676. *Thermochemical Studies. Part VIII.*[1] *Heats and Entropies of Reaction of Transition-metal Ions with 2,2′,2′′-Triaminotriethylamine.*

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The heats of reaction of 3*d* bivalent metal ions with 2,2′,2′′-triaminotriethylamine (tren) in 0·1M-potassium chloride at 25° have been measured calorimetrically. From these values and published values of free-energy changes the corresponding entropy changes have been calculated. The comparison of these thermodynamic functions with those for the $[\mathrm{M\ trien}]^{2+}$ and $[\mathrm{M\ en_2}]^{2+}$ ions confirms the *cis*-diaquo-octahedral structure for the tren-complexes of manganese, iron, nickel, and copper; it suggests the occurrence of a less hydrated structure for those of cobalt and zinc. The visible spectrum of the $[\mathrm{Co\ tren}]^{2+}$ ion shows quite different features from the spectra of the octahedral $[\mathrm{Co\ trien}]^{2+}$ and $[\mathrm{Co\ den_2}]^{2+}$ ions. Its magnetic moment (4·67 B.M.) indicates a high-spin configuration.

THE present study was undertaken to provide accurate thermodynamic data for the equilibria of complex formation in aqueous solution. In earlier studies in this series, the heats of formation of the complexes between bivalent metal cations from manganese to zinc and the polydentate amines ethylenediamine (en),[2] diethylenetriamine (den),[3]

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[1] Part VII, Paoletti, Ciampolini, and Vacca, *J. Phys. Chem.*, in the press.
[2] Ciampolini, Paoletti, and Sacconi, *J.*, 1960, 4553.
[3] Ciampolini, Paoletti, and Sacconi, *J.*, 1961, 2994.

and triethylenetetramine (trien)[4] were measured calorimetrically. That work has now been extended to the 1 : 1 metal complexes of 2,2′,2″-triaminotriethylamine (tren) $N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$, which is an isomer of the linear triethylenetetramine.

The stability constants of the complexes are already known.[5] For $[Cu\ tren]^{2+}$, the heat of formation has been previously calculated from the temperature coefficient of the equilibrium constant.[6]

EXPERIMENTAL

Materials.—2,2′,2″-Triphthalimidotriethylamine was prepared as described by Ristenpart.[7] It was refluxed with a stoicheiometric amount of ethanolic hydrazine for 0·5 hr., then acidified to Congo Red with hydrochloric acid, and the precipitate was separated and washed several times with water. On evaporation of the filtrate, the solid tetramine trihydrochloride was obtained. A large amount of this compound was also recovered in the purification of technical triethylenetetramine (Fluka)[1] and had an infrared spectrum (Nujol mull) identical with that of the synthetic specimen. The amine was obtained by adding a concentrated solution of sodium hydroxide to a saturated solution of the salt. The solution of the free amine was separated from sodium chloride and distilled *in vacuo*. The base was titrated against hydrochloric acid and proved to be 99·9% pure. It was dissolved in a carbon dioxide-free 0·1M-potassium chloride, and its concentration was determined potentiometrically by titration against hydrochloric acid.

The preparation and standardisation of the metal sulphate solutions have already been described.[2,3] The nitrogen was freed from oxygen by passage through copper gauze at 400°.

Calorimetric Measurements.—The calorimeter and the general procedure used were described in previous reports.[2-4] With manganese, iron, and cobalt, oxidation was avoided by bubbling a slow stream of nitrogen into the calorimetric solution. The final volume of the calorimetric liquid was about 930 ml.; the concentration of the metal complexes was about 0·01M. For each metal–base system two independent sets of runs were carried out with different solutions of the reactants.

Magnetic Measurements.—The magnetic susceptibility of the solution of the oxidisable $[Co\ tren]^{2+}$ complex was determined by using a Gouy-type magnetic balance.[8] The procedure used to avoid oxidation was identical with that employed with the $[Co\ trien]^{2+}$ ion.[4] The susceptibility of the Co tren SO_4 complex was determined according to the formula

$$\chi_g(\text{complex}) = [\chi_g(\text{solution})\text{-}(1 - x)\ \chi_g(\text{solvent})]x^{-1}$$

where x = fraction by weight of Co tren SO_4 in the solution. Diamagnetic corrections for the organic ligand were calculated from the Pascal constants.[9] The diamagnetic susceptibility of the sulphate ion was taken as -40×10^{-6}.[10]

Spectrophotometric Measurements.—The absorption spectra of the solutions were measured with a Beckmann D.U. spectrophotometer with 1 cm. stoppered silica cells. The solutions of the cobalt–amine complexes were prepared and transferred to the cell in an atmosphere of pure nitrogen as previously described.[3,4]

Results.—The Table reports the calorimetric data. The heat evolved in each experiment, corrected for the heat of dilution of the metal salt, is listed in the column headed Q. The molar enthalpy change, $-\Delta H$, is calculated by dividing the value of Q by the corresponding number of g.-ions of metal and by subtracting 265 cal. for manganese, 485 cal. for iron, and 235 cal. for the other ions. These corrections allow for the repression of the basic dissociation of the amine on complex formation and for the neutralisation of a proportion of the ligand with the iron system. The mean of the enthalpy changes for each metal is reported in the penultimate column. From these values and from the values of the stability constants obtained by Prue and Schwarzenbach,[5] corrected to 25° with the present ΔH values, the

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[4] Sacconi, Paoletti, and Ciampolini, *J.*, 1961, 5115.

[5] Prue and Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 963.

[6] Bertsch, Fernelius, and Block, *J. Phys. Chem.*, 1958, **62**, 444.

[7] Ristenpart, *Ber.*, 1896, **29**, 2530.

[8] Sacconi, Cini, Ciampolini, and Maggio, *J. Amer. Chem. Soc.*, 1960, **82**, 3487.

[9] Cf. Selwood, " Magnetochemistry," Interscience Publ. Inc., New York, 1956.

[10] Klemm, *Z. anorg. Chem.*, 1941, **246**, 347; cf. ref. 9, p. 78.

Calorimetric data and thermodynamic quantities for metal(II)–2,2′,2″-triaminotriethylamine systems in 0·1M-potassium chloride at 25°.

Metal	(10⁻⁵ mole)		tren (10⁻⁵ mole)	Q (cal.)	$-\Delta H$ (cal. mole^{-1})	$-\Delta H$ (mean) (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})
Manganese...	830		900	27·4	3034	3·00 ± 0·05	16·5 ± 0·5
	828		898	27·2	3026		
	867		940	28·3	2997		
	841		1137	27·2	2968		
	865		935	28·8	3069		
Iron	955	20 *	982	64·8	6294	6·30 ± 0·05	18·5 ± 0·5
	985	21 *	1012	66·3	6242		
	1079	23 *	1112	73·1	6286		
Cobalt	1008		1008	108·5	10,529	10·65 ± 0·15	22·0 ± 1·0
	1019		1019	109·7	10,526		
	1067		1067	115·9	10,632		
	1058		1059	117·0	10,824		
Nickel	992		992	152·0	15,098	15·15 ± 0·05	16·0 ± 0·5
	986		987	151·8	15,150		
	988		988	152·2	15,173		
	1001		1002	153·8	15,128		
	993		994	153·1	15,185		
Copper	954		954	197·7	20,478	20·40 ± 0·10	18·0 ± 1·0
	956		956	196·6	20,338		
	954		954	196·2	20,338		
	977		977	201·1	20,358		
Zinc	992		992	137·2	13,600	13·85 ± 0·20	19·5 ± 1·0
	987		987	137·0	13,643		
	990		989	138·6	14,000		
	894		894	124·8	13,966		
	918		918	128·8	14,031		

* Hydrochloric acid (10⁻⁵ mole) in the ferrous solution.

entropy changes have been calculated (last column). The results of the magnetic measurements carried out at 23° on an aqueous solution of Co tren SO_4 were: $x = 5{\cdot}04 \times 10^{-2}$; $\chi_g(\text{solution}) = 0{\cdot}84 \times 10^{-6}$; $\chi_g(\text{complex}) = 30{\cdot}25 \times 10^{-6}$; $\chi_M = 9112 \times 10^{-6}$; $\delta = 151{\cdot}10^{-6}$; $\chi_{Co^{2+}} = 9263 \times 10^{-6}$; $\mu_{\text{eff}} = 4{\cdot}67$ B.M.

The results of the spectrophotometric measurements were: $[\text{Co den}_2]^{2+}$, $\lambda_{\text{max.}}$ 1000 mμ (ε 4·7), λ_{sh} 540 (ε 6·5), $\lambda_{\text{max.}}$ 486 mμ (ε 12·6). $[\text{Co tren}]^{2+}$, $\lambda_{\text{max.}}$ 725 (ε 12·4), 574 (ε 42·2), 481 (ε 46·7), 300 mμ (ε 16·8). $[\text{Co trien}]^{2+}$, $\lambda_{\text{max.}}$ 1050 (ε 4·4), 484 mμ (ε 7·6). $[\text{Ni trien}]^{2+}$, $\lambda_{\text{max.}}$ 935 (ε 4·6), 565 (ε 5·9), 358 (ε 8·4), 316 mμ (ε 1·9).

DISCUSSION

The values of the heats of reaction (Table) show a steady increase from 3·0 kcal. mole^{-1} for manganese to 20·4 kcal. mole^{-1} for copper and then a fall to 13·85 kcal. mole^{-1} for zinc. With the exception of the value for zinc they are 3—5 kcal. mole^{-1} lower than the heats of the corresponding tetramino-complexes $[\text{M en}_2]^{2+}$ [2] This is, probably, a consequence of the steric strain imposed by the additional chelate ring and also of the lower strength of the metal–tertiary nitrogen bond than of the metal–primary nitrogen bond.[11] The values of the entropy changes are positive, ranging from 16 to 22 cal. deg.$^{-1}$ mole^{-1}, and are 9—20 cal. deg.$^{-1}$ mole^{-1} higher than those for the formation of the $[\text{M en}_2]^{2+}$ complexes.[2] The greater stability of the $[\text{M tren}]^{2+}$ complexes than of the $[\text{M en}_2]^{2+}$ ions (chelate effect) therefore arises essentially from the favourable entropy term.

In Fig. 1 the $-\Delta H$ values for the formation of the $[\text{M tren}]^{2+}$ and $[\text{M trien}]^{2+}$ complexes [3] are plotted against the atomic number of the metals. The differences between the two

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[11] Brown, McDanil, and Häfliger, in Braude and Nachod's " Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, 1955, p. 642; Sacconi, Lombardo, and Paoletti, *J. Amer. Chem. Soc.*, 1960, **82**, 4185; Sacconi and Lombardo, *ibid.*, p. 6266.

curves may be related to the stereochemistry of the complexes in the two series. At first, the 2,2′,2″-triaminotriethylamine complexes with bivalent transition-metal ions were all believed to be tetrahedral on account of the supposed structural inability of this ligand to fit on an octahedral co-ordination polyhedron.[12] Later, it was realised that 2,2′,2″-triaminotriethylamine can also give octahedral complexes. Jørgensen,[13] for instance, on the basis of spectrophotometric studies, showed that nickel–tren complexes, both in aqueous solution and in the solid state, have a *cis*-diaquo-octahedral structure. With the Ni tren$(CNS)_2$ compound, an octahedral structure has been definitely ascertained by *X*-ray analysis.[14]

Copper-tren Complex.—In order to explain the low heat of formation of the [Cu tren]$^{2+}$ complex (15·7 kcal. mole^{-1}) evaluated from the temperature coefficient of the stability constants, Bertsch, Fernelius, and Block [6] postulated a tetrahedral structure for this ion. On the other hand, Jørgensen [13] considered the visible absorption spectrum to indicate a *cis*-diaquo-octahedral structure. The present result is in agreement with the Jørgensen hypothesis as both the enthalpy and the entropy change for the formation of the [Cu tren]$^{2+}$ ion are very close to those for [Cu trien]$^{2+}$, which is thought to be octahedral.[3] The small difference between the heats of formation of [Cu tren]$^{2+}$ (20·40 kcal. mole^{-1}) and [Cu trien]$^{2+}$ (21·55 kcal. mole^{-1}) is not due to a different co-ordination number but probably arises because the former ion (*cis*-diaquo-octahedral) has lower crystal-field stabilisation energy than the latter (*trans*-diaquo-octahedral). Actually the tetragonal distortion of the crystal field, evaluated from the ratio between the wave-number of the " principal " band of the copper and nickel complexes,[15] is smaller in the [Cu tren]$^{2+}$ ion ($\nu_{Cu}/\nu_{Ni} = 1{\cdot}08$) [13] than in the [Cu trien]$^{2+}$ ion ($\nu_{Cu}/\nu_{Ni} = 1{\cdot}66$), and it is well known that with copper(II) the gain in the crystal-field stabilisation energy increases with the tetragonality.

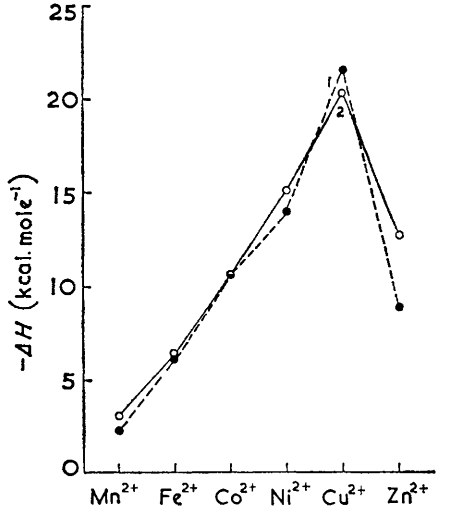

FIG. 1. Heats of formation of: (1) [M trien]$^{2+}$ ions; (2) [M tren]$^{2+}$ ions.

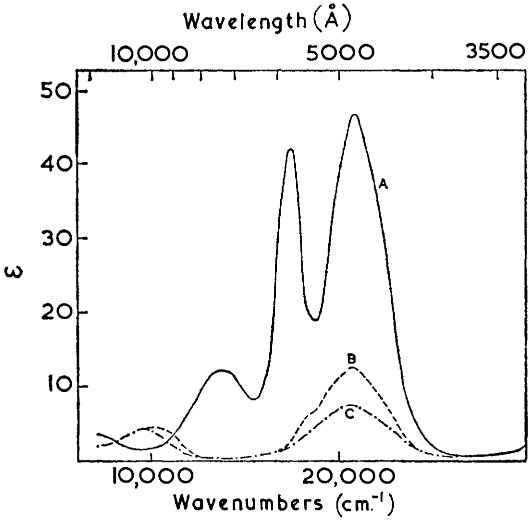

FIG. 2. Absorption spectra of complexes of cobalt and polyamines: A, [Co tren]$^{2+}$; B, [Co den_2]$^{2+}$; C, [Co trien]$^{2+}$.

Zinc–tren Complex.—The heat of formation of the [Zn tren]$^{2+}$ ion (13·85 kcal. mole^{-1})

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[12] Ackermann, Prue, and Schwarzenbach, *Nature*, 1949, **163**, 723.

[13] Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

[14] Hall and Woulfe, *Proc. Chem. Soc.*, 1958, 346.

[15] Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

is much higher than that of the tetrammine–zinc complexes [Zn trien]$^{2+}$ [3] and [Zn en_2]$^{2+}$ [2] (8·90 and 11·90 kcal. mole^{-1}, respectively) and falls surprisingly above that of the cobalt(II) analogue. Also the values of the entropy change reveal differing behaviour by these ligands in the reaction with zinc. Indeed in the [M tren]$^{2+}$ series the ΔS value for zinc complex falls in the range of values for the other cations whereas in the [M trien]$^{2+}$ and [M en_2]$^{2+}$ series it is markedly higher. Both these facts could be accounted for by the hypothesis that a smaller number of water molecules is released in the formation of [Zn tren]$^{2+}$ ion than in the formation of the tetrahedral ions [Zn trien]$^{2+}$ and [Zn en]$^{2+}$. It may be, therefore, that zinc exhibits a co-ordination number greater than four in the [Zn tren]$^{2+}$ complex. Such a supposition is not unfounded since, for example, both trigonal bipyramidal and square-pyrimidal structures [16] for some chelate complexes of zinc have been determined by *X*-ray analysis.

Cobalt–tren Complex.—The present magnetic measurements yield a value of 4·67 B.M. for the magnetic moment of the [Co tren]$^{2+}$ ion in aqueous solution. This ion, therefore, has the usual high-spin configuration of the amino–cobalt(II) complexes. Such a result contrasts with the statement by Jonassen *et al.*[17] that it has a low-spin configuration but is in agreement with the magnetic data of Barclay and Barnard [18] for the solids Co tren$(CNS)_2$ and Co tren I_2, 4·78 and 4·76 B. M., respectively. The [Co tren]$^{2+}$ complex exhibits an absorption spectrum which differs considerably from the spectra of the [Co trien]$^{2+}$ ion and of other definitely octahedral cobalt(II) complexes, *e.g.*, [Co den_2]$^{2+}$ (Fig. 2). Further, the entropy of formation for the [Co tren]$^{2+}$ ion is higher than for the other complexes of this series and also higher than for [Co trien]$^{2+}$. Thus it seems that in the reaction with 2,2′,2″-triaminotriethylamine the aqueous cobalt ion releases a greater number of water molecules than in these other cases. The heats of formation of the [Co tren]$^{2+}$ and [Co trien]$^{2+}$ complexes, however, are the same and thus such a hypothesis requires that a negligible heat effect results when the last water molecules are detached in the former case. This behaviour contrasts strongly with what happens with zinc. It must be remembered, in this connection, that Libus,[19] using the spectrophotometric technique, found that the equilibrium:

$$[Co(H_2O)_2X_4]^{2-} \rightleftharpoons [CoX_4]^{2-} + 2H_2O \quad (X = Cl, Br, I, CNS)$$

is practically independent of temperature. Thus this reaction occurs without measurable heat effect.

Comparison of the thermodynamic functions of the manganese–, iron–, and nickel–tren complexes with those of the [M trien]$^{2+}$ and [M en_2]$^{2+}$ complexes is in accord with an octahedral configuration.

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[16] Lippert and Trutere, *J.*, 1960, 4996; Corbridge and Cox, *J.*, 1956, 594; Hall and Moore, *Proc. Chem. Soc.*, 1960, 257.

[17] Jonassen and Strickland, *J. Amer. Chem. Soc.*, 1958, **80**, 312.

[18] Barclay and Barnard, *J.*, 1958, 2540.

[19] Libus, *Roczniki Chem.*, 1959, **33**, 931.