO_2(Ox)_2 \cdot HOx(s) \quad \Delta H_4 \quad (7)$$

[2a] L. Pokras and P. M. Bernays, THIS JOURNAL, **73**, 7 (1951).

[3] F. Frere, *ibid.*, **55**, 4362 (1933).

[4] F. Hecht and W. Reich-Rohrwig, *Monatsh. Chem.*, **53–54**, 596 (1929).

[5] G. B. Harvey, H. G. Heal, A. G. Maddock and E. L. Rowley, *J. Chem. Soc.*, 1010 (1947).

[6] L. Pokras, M. Kilpatrick and P. M. Bernays, THIS JOURNAL, **75**, 1254 (1953).

[7] T. Moeller and M. V. Ramaniah, *ibid.*, **75**, 3946 (1953); **76**, 5251 (1954).

[8] N. Eswaranarayana and Bh. S. V. Raghava Rao, *Anal. Chim. Acta*, **11**, 339 (1954).

[9] K. S. Venkateswarlu and Bh. S. V. Raghava Rao, *ibid.*, **12**, 554 (1955).

[10] T. Moeller and D. H. Wilkins, "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, p. 101.

[11] A. Classeen and J. Visser, *Rec. trav. chim.*, **65**, 211 (1946).

[12] F. Daniels, *et al.*, "Experimental Physical Chemistry," 4th Ed. McGraw-Hill Book Co., New York, N. Y., 1949, p. 462.

[13] F. D. Rossini, *et al.*, National Bureau of Standards, Circular No. 500, 462, 468 (1952).

[14] W. W. Wendlandt, *Anal. Chem.*, **30**, 56 (1958).

can be shown to be equal to

$$\Delta H_4 = \Delta H_2 + \Delta H_3 - \Delta H_1$$

The heats of solvation of the thorium and uranium(VI) chelates are given in Tables I and II. Since the metal chelate to water mole ratios were of the order of 1:10,000, the resultant heats of solution were assumed to be at infinite dilution. This assumption was considered valid since the heat of solution values were independent of the sample size.

TABLE I

HEATS OF SOLUTION OF THORIUM AND URANIUM(VI) 8-QUINOLINOL CHELATES IN 3.0 N HYDROCHLORIC ACID AT 25°

Compound	Sample wt., g.	Heat of soln., kcal./mole	Av., kcal./mole
		$-\Delta H_1$	
$Th(C_9H_6NO)_4 \cdot C_9H_6NOH$	0.6707	36.4	36.4 ± 0.2
	.2558	36.5	
	.3874	36.2	
		$-\Delta H_2$	
$Th(C_9H_6NO)_4$	0.5011	40.1	40.1 ± 0.2
	0.1424	40.0	
		$-\Delta H_1$	
$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$	0.6717	11.8	11.9 ± 0.1
	0.5504	11.9	
		$-\Delta H_2$	
$UO_2(C_9H_6NO)_2$	0.4002	14.0	
	.3969	13.9	14.0 ± 0.1
	.8089	14.1	
		$-\Delta H_3$	
C_9H_6NOH	1.2315	2.7	
	1.4038	2.9	2.8 ± 0.1
	1.3893	3.0	
	0.4062	2.6	

TABLE II

THE AVERAGE SOLVATE MOLECULE INTERACTION ENERGIES IN THE THORIUM AND URANIUM(VI) 8-QUINOLINOL CHELATES AT 25°

Metal chelate	$-\Delta H_1$[a]	$-\Delta H_2$	$-\Delta H_3$	$-\Delta H_4$
Thorium	36.4 ± 0.2	40.1 ± 0.2	2.8 ± 0.1	6.5 ± 0.2
Uranium(VI)	11.9 ± 0.1	14.0 ± 0.1	2.8 ± 0.1	4.9 ± 0.2

[a] All ΔH values in kcal./mole.

Kinetic Studies.—The method of Freeman and Carroll[15] was used to study the kinetics of the thermal decomposition process. In this method, from a single thermogram, the order of reaction as well as the activation energy can be calculated. Assuming that the volume of the reaction mixture does not change appreciably, the following equation is used to evaluate the reaction kinetics

$$\frac{-E^*/2.3R\ \Delta\,(1/T)}{\Delta \log W_r} = -x + \frac{\Delta \log dw/ft}{\Delta \log W_r}$$

where $W_r = w_c - w$; w_c is the weight loss at the completion of the reaction and w is the total weight loss up to time t.

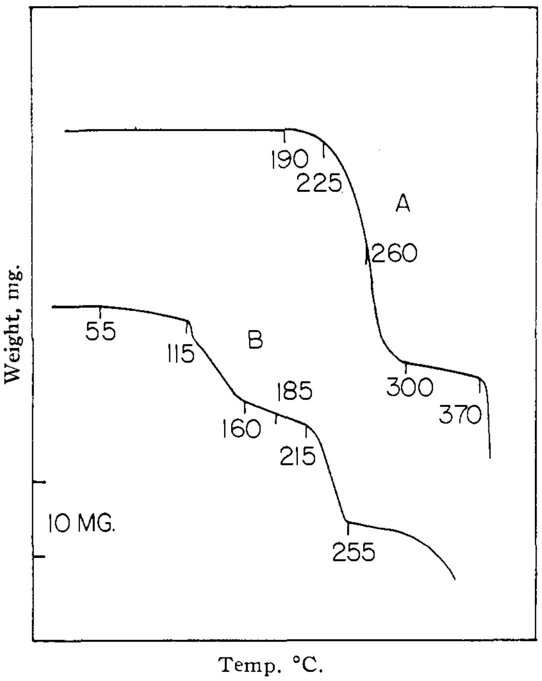

Fig. 1.—Thermograms of the thorium and uranium chelates: A, $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$; B, $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$.

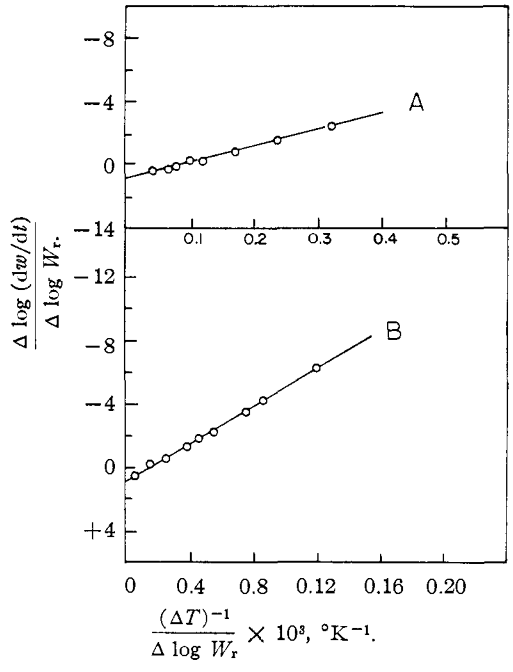

Fig. 2.—Kinetics of the thermal decomposition reaction: A, thorium chelate; B, uranium chelate.

By use of the thermograms given in Fig. 1, a graph of (Δ log dw/dt/Δ log W$_r$) $vs.$ Δ $(T^{-1})/\Delta \log W_r$ is given in Fig. 2. From the slope of curve, the E^* was calculated and from the intercept, the order of reaction was found. The results of these calculations are given in Table III. The kinetic data are presented for only the second step of the decomposition reaction of the thorium chelate. An attempt was made to evaluate the kinetics of the first step but a straight line relationship could not be obtained. Apparently, the evolution of the first molecule of 8-quinolinol is quite complex. As was expected, the thermal decomposition reaction was first order. It appears somewhat unusual that the E^* for the thorium chelate

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(15) E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).

Table III

Activation Energy and Order of Reaction for the Thermal Decomposition of the Uranium and Thorium Chelates

Reaction	Reaction order	E^*, kcal./mole
$UO_2(Ox)_2\cdot HOx = UO_2(Ox)_2 + HOx$	1	26 ± 2[a]
$[Th(Ox)_4]_2\cdot HOx = 2Th(Ox)_4 + HOx$	1	42 ± 4[a]

[a] Average of two separate thermograms.

(second step) should be much larger than that of the uranium chelate.

The thermograms of the thorium and uranium chelates are given in Fig. 1. While the uranium chelate loses 8-quinolinol in one step, it is apparent that this is a two step process in the thorium chelate. Borrel and Paris[16] also recognized this and proposed that the first step consisted of an intramolecular dehydration, resulting in the formation of $Th(C_9H_6NO)_4\cdot(C_9H_6NO)_2O$ and H_2O. Further heating resulted in the volatilization of $(C_9H_6NO)_2O$, leaving $Th(C_9H_6NO)_4$. However, on this basis, the weight loss for the dehydration reaction would be 0.96%; for the second step, it would be 16.18%.

The data in Table IV are in disagreement with this type of decomposition mechanism. There is better agreement with the data if the thorium chelate decomposes thermally according to the reactions

$$2Th(C_9H_6NO)_4\cdot C_9H_6NOH = [Th(C_9H_6NO)_4]_2\cdot C_9H_6NOH + C_9H_6NOH \quad (1)$$

$$[Th(C_9H_6NO)_4]_2\cdot C_9H_6NOH = 2Th(C_9H_6NO)_4 + C_9H_6NOH \quad (2)$$

Table IV

Weight Loss Data for the Thorium 8-Quinolinol Chelates

Run no.	Eq. 1, % (from 55 to 185°) Found	Theor.	Eq. 2, % (from 185 to 25) Found	Theor.
436	7.64	7.77	8.64	8.42
435	7.21		8.57	
437	7.71		8.36	
428	6.90		8.52	
431	6.43		8.30	

Discussion

From the magnitude of the heats of solvation, the 8-quinolinol is thought to be held in the crystal lattice by weak electrostatic forces. The values found for the thorium and uranium chelates are larger than the 1 kcal./mole estimated for the scandium chelate.[6]

Since the structures of the metal chelates are unknown, it is difficult to understand the exact nature of the bonding in the crystal lattice. If a layer structure is assumed, bonding similar to that found for chloroform in the chloroform bearing chromium, iron and aluminum acetylacetonates[17] might be expected. The chloroform interaction energy in the metal chelates is about 6.5 kcal./mole of chloroform, a value very similar to that found for 8-quinolinol in this investigation.

Acknowledgment.—The financial assistance of a grant from the Research Corporation is gratefully acknowledged.

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[16] M. Borrel and R. Paris, *Anal. Chim. Acta*, **4**, 267 (1950).

[17] J. F. Steinback and J. H. Burns, THIS JOURNAL, **80**, 1839 (1958).

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL SCIENCES, UNIVERSITY OF CALIFORNIA, RIVERSIDE]

Properties and Infrared Spectra of Ethylenediaminetetraacetic Acid Complexes. II. Chelates of Divalent Ions[1]

BY DONALD T. SAWYER AND PAUL J. PAULSEN

RECEIVED JULY 30, 1958

Infrared spectra have been recorded for the EDTA chelates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II). The data, when related to other studies, indicate that the bonding between ligand and metal ion is primarily ionic. Correlations are made between the various functional groups and their resulting absorption peaks. The sodium salts for this group of chelates have been synthesized and isolated.

The chelates formed between the ions of the alkaline earths and ethylenediaminetetraacetic acid (hereafter referred to as EDTA) have been discussed in relation to their infrared spectra in the previous paper of this series.[2] Because EDTA also forms stable complexes with other divalent metal ions, the study of their infrared spectra is of interest and has led to an investigation of the EDTA chelates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II). Although the solution properties of these chelates have been extensively studied,[3-5] little is known of their properties in the solid phase. Also, the type of bonding between the metal ion and the ligand has not been established.

The bonding between the above ions and the ligand would be expected to be primarily ionic,[6] but data are not available to confirm this supposition. The use of the infrared technique to determine whether the bonding in EDTA chelates is ionic or covalent has been reviewed previously.[2] As the

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[1] This research was supported by a grant-in-aid from the Research Corporation. Presented before the Analytical Division of the American Chemical Society in Chicago, Illinois, September, 1958.

[2] D. T. Sawyer and Paul J. Paulsen, THIS JOURNAL, **80**, 1597 (1958).

[3] R. W. Schmid and C. N. Reilley, *ibid.*, **78**, 5513 (1956).

[4] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

[5] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 537.

[6] J. C. Bailar, Jr., "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, p. 217-218.