

sents the tocopherol level for heart and the y -axis the tocopherol level for liver and spleen, respectively, the regression lines for the averages of the groups will pass through zero and they are significantly straight lines. This indicates that the relationship between the tocopherol levels in heart, liver, and spleen are linear. From the angle of the regression lines for the average values of the groups, it is possible to state the general relationship between the tocopherol content of heart, liver, and spleen to be about 8: 5: 3. This relationship applies to all groups, fresh normal material, autopsy material in which the tocopherol level may sink after death, and material from animals with vitamin E deficiency.

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Metal Ammine Formation in Solution

XI. Stability of Ethylenediamine Complexes and the Coordination Number of Chromium(II)

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The coordination compounds of chromium(II) have been studied for many years; however, no stability constants have been reported for any of its complexes, nor has any experimental evidence been given of its coordination number. The difficulty of preparing chromium(II) solutions free from other metals (or acetate), the instability of chromium(II) toward oxidation, and the strong tendency of chromium(II) to form insoluble basic salts are serious obstacles to such an investigation. From the ligand field theory it is postulated¹ that chromium(II) complexes should show simi-

arity with copper(II) complexes, *i. e.* have a tetragonal bipyramidal configuration and the metal ion a characteristic coordination number of four. This has been verified by establishing the formation curve for the chromium(II) ethylenediamine complexes. Studies with other amines are in progress and will be reported elsewhere.

Solutions containing *ca.* 0.04 M chromous chloride, 0.35 M hydrochloric acid, and 1 M potassium chloride were titrated with concentrated solutions of ethylenediamine (*ca.* 5 M, and 1 M KCl), the hydrogen ion concentration being determined with the glass electrode. It was shown spectrophotometrically that below 6 M chloride ion, chloro complexes are insignificant. The formation curves giving the average ligand number as function of the exponent of the free ethylenediamine concentration were calculated according to Bjerrum². Three independent titrations are represented in Fig. 1. The fulldrawn curve is the theoretical formation curve calculated from the stability constants obtained. With a concentration of free amine higher than *ca.* 0.1 M, there is a considerable scatter in the experimental points because of the high initial acid concentration required to prevent precipitation of hydroxy compounds during the course of the titration. However, it is evident that the formation function of Cr(II)-en levels off at $\bar{n} = 2$. Preliminary spectrophotometric measurements show qualitatively that the bis(ethylenediamine) chromous ion has only a very slight tendency to take up more ethylenediamine. Further it is interesting to see that there is a distinct "pentammine" effect in the spectra just as in the corresponding cupric systems^{3,4} (see Table 1).

Table 1. Data for the absorption maximum of the aquo chromous ion and two chromium(II) ethylenediamine solutions.

$C_{Cr(II)}$ mole/l	C_{en} mole/l	λ_{max} $\mu\mu$	$1/\lambda_{max}$ cm^{-1}	ϵ_{max}
0.212	0	714	14 000	4.7
0.0375	0.57	547	18 300	25.1
0.0351	10.8	571	17 500	17.1

The consecutive formation constants were calculated in the usual way^{2,5}, and found to be $\log K_1 = 5.145$, $\log K_2 = 4.035$ at 25°. In Table 2 these values are compared with the earlier determined constants for the other divalent transition group

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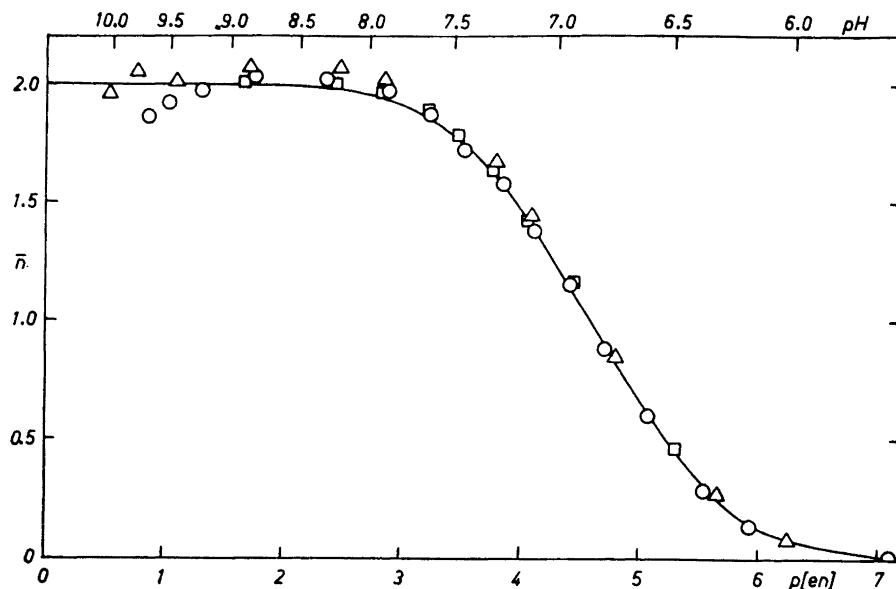


Fig. 1. Formation curve for Cr(II)-ethylenediamine system at 25°.

Titration with initial concentrations:

- , 0.344 M HCl, 0.0459 M CrCl₂, 0.96 M KCl
 △, 0.355 M HCl, 0.0366 M CrCl₂, 1.02 M KCl
 □, 0.355 M HCl, 0.0366 M CrCl₂, 1.02 M KCl

metals under similar conditions (25°, $\mu \sim 1.4$) *.

The crystal field stabilization is calculated as previously described^{1,7}, and the data show that chromium(II) has a rather

* See Refs. 2,4-6. The manganous constants are converted from 30° to 25° by addition of 0.04 to log K_n , the ferrous constants by addition of 0.06, and the cobaltous constants by addition of 0.08.

high stabilization compared to the other transition group metals. From Table 1 it is seen that the bis(ethylenediamine)-chromium(II) ion is displaced 18 300–14 000 = 4 300 cm⁻¹ relative to the aquo ion. The corresponding displacement of the planar bis(ethylenediamine)copper(II) ion is not much higher, 18 200–12 600 = 5 600 cm⁻¹. This shows that the tetragonal distortion is of the same order of magnitude in the two cases, and considering that the

Table 2. Consecutive formation constants K_n and estimated ligand field stabilizations for the ethylenediamine complexes of the divalent transition group metals.

	d ⁴ Cr ⁺⁺	d ⁵ Mn ⁺⁺	d ⁶ Fe ⁺⁺	d ⁷ Co ⁺⁺	d ⁸ Ni ⁺⁺	d ⁹ Cu ⁺⁺	d ¹⁰ Zn ⁺⁺
log K_1	5.15	2.77	4.34	5.97	7.51	10.72	5.92
Stabilization	3.00	0	0.94	1.94	2.85	5.43	0
log K_2	4.04	2.10	3.31	4.91	6.35	9.31	5.15
Stabilization	2.55	0	0.60	1.59	2.42	4.77	0
log K_3	—	0.92	2.05	3.18	4.42	—1.0	1.86
Stabilization	< -1	0	0.94	1.88	2.93	—2.7	0

complexity constants are much higher in the copper than in the chromium system, it can be concluded that the 3rd formation constant must be exceedingly small in the last mentioned case. Also the relatively small "pentammine" effect in the chromous system gives evidence for this.

Experimental. Chromous solutions were prepared by dissolving electrolytically purified chromium metal (kindly furnished by E. I. du Pont de Nemours and Co.) in hot oxygenfree hydrochloric acid to give solutions containing ca. 0.2 M chromous chloride and 0.2 M hydrochloric acid. Chromium(II) was determined by titration with potassium iodate⁸, hydrochloric acid by potentiometric titration with sodium hydroxide, and chromium(III) spectrophotometrically. The solution used contained less than 2% of the chromium as chromic ion which was ignored. The chromium(II) solution was always under a positive pressure of nitrogen, and all other solutions were made oxygenfree by bubbling with nitrogen. The ethylenediamine hydrate was specially purified by Carbide and Carbon Chemicals Company and distilled through a column. It was diluted with an equal volume of 2 M potassium chloride and swept with nitrogen before use.

The titrations were performed under nitrogen in a thermostated cell at 25°C. The cell E.M.F. was measured with a Radiometer pH meter, model PHM 3, using a glass electrode which had been tested for linear response to pH. The acidity constants of the ethylenediamine ($pK_{\text{enH}_2} = 7.44$, $pK_{\text{enH}} = 10.06$) were determined by titrating solutions of the same composition as for the complexity titrations, replacing the chromous chloride with an equivalent amount of barium chloride².

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The Preparation of Benzene-1,2,4-trisulphonic Acid

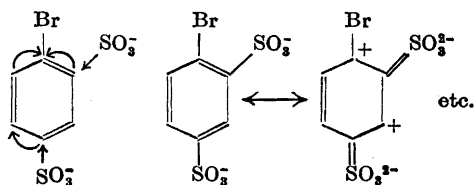
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As a part of the preliminaries for an investigation on the adsorption of benzene sulphonic acids and naphthalene sulphonic acids on aluminium oxide, asymmetrical benzene trisulphonic acid has been prepared.

After unsuccessful experiments with the method of Gattermann^{1,2}, involving the use of aniline-2,4-disulphonic acid, and after attempts to develop sulphonation products of thiophenyl derivatives, refluxing³ a solution of the sodium salt of bromobenzene-2,4-disulphonic acid⁴⁻⁷ and sodium sulphite for 6 h in the presence of some cupric sulphate turned out to be a simple and successful method.⁸ Benzene-1,4-disulphonic acid⁸ was prepared from bromobenzene-4-sulphonic acid⁹ as a preparatory study of this method.

Compared with the preparation of benzene sulphonic acid from bromobenzene, which is achieved by heating bromobenzene with a solution of sodium sulphite and cupric sulphate at 180–200°C for 7 h, the displacement of bromine from bromobenzene-2,4-disulphonic acid is clearly facilitated. As the reaction is carried out in a neutral solution, it gives some valuable information on the relative strengths of the inductive and mesomeric effects operating from the two sulphonate groups. The inductive effect (I) is opposite to the mesomeric effect (II).



I. + I effect II. — M effect

The displacement of bromine is a nucleophilic reaction: