[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Proton Spin Relaxation in Aqueous Solutions of Paramagnetic Ions. IV. Temperature Dependence in Solutions of Copper(II)–Ethylenediamine Complexes[1,2]

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Proton spin relaxation times, T_1 and T_2, were measured in aqueous copper(II)–ethylenediamine solutions in the temperature range 4 to 88°. Activation energies, or effective energy barriers, obtained for ion rotation (tumbling) are: $Cu(H_2O)_6^{++}$, 5.1 kcal./mole; $Cu(en)(H_2O)_4^{++}$, 4.5 kcal./mole; $Cu(en)_2(H_2O)_2^{++}$, 3.9 kcal./mole; $Cu(en)_2(H_2O)_2^{++}$ with excess ethylenediamine, 3.5 kcal./mole. The difference in the last two is attributed to differences in ion–solvent interaction with respect to rotation about different complex ion axes. The activation energy for exchange of N–H protons with those of solvent was found to be 4.5 kcal./mole. Bimolecular exchange of ethylenediamine between the bis complex and free solution is suggested as a path for proton exchange.

The dependence of proton longitudinal (thermal) and transverse (phase memory) relaxation times, T_1 and T_2, in aqueous solutions of paramagnetic ions upon proton resonance frequency and temperature has been considered in detail in two recent papers[4,5] and in earlier references cited there. Further discussion was presented in the preceding paper of this series[2] in which the effect of complex formation by copper(II) ions with ethylenediamine upon proton relaxation was considered in detail. Interpretation of the results reported here is based on conclusions drawn in that report and specific items are recalled in the following discussion.

The effect of temperature on proton relaxation times in copper(II)–ethylenediamine solutions is examined in this work and temperature factors are obtained for the correlation times and exchange rates which control the contributions of various mechanisms to the observed T_1 and T_2. The general approach suggested by Bernheim, Brown, Gutowsky and Woessner[5] is followed where it is applicable.

Experimental

Reagent grade copper(II) nitrate and technical ethylenediamine[6] were used in the preparation of solutions as described previously.[2] Ethylenediamine was redistilled before use.

Relaxation times were measured by "spin-echo" methods using techniques discussed in previous papers.[4,7] For T_2 a 120°–120° double-pulse method was used, with corrections for rectifier non-linearity. T_1 was determined using a 90°–90°–90° triple-pulse recovery method and, alternatively, by a similar triple-pulse decay method, with corrections for non-linearity. Results of the two T_1 methods were in good agreement in all cases reported here. Measurements were made at a proton resonance frequency of 29.0 Mc./sec., corresponding to a fixed magnetic field strength of 6810 oersteds.

Sample temperatures were regulated to ±1° using a cylindrical jacket around the sample coil through which a glycol–water mixture was circulated from an external thermostated reservoir. Care was taken to allow samples to reach thermal equilibrium before any measurements were made.

Results and Discussion

Hexaaquocopper(II) Nitrate Solutions.—Experimental values of proton T_1 and T_2 as functions of temperature for 0.05 M $Cu(H_2O)_6^{++}$ solutions are shown in Fig. 1. It has been reported[2,4,5] that both longitudinal and transverse relaxation in such solutions occur as a result of dipolar interaction only. The temperature variation of T_1 and T_2 is expected to be attributable primarily to changes in the dipolar correlation time, τ_c, which has been identified with the correlation time for rotation (tumbling) of the hydrated ion. Thus, τ_c has an exponential dependence on temperature[5]

$$\tau_c = \tau_c^\circ \exp(V_c/RT) \qquad (1)$$

in which V_c is the activation energy for ion tumbling. Use of the term activation energy for a process of this kind is not strictly justified but is retained here for convenience of reference.

Incorporation of equation 1 into the appropriate Solomon expressions[4,5,8] gives for T_1 and T_2

$$1/T_1 = (4/30)[S(S+1)g^2\beta^2\gamma_I^2 p\tau_c^\circ \exp(V_c/RT)/r^6] \times [3 + 7/\{1 + \omega_s^2\tau_c^{\circ 2}\exp(2V_c/RT)\}] \qquad (2)$$

$$1/T_2 = (4/60)[S(S+1)g^2\beta^2\gamma_I^2 p\tau_c^\circ \exp(V_c/RT)/r^6] \times [7 + 13/\{1 + \omega_s^2\tau_c^{\circ 2}\exp(2V_c/RT)\}] \qquad (3)$$

in which γ_I is the proton gyromagnetic ratio, r is the ion–proton internuclear distance, p is the probability that a proton occupy a position in the coördination sphere of the paramagnetic ions, and ω_s is the electron precessional frequency at the given fixed magnetic field strength. In either the high frequency ($\omega_s^2\tau_c^2 >> 1$) or low frequency ($\omega_s^2\tau_c^2 << 1$) limit, both t_1 and t_2 should exhibit exponential temperature dependence. However, in the region in which $\omega_s\tau_c \cong 1$, appreciable departure from strict exponential behavior is predicted. Noting that $\tau_c = 2 \times 10^{-11}$ sec. for aqueous $Cu(H_2O)_6^{++}$[2,4] at 27°, it is apparent that neither limiting approximation may be made with any assurance. τ_c was determined in the earlier work by two independent methods whose results differed by 10%. The value of τ_c obtained from the critical resonance frequency, at which $\omega_s\tau_c = 1$, is estimated to have a standard error of *ca.* 10%. In the following calculations a change in τ_c of 10% results in a value of V_c differing from that reported by approximately 0.1 kcal./mole.

Values of V_c were obtained by fitting theoretical curves of the form of equations 2 and 3 (using $\tau_c = 2 \times 10^{-11}$ sec.) to the experimental data. Best fit

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[1] This work was supported by a grant from the Robert A. Welch Foundation, Houston, Texas. Some of the results were discussed at the 136th National Meeting, American Chemical Society, Atlantic City, New Jersey, September, 1959.

[2] Paper III: L. O. Morgan, J. Murphy and P. F. Cox, THIS JOURNAL, **81**, 5043 (1959).

[3] Magnolia Petroleum Company Fellow, 1958–1959.

[4] L. O. Morgan and A. W. Nolle, *J. Chem. Phys.*, **31**, 365 (1959).

[5] R. A. Bernheim, T. H. Brown, H. S. Gutowsky and D. E. Woessner, *ibid.*, **30**, 950 (1959).

[6] Distillation Products Industries Division, Eastman Organic Chemicals, Rochester, N. Y.

[7] A. W. Nolle and L. O. Morgan, *J. Chem. Phys.*, **26**, 642 (1957).

[8] I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

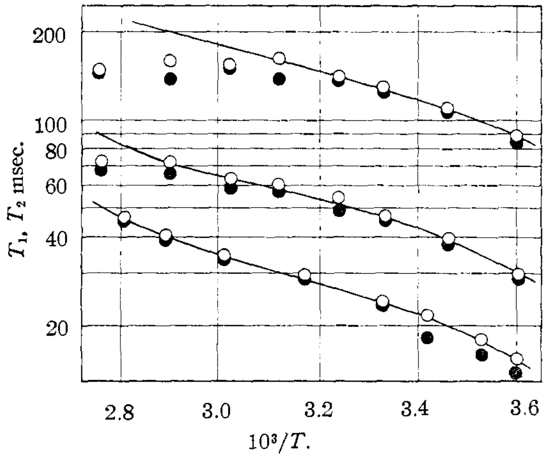

Fig. 1.—T_1 and T_2 as functions of temperature for: lower curve. 0.05 M copper (II) nitrate; middle curve, 0.05 M copper(II) nitrate with 0.05 M ethylenediamine; upper curve, 0.05 M copper(II) nitrate with 0.10 M ethylenediamine. Solid lines represent theoretical curves (T_1) for temperature dependence predicted for the reported V_c.

was determined by the method of least squares. Within the expected experimental error the same value was obtained for both T_1 and T_2 data: 5.1 kcal./mole (Table I).[9] The appropriate theoretical curve is shown with the experimental data in Fig. 1.

Table I

Activation Energies for Dipolar Relaxation

Paramagnetic ion	V_c (kcal./mole)	τ_c° (sec.)
$Cu(H_2O)_6^{++}$	5.1	3.7×10^{-15}
$Cu(en)(H_2O)_4^{++}$	4.5	1.0×10^{-15}
$Cu(en)_2(H_2O)_2^{++}$	3.9	3.0×10^{-14}
$Cu(en)_2(H_2O)_2^{++}$ (with 0.053 M en excess)	3.5	5.5×10^{-14}

Tetraaquoethylenediaminecopper(II) Nitrate Solutions.—The dipolar mechanism is also responsible for the observed relaxation in solutions containing 0.05 M $Cu(en)(H_2O)_4^{++}$ (Fig. 1). There is no apparent contribution from rapid exchange of N–H protons of the ethylenediamine ligand, except perhaps at the highest experimental temperatures. In the low and intermediate temperature regions the observed relaxation times are explicable in terms of the number of exchangeable O–H protons in the coördination sphere of the paramagnetic ion. Equations 2 and 3 are equally applicable in this case, noting that the value of p is expected to be $^2/_3$ of that for equivalent $Cu(H_2O)_6^{++}$ solutions. V_c is 4.5 kcal./mole (Table I) and the corresponding theoretical curve is shown in Fig. 1. τ_c was assumed to be approximately 2×10^{-11} sec. at 27° for this complex and those considered in the following sections on the basis of frequency dependence data reported previously.[2] Although t_1 was measured for each of the solutions at only three resonance frequencies, the experimental values in each case were represented very closely by theoretical frequency dependence curves based on $\tau_c = 2 \times 10^{-11}$ sec. Allowing the maximum probable experimental error for each of the t_1 values it is estimated that the reported τ_c is correct to within *ca.* 20%. That corresponds to ±0.2 kcal./mole in the calculated values of V_c.

Diaquobisethylenediaminecopper(II) Nitrate Solutions.—In the absence of ethylenediamine in excess of that required for the formation of $Cu(en)_2(H_2O)_2^{++}$, relaxation in 0.05 M solutions may be explained on the basis of the dipolar mechanism alone, in the lower range of temperatures. V_c is 3.9 kcal./mole (Table I, theoretical curve shown in Fig. 1).

The high temperature values of T_1 and T_2 observed in this case cannot be fitted by any theoretical curve of the assumed form using single values of τ_c and V_c. However, N–H proton exchange may be expected to contribute significantly to the observed relaxation at high temperatures. Assuming the additional relaxation to be proton exchange rate controlled and analyzing the data in a manner analogous to that described in the following section, relaxation rate constants for the three highest temperatures are 0.76, 1.25, and 2.31 sec.$^{-1}$. These values give an estimated activation energy for proton exchange of approximately 8 kcal./mole.

Diaquobisethylenediaminecopper(II) Nitrate in Solutions Containing an Excess of Ethylenediamine.—In 0.05 M copper(II) solutions containing more than 0.01 M ethylenediamine in excess of that required for formation of the bis complex the contribution of isotropic spin exchange (scalar coupling of electron and proton spins) to transverse relaxation is large. This arises through rapid exchange of ligand N–H protons, which are strongly coupled to the electron spin system through the Cu–N bonds. The appropriate correlation time, τ_e, for the isotropic spin exchange process is presumably the electron spin relaxation time, τ_s, which is expected to be of the order of 10^{-8}–10^{-7} sec. Observed values of t_1 and t_2 are given by

$$1/T_1(\text{obsd.}) = 1/T_1(\text{dip}) + 1/T_1(\text{ex}) \quad (4)$$

$$1/T_2(\text{obsd.}) = 1/T_2(\text{dip}) + 1/T_2(\text{ex}) \quad (5)$$

The appropriate spin exchange contributions are[10] (for infinitely rapid exchange)

$$1/T_1(\text{ex}) = 2/3[S(S+1)A^2p/\hbar^2][\tau_e/(1+\omega_s^2\tau_e^2)] \quad (6$$

$$1/T_2(\text{ex}) = 1/3[S(S+1)A^2p/\hbar^2][\tau_e+\tau_e/(1+\omega_s^2\tau_e^2)] \quad (7)$$

At 29.0 Mc./sec. $\omega_s^2\tau_e^2 >> 1$ and $1/T_1(\text{ex})$ is negligible. For ethylenediamine concentrations in the range 0.01 to 0.10 M the first-order proton exchange rate constant (for N–H protons) k satisfies the condition

$$1/T_2(\text{bis}) < k << [1/T_2(\text{comp})][P_N] \quad (8)$$

$$P_N = 8[Cu(en)_2(H_2O)_2^{++}]/[H]_{tot} \quad (9)$$

in which T_2(bis) is the observed transverse relaxation time for a solution containing an equivalent concentration of bis complex with no excess ethylenediamine (negligible N–H proton exchange), T_2(comp) is the transverse relaxation time for N–H

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[9] Bernheim, Brown, Gutowsky and Woessner (ref. 5) found V_c = 2.48 kcal./mole for copper(II) solutions using data taken at 20 Mc./sec. Using $\tau_c = 2 \times 10^{-11}$ sec. it may be shown that the exponential approximation does not apply in any part of their experimental temperature range for copper(II) solutions. The same is true for gadolinium(III) solutions. The values 5.5 and 1.5 kcal./mole reported for manganese(II) and cobalt(II) solutions, respectively, are approximately correct.

[10] N. Bloembergen, *J. Chem. Phys.*, **27**, 572 (1957), and references cited there; *ibid.*, **27**, 595 (1957).

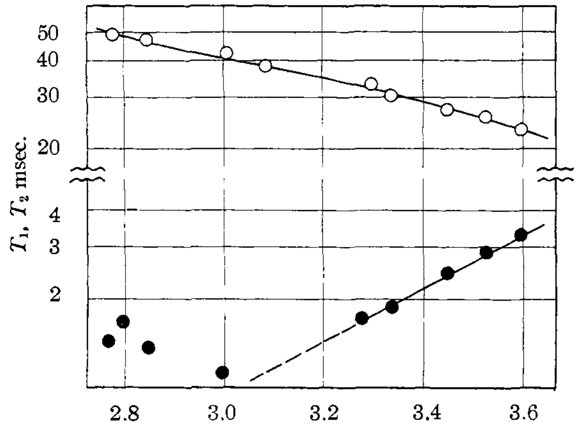

Fig. 2.—T_1 and T_2 as functions of temperature for 0.05 M copper(II) nitrate with 0.153 M ethylenediamine. The upper solid line represents the predicted T_1 temperature dependence for V_c = 3.5 kcal./mole.

protons in the complex, and $[H]_{tot}$ is the total concentration of exchangeable protons in the system. Transverse relaxation is assumed to be complete within the residence time of the N–H protons[11] and the over-all proton transverse relaxation rate attributable to N–H proton exchange is determined by k

$$1/T_2(\text{obsd.}) - 1/T_2(\text{bis}) = k \qquad (10)$$

T_2 as a function of temperature for 0.05 M $Cu(en)_2(H_2O)_2^{++}$, 0.053 M ethylenediamine solution is shown in Fig. 2. In the lower temperature range a reasonably good exponential relation is observed, while at higher temperatures deviations are of such a nature as to suggest that the simplifying assumption (10) no longer applies.

It has been shown[2] that N–H proton exchange follows a bimolecular rate law in these systems

$$R = 2k[H_2O] = k_H'[Cu(en)_2(H_2O)_2^{++}][en] \qquad (11)$$

in which k_H' is the bimolecular rate constant expressed in terms of proton exchange. In Fig. 3, k_H' is shown as a function of temperature, using only data for which (10) applies. Additional values, obtained at other concentrations of complex and ethylenediamine are included to permit extension of the line to higher temperatures while retaining the validity of (10). The activation energy V_h for the exchange process was evaluated from

$$k_H' = k_H'^0 \exp(-V_h/RT) \qquad (12)$$

to obtain V_h = 4.5 kcal./mole and $k_H'^0 = 4.4 \times 10^{10}$ sec.$^{-1}$.

With respect to T_1, mixing of ligand N–H protons with those of solvent is essentially complete at ethylenediamine concentrations in excess of 0.01 M (for 0.05 M $Cu(en)_2(H_2O)_2^{++}$ solutions) and the isotropic spin exchange mechanism does not apply, as has been shown. Thus, the dipolar relaxation mechanism is the principal contributor to thermal relaxation, with the important additional feature that N–H protons now participate in the

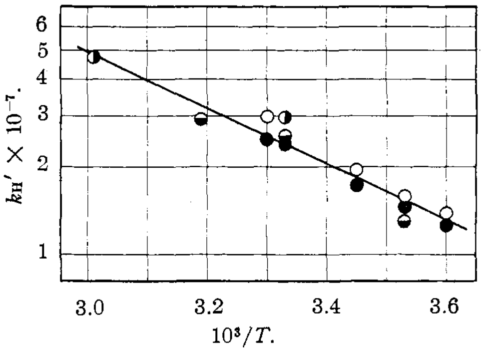

Fig. 3.—k_H' as a function of temperature: 0.05 M copper(II) nitrate with 0.115 M ethylenediamine: 0.05 M copper(II) nitrate with 0.153 M ethylenediamine: 0.02 M copper(II) nitrate with 0.058 M ethylenediamine: 0.02 M copper(II) nitrate with 0.096 M ethylenediamine. The solid line represents the predicted temperature dependence of k_H' for V_h = 4.8 kcal./mole.

over-all proton relaxation. V_c is found to be 3.5 kcal./mole (Table I, theoretical curve shown in Fig. 2). In this case a good fit to the experimental data is obtained over the entire temperature range because rapid N–H proton exchange occurs throughout the range.

General.—Decrease of V_c with increasing substitution of ethylenediamine for water molecules in the paramagnetic complex ion is to be expected. While the complex ionic radius increases to some extent, the degree of ion–solvent interaction should decrease to an even greater extent. In essence, the ion presents a hydrocarbon-like surface to the solvent wherever an ethylenediamine ligand is located.

At first glance it might appear surprising that V_c for the bis complex in excess ethylenediamine is less than that for the same complex in the absence of excess ethylenediamine. However, relaxation in the latter instance is primarily attributable to O–H protons in axial positions in the complex. The perturbation leading to magnetic dipolar interaction in that case is probably end-over-end tumbling. In an excess of ethylenediamine, N–H protons exchange rapidly and, therefore, contribute to the observed relaxation of solvent protons. Magnetic dipolar interaction of those protons with the central ions includes that resulting from rotation about the fourfold symmetry axis, for which the activation energy, or effective energy barrier, should be significantly smaller.

The most plausible, although not the only, interpretation of the bimolecular rate law observed for N–H proton exchange is that the exchange occurs through molecular exchange of ethylenediamine molecules between complex and solution, followed by rapid proton exchange between free ethylenediamine and solvent water. In their study of exchange in transition metal–ethylenediamine complex solutions, Popplewell and Wilkins[12] reported that the ethylenediamine–$Cu(en)_2(H_2O)_2^{++}$ exchange rate was too large to be measured by radiochemical methods. In the general consideration of their results it was concluded that exchange by

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[11] In order to set a reasonable upper limit to T_2(comp), T_2 was measured in 0.01 M copper(II) nitrate, 0.90 M ethylenediamine solution. T_2 was found to be 2.0 msec. at 27°, which gives $T_2(\text{comp}) \leq 1.4 \times 10^{-4}$ sec.

[12] D. S. Popplewell and R. G. Wilkins, *J. Chem. Soc.*, 4098 (1955); *Rec. trav. chim.*, **75**, 815 (1956).

the dissociative path is probably very rapid even in alkaline solution at 0° and, further, that a bimolecular path is expected to be important because of the possibility of forming a transition state by attachment of an ethylenediamine molecule in an axial position. Thus, bimolecular exchange may occur through rapid formation and dissociation of the tris complex, in spite of its low thermodynamic stability constant.[13] Bjerrum and Nielsen suggested that the third ethylenediamine molecule in the tris complex is monodentate and that copper(II) has coördination number 5 in the complex. Although such a structure may be involved as an initial step in the reaction, it cannot be the only form of the tris complex. If proton exchange results reported in this paper are indeed explained by the bimolecular exchange of ethylenediamine, it is necessary that the ethylenediamine ligands be equivalent in some intermediate or transition state, most probably one having nearly octahedral symmetry. It should be noted that the bimolecular exchange rate constant expressed in terms of ethylenediamine exchange is

$$k_{en}' = k_H'/4 \qquad (13)$$

because there are four exchangeable protons in each ethylenediamine molecule.

The observed activation energy, 4.5 kcal./mole, is abnormally low for unimolecular (or pseudo-unimolecular) dissociation of a transition metal–ethylenediamine chelate. However, it is quite reasonable for an "associative" reaction

$$Cu(en)_2(H_2O)_2^{++} + en \longrightarrow Cu(en)_3^{++} + 2H_2O \qquad (14)$$

If that reaction involves the rate-determining step in proton exchange, the ensuing "dissociation"

$$Cu(en)_3^{++} + 2H_2O \longrightarrow Cu(en)_2(H_2O)_2^{++} + en \qquad (15)$$

must be rapid, in spite of an anticipated high activation energy, because of a large entropy of activation.

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(13) J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

The Infrared Spectra of Some Thiocyanatocobalt Ammines

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The infrared spectra of a series of thiocyanatocobalt ammines has been obtained in the region from 680 to 4000 cm.$^{-1}$. The spectra strongly suggest the formation of a double bond between the ligand and the metal with resulting loss of triple bond character in the C–N bond and gain of double bond character in the C–S bond. It has been shown that coördinated and ionic thiocyanate can be differentiated readily by examination of their infrared spectra. Bridging by thiocyanate occurs in some of the thiocyanatocobalt ammine–silver addition compounds and can be detected by observing the C–N frequency of the adduct. Assignment of bands in the infrared spectra of some acido bisethylenediamine complexes to various N–H vibrations has been made and a means for differentiating *cis*- and *trans*-isomers of these compounds by the number of bands in the 1120–1150 cm.$^{-1}$ region proposed.

The introduction of the thiocyanato group into the coördination sphere of various cobalt ammines gives rise to a series of compounds which differ markedly in chemical and physical properties from the usual halo-substituted acido cobalt ammines. For example, the thiocyanato ligand of the thiocyanatocobalt ammines is more resistant to replacement by the anions of strong mineral acids or by water[2] than are the comparable chloro- or bromocobalt ammines which undergo replacement reactions readily.[3]

Further, the thiocyanato ligand is difunctional, with both the nitrogen and the sulfur atoms potentially able to act as electron pair donors. Thiocyanate coördinates to cobalt with the formation of metal–NCS bonds and to mercury or platinum with the formation of metal–SCN bonds. Even after coördination through the nitrogen end of the molecule, the sulfur end appears to remain able to donate electrons in coördinate covalent bond formation with such metal ions as mercury(II) or silver (I). Werner[4] believed that in the thiocyanatocobalt ammines, the bonding of the ligand to the metal is through nitrogen and has claimed that the formation of the silver addition products of these ammines is due to the coördination of the heavy metal ion to the free sulfur end of the ligand. Waggener, *et al.*,[5] have demonstrated the existence of a metal to nitrogen bond in the thiocyanatocobalt ammines and their chromium analogs and have shown both that the silver adducts are much less stable than Werner had supposed and that mercury(II) ion also forms adducts with thiocyanato complexes.

In this study, the infrared spectra of a series of thiocyanatocobalt ammines and related thiocyanato complexes were obtained in an effort to determine the nature of the bonding within the thiocyanato ligand and by inference, the bonding between the ligand and the metal. Further, the difference between coördinated and uncoördinated thiocyanate and the nature of the silver adducts of some thiocyanatocobalt ammines were investigated. Finally, information leading to the assignment of various N–H vibrations in the spectra of the ethylenediamine cobalt complexes was obtained.

Experimental

Preparation of Compounds.—The preparation of pure salts of the thiocyanatocobalt ammines followed the methods of Werner and Muller.[6]

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(1) This material was taken from the Ph.D. dissertation of Mark M. Chamberlain, University of Illinois, June, 1956.

(2) J. Sand and G. Bokman, *Ber.*, **40**, 4497 (1907).

(3) A. Werner, *Z. anorg. allgem. Chem.*, **22**, 91 (1900).

(4) A. Werner, *Ann.*, **386**, 1 (1912).

(5) W. C. Waggener, J. A. Mattern and G. H. Cartledge, Abstracts of papers, 122nd National Meeting, American Chemical Society, September, 1952, page 19-P; W. C. Waggener, private communication.

(6) A. Werner and H. Muller, *Z. anorg. allgem. Chem.*, **22**, 91 (1900).