TABLE I

Ethylene, ml.	Ratio C_2H_4 (free): C_2H_4 (coord.)	Location of n.m.r. absorption of ethylene, p.p.m.
0	0	−4.83
2	0.6	−4.90
4	1.3	−5.00
6	1.9	−5.10
8	2.6	−5.15
25	∞	−5.37

trometer and a Varian Model V-4340 variable temperature probe accessory. As the temperature was reduced the location of the absorption ascribed to ethylene shifted downfield as follows: 0° (δ −4.82 p.p.m.); −25° (−4.85 p.p.m.); −50° (−4.93 p.p.m.)· −75° (−5.13 p.p.m.).

Exchange Experiments. C_2D_4 and $[(C_2H_4)PtCl_3]^-$.—A solution of 0.15 g. of $[(C_2H_4)PtCl_2]_2$ (0.5 mmole of coordinated ethylene) in 5 ml. of 1 M methanolic HCl was put in a flask containing a magnetic stirrer. The flask was chilled to −80° and evacuated. Then, 15 ml. of C_2D_4 (0.6 mmole) was admitted, and the mixture was stirred vigorously for 1 min. Ethylene was quickly distilled into an evacuated flask chilled in liquid nitrogen and analyzed by mass spectroscopy. The gas was 54% C_2D_4 and 46% C_2H_4.

$K[(C_2D_4)PtCl_3]$ **and** $(acac)Rh(C_2H_4)_2$.—$K[(C_2D_4)PtCl_3]$ was prepared by charging into a liquid nitrogen cooled, heavy-walled 4.5-ml. tube, 0.42 g. of K_2PtCl_4 (1 mmole), 2 ml. of H_2O, 0.25 ml. of concentrated HCl solution, and 25 ml. of gaseous C_2D_4 (1 mmole). The tube was sealed and agitated at 25° for 2 days during which time the color changed from red to yellow, corresponding to formation of Zeise's salt. About 1 ml. of water was removed by distillation at reduced pressure, and the residue cooled to give 0.3 g. (75% yield) of $K[(C_2D_4)PtCl_3] \cdot H_2O$.

The exchange reaction was accomplished by mixing a solution of 0.1 g. of $K[(C_2D_4)PtCl_3] \cdot H_2O$ (0.26 mmole) in 3 ml. of ethanol with a solution of 0.035 g. of $(acac)Rh(C_2H_4)_2$ (0.13 mmole) in 2 ml. of ethanol. After 30 sec. the reaction mixture was divided

into two equal parts. One was immediately poured into 30 ml. of chloroform to precipitate the platinum complex, but hold the rhodium complex in solution. The other aliquot was diluted with 30 ml. of water to precipitate the rhodium complex. The complexes were recovered from the suspensions by centrifuge. Each was treated in an infrared gas cell with an ethylene glycol solution of sodium cyanide and both gave equal amounts of C_2D_4 and C_2H_4 as judged from the O.D. of the absorptions at 10.5 (C_2H_4) and 13.9 μ (C_2D_4).

Attempt to Demonstrate the Formation of $[(C_2H_4)_2PtCl_2]$ **in Solution.**—The apparatus consisted of a flask (with a side arm and magnetic stirrer) attached through a three-way T-stopcock to an open-end manometer made of capillary tubing. The apparatus was designed to minimize free space. The flask was charged with 2.00 ml. of acetone, and a magnetized tube holding 0.030 g. of $[(C_2H_4)PtCl_2]_2$ was inserted in the side arm. The acetone was frozen in liquid nitrogen and the apparatus evacuated. Next the flask was warmed to −36°, and the acetone was saturated with ethylene introduced through the stopcock (27 ml. (N.T.P.) of ethylene was required). The apparatus was closed and the $[(C_2H_4)PtCl_2]_2$ added to the acetone. The pressure of the system increased by 1 mm. Conversion of all the $[(C_2H_4)PtCl_2]_2$ into $(C_2H_4)_2PtCl_2$ would have led to absorption of 2.24 ml. of ethylene and a pressure drop of 63 mm.

Synthesis of Zeise's Salt.—A stirred flask was charged with 8.3 g. of K_2PtCl_4 (0.02 mole), 40 ml. of H_2O, and 5 ml. of concentrated HCl. The flask was swept free of air with ethylene, and 0.2 g. of $SnCl_2 \cdot 2H_2O$ was added. The mixture was stirred and ethylene was introduced at about 1.5 atm. Absorption of ethylene was nearly complete in 3 hr., and the reaction mixture was chilled to 0°. The reaction solution was siphoned from the product under nitrogen, and the crystals were washed with 10 ml. of methanol cooled to 0°. The yield was 5.4 g. (70% conversion).

The reaction solution from the first synthesis was used as the solvent for 8.3 g. of K_2PtCl_4 in a second synthesis conducted as the first. The yield of $K[(C_2H_4)PtCl_3] \cdot H_2O$ was 7.6 g. (98% conversion).

Complexes of Chromium(II) with Diethylenetriamine and Triethylenetetramine[1]

BY ROBERT L. PECSOK, RONALD A. GARBER, AND L. DONALD SHIELDS

The Cr(II)–dien and Cr(II)–trien systems have been studied using potentiometric, spectrophotometric, and magnetic methods. All pK values refer to concentration quotients obtained at an ionic strength of 0.1 F. Values of pK_H for dien and trien have been determined at 26°; dien: $pK_1 = 4.22$, $pK_2 = 8.95$, $pK_3 = 9.79$; trien: $pK_1 = 3.37$, $pK_2 = 6.62$, $pK_3 = 9.09$, $pK_4 = 9.69$. The pK_H values for trien have been redetermined at 20°: $pK_1 = 3.55$, $pK_2 = 6.76$, $pK_3 = 9.26$, $pK_4 = 9.80$. These studies indicate the existence of the complexes mono(dien)–Cr(II), bis(dien)–Cr(II), and mono(trien)–Cr(II) with respective log K_f values of 6.71, 2.69, and 7.71 at 20° and 6.78, 2.6, and 8.0 at 26°. Magnetic measurements using an n.m.r. technique indicate that the bis(dien)–Cr(II) and mono(trien)–Cr(II) complexes have four unpaired electrons. It is postulated that all of these complexes have distorted octahedral configurations with water molecules filling the remaining positions not occupied by the amine nitrogen atoms.

Introduction

In previous potentiometric and spectrophotometric studies of the complexes of chromium(II) with ethyl-

enediamine in aqueous solution, Pecsok and Bjerrum[2] established the existence of mono and bis complexes and determined the consecutive formation constants for these complexes. In the ethylenediamine study, it was suggested that chromium(II) forms planar com-

(2) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

plexes with a coordination number of four. Further studies of other chromium(II)–polyamine systems using tridentate and tetradentate ligands should yield significant additional information concerning the coordination number of the Cr(II) ion and the structure and stability of its complexes.

In this study we have investigated the systems chromium(II)–diethylenetriamine and chromium(II)–triethylenetetramine. Using potentiometric methods we have determined the consecutive acidity constants at 26° and 0.1 F ionic strength for diethylenetriamine (hereafter referred to as dien) and triethylenetetramine (hereafter referred to as trien). We also have redetermined the consecutive acidity constants for trien at 20.0° and 0.10 F ionic strength. Values for the formation constants of the mono and bis complexes of dien with chromium(II) and the mono complex of trien at 26 and 20.0° at 0.10 F ionic strength have been determined.

Experimental

Reagents.—Chromium(II) chloride solutions were prepared from primary standard potassium dichromate as previously described by reduction with hydrogen peroxide and electrolysis at a mercury cathode.[8] The Cr(II) content was determined by indirect potentiometric titration with ceric solution after adding an excess of iron(III). The Cr(III) content was determined spectrophotometrically and found to be less than 0.1% of the total Cr. The acidity of the Cr(II) solutions was determined by potentiometric titration to pH 4.7 with standardized sodium hydroxide.

Technical grade dien (Eastman Kodak Co.) was doubly distilled from metallic sodium under 1 mm. pressure at 64–67°. About 300 g. of the distillate then was dissolved in 750 ml. of 95% ethanol, 150 ml. of 8.5 F hydrochloric acid (in ethanol) was added, and the mixture was cooled to 0°. The white crystals formed were collected by filtration, washed with diethyl ether, dried by suction, and stored in a vacuum desiccator. Potentiometric titrations of the dien salt with standardized sodium hydroxide and hydrochloric acid solutions indicated that the crystals were 16.70% dien monohydrochloride and 83.30% dien dihydrochloride. Microanalyses for carbon, hydrogen, nitrogen, and chlorine confirmed this composition. *Anal.* Calcd.: C, 28.47; H, 8.84; Cl, 37.78; N, 24.90. Found: C, 28.68; H, 8.56; Cl, 37.19; N, 24.69. Aqueous stock solutions of dien were prepared using the assayed salt crystals and oxygen-free distilled water. These solutions were placed in storage burets under 1.5 atm. of purified nitrogen.

Technical grade trien (Eastman Kodak Co.) was doubly distilled from molten sodium under 1 mm. pressure at 106–110°. A solution of 160 g. of the distillate in 500 ml. of 95% ethanol at 0° was treated with 113 ml. of 8.5 F ethanolic hydrochloric acid. The white precipitate formed was removed by filtration and discarded. About 100 ml. of 8.5 F ethanolic hydrochloric acid was added to the filtrate at 0° and the resultant white crystals were collected by filtration. Five recrystallizations from 95% ethanol produced white crystalline plates which were washed with diethyl ether, dried by suction, and stored in a vacuum desiccator. Potentiometric titrations indicated that the composition was 98.2% trien dihydrochloride and 1.3% trien trihydrochloride, thus suggesting the presence of 0.5% water. Microanalyses of the crystals for carbon, hydrogen, nitrogen, and chlorine agreed with this composition. *Anal.* Calcd.: C, 32.64; H, 9.20; Cl, 32.30; N, 25.38. Found: C, 32.67; H, 9.23; Cl, 31.86; N, 24.44 trien stock solutions were prepared with degassed distilled water, transferred to a storage buret, and then placed under 1.5 atm. of purified nitrogen.

(3) R. L. Pecsok and W. P. Schaefer, *J. Am. Chem. Soc.*, **83**, 62 (1961).

Reagent grade potassium chloride was used to adjust the ionic strength of all solutions to approximately 0.10 F.

Hydronium Ion Concentration Measurements.—Measurements of the hydronium ion concentration were made with Radiometer PHM4C meters using Radiometer G202B and G202C glass electrodes. The electrode systems were calibrated several times each day with standard solutions of known hydrochloric acid concentration also containing potassium chloride to give 0.10 F ionic strength. A thermostated cell with positive nitrogen pressure (5 cm. of H_2O) was used in the potentiometric work performed at 20° and 0.10 F ionic strength. The titrations were performed by adding increments of the stock Cr(II) solution to oxygen-free reaction mixture containing potassium chloride, dien or trien, and sodium hydroxide sufficient to establish the final hydronium ion concentration at the desired value.

Spectrophotometric Measurements.—All spectra were measured with a Cary Model 14 recording spectrophotometer. The Cr(II) solutions were measured in a 10-cm. cell with standard taper fittings. The Cr(II) complex solutions prepared in an electrolytic beaker were transferred to the spectral cell by the force of nitrogen pressure within the beaker through an outlet tube to a nitrogen-flushed cell. The solutions to be studied spectrophotometrically were prepared at room temperature (26 ± 1°) because of the inconvenience involved in manipulating the beaker and spectral cell in a constant-temperature bath.
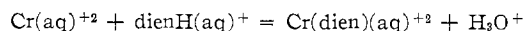
Nuclear Magnetic Resonance Measurements.—All nuclear magnetic moment measurements were made with a Varian Associates Model A-60 analytical n.m.r. spectrometer.
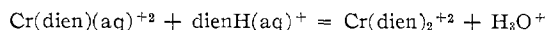
Results

Determination of pK_H Values for dien and trien.—Stock solutions of dien and trien, with the ionic strength maintained constant, were titrated with standardized sodium hydroxide and groups of points taken around $\bar{n}$ values of 2.4, 1.8, and 0.5 for dien and $\bar{n}$ values of 3.5, 2.4, 1.5, and 0.5 for trien.

Jonassen's formulas[4] for the calculation of the pK_H values were used. The values obtained for dien in 0.1 F ionic strength at 26° are: $pK_1 = 4.22$, $pK_2 = 8.95$, $pK_3 = 9.79$. For the same at 20° we used values previously reported by Prue and Schwarzenbach[5]: $pK_1 = 4.34$, $pK_2 = 9.13$, $pK_3 = 9.94$. The values for trien in 0.1 F ionic strength at 26° are: $pK_1 = 3.37$, $pK_2 = 6.62$, $pK_3 = 9.09$, $pK_4 = 9.69$; and at 20°, $pK_1 = 3.55$, $pK_2 = 6.76$, $pK_3 = 9.26$, $pK_4 = 9.80$.

Titration of the Cr(II)–dien System.—Following Bjerrum's treatment,[6,7] the complexation reactions in this system can be represented as

$$Cr(aq)^{+2} + dienH(aq)^+ = Cr(dien)(aq)^{+2} + H_3O^+$$

and

$$Cr(dien)(aq)^{+2} + dienH(aq)^+ = Cr(dien)_2^{+2} + H_3O^+$$

and we define

$$K_1 = [Cr(dien)(aq)^{+2}]/[Cr(aq)^{+2}][dien] \qquad (1)$$

$$K_2 = [Cr(dien)_2^{+2}]/[Cr(dien)(aq)^{+2}][dien] \qquad (2)$$

The concentration of the bis complex can be neglected at $\bar{n} = 0.50$ if the values of K_1 and K_2 differ greatly. Then $K_1 = $ [dien] at $\bar{n} = 0.50$. Similarly, $K_2 = $ [dien] at $\bar{n} = 1.50$.

(4) H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm, and R. M. Rogan, *ibid.*, **72**, 2430 (1950).

(5) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(7) H. B. Jonassen, R. B. LeBlanc, and R. M. Logan, *J. Am. Chem. Soc.*, **72**, 4968 (1950).

We determine the formation curve from $\bar{n} = 0$ to $\bar{n} = 1$ from the relations given: C_M is the total concentration of Cr^{+2} in system in all forms, C_D is the total concentration of dien present in all forms, C_H is the total concentration of H^+ in system in all forms, C_S is the total concentration of H^+ bound to dien, C_D^* is the total concentration of dien not bound in metal complex, C_D^{**} is the concentration of dien bound in metal complex, $\bar{n}_H$ is the average number of hydrogens bound per noncomplexed dien molecule, and $\bar{n}$ is the average number of dien molecules bound per metal ion.

We can control and have accurate knowledge of the parameters C_M, C_H, and C_D, and we can measure $[H_3O^+]$. From this measurement we may calculate values for all of the other terms above from the relationships

$$C_S = C_H - [H_3O^+] + [OH^-] \tag{3}$$

$$C_D^* = C_S/\bar{n}_H \tag{4}$$

We may calculate C_D^* from eq. 4

$$C_D^{**} = C_D - C_D^* \tag{5}$$

Thus

$$\bar{n} = C_D^{**}/C_M \tag{6}$$

and

$$[dien] = \alpha C_D^* \tag{7}$$

where α is the fraction of uncomplexed dien present as proton-free dien. All of the necessary concentrations are known and we now may solve for K_1 using eq. 1 and for K_2 using eq. 2. With the relationships given above and the acidity constants for dien given by Prue and Schwarzenbach,[5] an experimental Bjerrum formation curve may be obtained for the chromium(II)–dien system.[8] The graphic solution for the value of log K_1 at $\bar{n} = 0.5$ gives 6.73. Analysis of thirteen points on the formation curve, all with varying total metal ion, total dien, and total hydrogen ion concentrations, yields an average value of 6.71 for log K_1 at 20° with an average deviation of ±0.02 log unit. The graphic solution for the value of log K_2 at $\bar{n} = 1.5$ gives 2.61. Analysis of fifteen points on the formation curve, all representing different total metal ion, total dien, and total hydrogen ion concentrations, provides an average value of 2.63 for log K_2 at 20° with an average deviation of ±0.02 log unit. The constancy of the formation constant values indicates that there is insignificant oxidation of chromium(II) during the time of the titrations.

Spectra of Cr(II)–dien Solutions.—All solutions contained 20 ml. of a stock solution of dien dihydrochloride (0.0723 F). Varying amounts of acid and base and 0.1 F potassium chloride were added so that

(8) Pertinent data for the formation curves have been deposited as Document No. 8241 with ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I

WAVE LENGTHS OF MAXIMUM ABSORPTION AND MOLAR EXTINCTION COEFFICIENTS OF Cr(II)–dien SOLUTIONS

$-\log$ [H_3O^+]	pA	Abs. max., $m\mu$	ϵ_M	x	log K_1
4.38	11.79	710	4.83	0	
4.77	10.87	710	6.40	0.035	
5.26	9.85	710	6.76	0.037	
6.00	8.34	670	7.97	0.162	
6.47	7.41	620	9.29	0.212	6.84
6.64	7.08	613	14.97	0.398	6.90
6.66	7.03	613	15.4	0.413	6.88
6.69	6.91	614	15.8	0.425	6.78
6.81	6.74	614	18.6	0.516	6.77
7.12	6.13	612	25.7	0.748	6.60
7.26	5.84	614	28.7	0.846	6.59
7.92	4.55	610	32.0	0.952	6.85
8.33	3.81	603	32.6	0.973	
8.91	2.81	597–598	34.4		
9.51	2.18	588	38.7		
10.07	1.84	586–587	38.9		
10.48	1.71	582–583	39.7		
11.43	1.62	575	43.0		
11.62	1.62	563	49.7		

Av. 6.78 ± 0.12

after the addition of 2 ml. of Cr(II) solution, the final volume would be about 50 ml. and the ionic strength 0.1 F. The wave length of maximum absorption and the measured extinction coefficients, based on total chromium concentration, for a series of Cr(II)–dien solutions of varying acidity are listed in Table I.

The absorption peak at 710 $m\mu$ (ϵ 4.83) in the most acid solutions is due to the $Cr(H_2O)_6^{+2}$ species. As the acidity decreases, more unprotonated dien is available for complexation and the mono(dien)–Cr(II) complex forms. Its absorption peak is at 614 $m\mu$ (ϵ 32.3). At values of $-\log [H_3O^+]$ of 8 and above, the bis(dien) species begins to appear in appreciable quantity. Its absorption maximum occurs at about 587 $m\mu$ (ϵ 38.8). If $-\log[H_3O^+]$ is raised above 11, turbidity occurs, probably due to the formation of a hydroxy species.

In order to calculate K_1 of the mono(dien)–Cr(II) complex, the concentration of three species must be known (eq. 1). The concentration of uncomplexed and unprotonated amine is a function only of the hydronium ion concentration, the concentration of total dien, and the acid dissociation constants, all of which are known in any given solution. The relative mole fractions of the mono(dien)–Cr(II) and hexaaquo Cr(II) ions may be calculated from

$$\epsilon_M = A/bC_M = (1 - x)\epsilon_{Cr(aq)} + x\epsilon_{Cr(dien)} \tag{8}$$

where the measured absorbance, A, and the molar extinction coefficient, ϵ, refer to a particular wave length, and x is the mole fraction of Cr(II) existing as Cr(dien). The appropriate values for ϵ at all wave lengths were obtained from spectra of solutions containing a single Cr(II) species; i.e., at pA = 12, 4, and 2, where the $Cr^{II}(aq)$, $Cr^{II}dien$, and $Cr^{II}(dien)_2$ species predominate, respectively. To minimize error, the wave length chosen was usually that of the absorption maximum for the mixed solution. The values of K_1

obtained from these data are listed in Table I. The bis(dien)–Cr(II) complex is formed over a very small range in pA, and the molar extinction coefficients of the mono and bis complexes are nearly the same; therefore, a calculation of K_2 was not meaningful.

Titration of the Cr(II)–trien System.—The complexation reaction in this system can be represented as

$$Cr(aq)^{+2} + trienH(aq)^+ = Cr(trien)(aq)^{+2} + H_3O^+$$
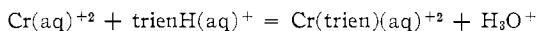
and we may write

$$K_1 = [Cr(trien)(aq)^{2+}]/[Cr(aq)^{+2}][trien] \quad (9)$$

By a simple modification of the Cr–dien calculations allowing for the fourth acidity constant of trien, analogous equations can be derived for the trien system.[9]

Thirteen points were measured along the titration curve from which values for $\bar{n}$ and p[trien] were computed and a formation curve constructed.[8] Values for log K_1 varied from 7.55 at $\bar{n} = 0.650$ to 7.82 at $\bar{n} = 0.272$ with an average value of log $K_1 = 7.71 \pm 0.08$. This slight trend of log K_1 to increase as $\bar{n}$ decreases is probably due to extraneous oxidation of the complex. A point by point determination would probably yield a better value for the formation constant. This technique has been applied in the Cr(II)–EDTA case with excellent results.[10]

Spectra of Cr(II)–trien Solutions.—All solutions contained 20 ml. of a stock solution of trien dihydrochloride (0.0506 F). Varying amounts of acid and base and 0.1 F potassium chloride were added, so that after the addition of about 2 ml. of Cr(II) solution, the final volume would be about 50 ml. and the ionic strength 0.1 F.

The wave length of maximum absorption and the measured extinction coefficients, based on total chromium concentration, of a series of Cr(II)–trien solutions of varying acidity are listed in Table II.

TABLE II
WAVE LENGTH OF MAXIMUM ABSORPTION AND MOLAR
EXTINCTION COEFFICIENTS OF Cr(II)–trien SOLUTIONS

$-\log [H_3O^+]$	pA	Abs. max., $m\mu$	ϵ_M
5.32	11.23	691	7.36
5.92	9.48	643	12.1
6.25	8.55	619	20.0
6.51	7.85	618	28.8
6.59	7.66	612–613	30.4
6.65	7.51	610–611	32.8
6.92	6.84	609	37.8
7.19	6.26	602–603	42.7
7.58	5.42	598	44.6
8.55	3.56	592	46.1
8.94	2.92	590	45.9
8.99	2.85	590	45.0
9.41	2.40	586	49.2
9.91	2.05	566	49.6

The absorption peak of the trien complex occurs at 591 $m\mu$ (ϵ 46.0). The continuing decrease in wave length of the maximum after complete formation of the trien complex is accompanied by a slight turbidity and

may be due to the formation of a hydroxy species or the precipitation of $Cr(OH)_2$.

In a manner similar to that for the dien complexes, we can calculate K_1 for the mono(trien) complex. The values of log K_1 for three points are 7.85, 7.89, and 8.02. The average value is 7.9 $\pm$ 0.1. The accuracy of this determination is not as great as that for the formation constants of the dien complexes because of the decreased stability of the trien complex with respect to oxidation.

Magnetic Moment Measurements.—In order to determine the magnetic moments of the Cr(II) complexes which were prepared, attempts were made to measure their magnetic susceptibilities on a Gouy balance. Although the magnetic susceptibility of the Cr(II) chloride solution was obtained in this way, only erratic results were possible for the dien and trien complexes because of their decreased stability and the time necessary for the balance procedure.

Roberts[11] states that the width of a nuclear magnetic resonance line is determined by the transverse relaxation time, T_2, which is a measure of how fast nuclei return to an average magnetic state after an external magnetic field is removed. The width of the line at one-half full signal strength is numerically equal to $1/T_2$.

Bloch and his co-workers[12] originally showed that the addition of paramagnetic ions to water affects the relaxation time. Then, Bloembergen, Purcell, and Pound[13] showed that the relaxation time is inversely proportional to the concentration of paramagnetic ions. In some cases the relaxation time is also proportional to the square of the effective magnetic moment of the paramagnetic ion. This latter relationship was found to hold for the Er(III), Fe(III), Cr(III), and Cu(II) ions. Large deviations were found for the Co(II), Ni(II), and $Fe(CN)_6^{-3}$ ions and were attributed to nondiagonal elements which are ineffective in producing relaxation.

Several solutions of copper sulfate were prepared. Their concentrations ranged from 10^{19} to 10^{20} ions/cc. (0.016 to 0.16 F). The sample was introduced into an n.m.r. tube and the spectrum measured. It was found that the half-width of the water proton resonance peak of these solutions was directly proportional to the concentration of the paramagnetic ion, Cu(II).

Then the half-width of the corresponding line resulting from a 0.0829 F solution of Cr(II) chloride was measured. In a similar manner solutions of Cr(II)–dien and Cr(II)–trien were also investigated. All Cr(II) solutions were swept with prepurified nitrogen as they were introduced into the sample tubes. Table III shows the results of these measurements. All samples were run at the same sweep width and sweep time so that half-widths of resonance peaks would be measured in cm. and compared. The magnetic moments for the Cr(II) species were calculated from the relation

(9) H. B. Jonassen and A. W. Meibohm, *J. Phys. Chem.*, **55**, 726 (1951).
(10) R. L. Pecsok, L. D. Shields, and W. P. Schaefer, *Inorg. Chem.*, **3**, 114 (1964).

(11) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 97, 98
(12) F. Bloch, W. W. Hansen, and M. Packard, *Phys. Rev.*, **70**, 474 (1946).
(13) N. Bloembergen, E. M. Purcell, and R. V. Pound, *ibid.*, **73**, 679 (1948).

$$\Delta\nu = k^* N_{ion}\mu_{eff}^2 \qquad (10)$$

where $\Delta\nu$ is the half-width of the peak, k^* is a proportionality constant determined from the average value of the copper measurements ($k^* = 9.55 \times 10^{-21}$), N_{ion} is the concentration of Cr(II) species in 10^{19} ions/cc., and μ_{eff} is the effective magnetic moment.

The slightly low result for the second trien solution is probably due to oxidation. These solutions are less stable than those containing dien. Nevertheless, all magnetic moments are approximately that expected for a system with four unpaired electrons.

<div align="center">

TABLE III

MAGNETIC MOMENT BY MEANS OF
NUCLEAR MAGNETIC RESONANCE

</div>

Sample	Concn., M	Concn., 10^{19} ions/cc.	Half-width, cm.	Mag. mom., B.M.
CuSO$_4$	0.0169	1.02	0.42	2.0[a]
CuSO$_4$	.0421	2.54	0.94	2.0[a]
CuSO$_4$	.0842	5.08	1.85	2.0[a]
CrCl$_2$	.0829	5.00	11.48	4.90
Cr(dien)$_2^{+2}$	.0178	1.07	2.52	4.96
Cr(trien)$^{+2}$	.0189	1.14	2.68	4.96
Cr(trien)$^{+2}$	.0209	1.26	2.71	4.75

[a] Assumed value.

Discussion

The Coordination Number of Cr(II).—The results of these studies provide evidence that the Cr(II) ion has a coordination number of six, a view recently advanced in our studies of the Cr(II)–EDTA system.[10]

The formation curve for the Cr(II)–dien system shows that two molecules of dien are coordinated to the central Cr(II) ion. Fisher–Taylor–Hirschfelder molecular models of the bis(dien)–Cr(II) ion indicate that there is no steric hindrance to prevent the coordination of all three nitrogens on the second dien molecule. However, Kling and Schläfer have suggested that the corresponding bis(dien)–Cr(III) complex involves the coordination of only five nitrogens.[14]

Even if the sixth nitrogen is not coordinated to the central chromium atom, it seems reasonable to assume that this place is filled by a water molecule, creating a somewhat distorted octahedral arrangement.

The formation curve for the Cr(II)–trien system shows that only one molecule of trien is complexed to the central chromium atom. This tells us nothing about the coordination number since two water molecules could be coordinated to complete an octahedral configuration.

If the bis(dien)–Cr(II) complex is assumed to be octahedral, the relatively small shift in wave length of

(14) O. Kling and H. L. Schläfer, *Z. anorg. allgem. Chem.*, **313**, 187 (1961).

the absorption maximum in going to the trien complex would indicate an octahedral configuration there too.

The absorption peak of the mono(dien) complex is at 614 mμ, while the bis species absorbs at about 587 mμ. In the case of Cr(II)–trien, the peak is at about 591 mμ. Thus, the addition of a fourth nitrogen to the inner coordination sphere has lowered the wave length of maximum absorption as it does in the case of Cu(II), where the corresponding wave lengths are 610 and 575 mμ.

dien and trien Complexes of the Divalent Metal Ions of the First Transition Series.—With the completion of this study, the first and second formation constants for all of the dien and trien complexes of the divalent members of the first transition series (with the exception of V(II)) have been determined. These values are listed in Table IV.

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TABLE IV

FORMATION CONSTANTS FOR dien AND trien COMPLEXES OF THE
DIVALENT METALS OF THE FIRST TRANSITION SERIES AT 20°
AND 0.1 F IONIC STRENGTH

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Metal ion	dien[a] log K_1	dien[a] log K_2	trien[b] log K_1
Cr(II)	6.71	2.69	7.71
Mn(II)	3.8	2.8	4.9
Fe(II)	6.0	4.1	7.8
Co(II)	8.1	6.0	11.0
Ni(II)	10.7	8.25	14.0
Cu(II)	16.0	5.3	20.4
Zn(II)	8.9	5.5	12.1

[a] From ref. 5, except for Cr(II).   [b] From G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950), except for Cr(II).

Examination of Table IV clearly indicates that the greatest differences between the first and second formation constants occur with Cr(II) and Cu(II). It should be pointed out that these results are entirely consistent with the smaller tendency of these cations to exhibit a coordination number of six and form stable octahedral complexes relative to the other members of the series.

The formation constant for mono(dien)–Cr(II) is greater than those for the corresponding Mn(II) and Fe(II) complexes. We suggest that the three nitrogen atoms of the molecule lie in a plane with water molecules occupying the fourth coordination position of the plane and two coordination positions above and below the plane. This type of configuration would provide greater ligand field stabilization for the Cr(II) complex than could be provided by any configuration of the Mn(II) or Fe(II) complexes. This greater ligand field stabilization would account for the formation constant for mono(dien)–Cr(II) being greater than the formation constants for the Mn(II) and Fe(II) complexes.