

574. *Thermochemical Studies. Part IV.¹ Heats and Entropies of Reaction of Transition-metal Ions with Diethylenetriamine.*

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Values (valid for solutions in 0.1M-potassium chloride at 25°) for the heats of formation of successive step-complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with diethylenetriamine have been measured calorimetrically. These values have then been used for calculating the corresponding entropy changes. The enthalpy changes in the formation of metal complexes with two molecules of diethylenetriamine are generally less negative by 3—4 kcal. mole⁻¹ than those for the corresponding trisethylenediamine complexes. The favourable entropy factor, however, gives these complexes stabilities practically equal to those of the trisethylenediamine complex ions. For each metal, with the exception of copper, the value of ΔH_2 is more negative than that of ΔH_1 . The small negative value of ΔH_1 for the species $[\text{Zn den}]^{2+}$ is ascribed to the formation of a tetrahedral complex, a hypothesis which is supported by the exceptionally large entropy term $\Delta S_1 = +18.5$ cal. degree⁻¹ mole⁻¹.

In a previous determination of the heats of formation of the complex ions of ethylenediamine with manganese(II), iron(II), cobalt(II), nickel(II), and zinc(II) in M-potassium chloride,¹ it was found that the values of ΔH_{1-3} , corrected for the crystal-field stabilisation energy and plotted against atomic number, increased monotonically from manganese to zinc and lay on a curve above the straight line manganese-zinc.

To extend these results, the heats of formation of analogous complexes of diethylenetriamine, $\text{NH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2$, with the transition ions from manganese to zinc have been measured by a direct calorimetric method. The visible spectra were also investigated in order to determine the value of Dq needed to calculate the crystal-field stabilisation energy.

Since the values of the equilibrium constants of most of these ions reported in the literature² had been determined in 0.1M-potassium chloride, this ionic medium was chosen for the measurements. It has the advantage over M-potassium chloride that complications due to the formation of chloro-complexes are avoided. Since it is a tridentate ligand, diethylenetriamine enables the influence of chelation on the stability of the complexes to be studied.

Incomplete data on the enthalpy of formation of metal complexes with diethylenetriamine are recorded in the literature.^{3,4} These are, however, not completely reliable since they were determined, not by a direct calorimetric method, but by measuring the temperature coefficient of the equilibrium constant.

¹ Part III, Ciampolini, Paoletti, and Sacconi, *J.*, 1960, 4553.

² Prue and Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 985.

³ Jonassen, Hurst, LeBlanc, and Meibohm, *J. Phys. Chem.*, 1952, **56**, 16.

⁴ McIntyre, jun., Block, and Fernelius, *J. Amer. Chem. Soc.*, 1959, **81**, 529.

EXPERIMENTAL

Materials.—Diethylenetriamine (den) was distilled twice through a Todd column. The cut used (n_D^{25} 1.4815; d_4^{25} 0.9456) was titrated potentiometrically against hydrochloric acid and found to be 99.6% pure. This base was dissolved in a carbon dioxide-free 0.1M-potassium chloride and its concentration determined potentiometrically against hydrochloric acid.

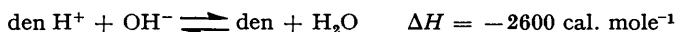
The solutions of reagent-grade manganous, cobaltous, nickel, copper and zinc sulphates were about 0.4M. Manganese was determined by potentiometric titration with a standard solution of potassium permanganate, cobalt and zinc gravimetrically as anthranilates, nickel with dimethylglyoxime, and copper by electrodeposition. The ferrous sulphate solution was roughly molar with respect to the metal salt and 0.015N with respect to the hydrochloric acid. Its preparation and mode of preservation are described elsewhere.¹ Nitrogen and hydrogen were purified by being passed through copper gauze at 400°.

Calorimetric Measurements.—The calorimeter used to measure the heats of reaction between diethylenetriamine and the metal ions was the same as that described for the measurements of the heat of formation of the ethylenediamine complexes,¹ and the same experimental procedure was adopted. With copper, buffering was necessary to avoid the formation of the complex ion [Cu den(OH)]⁺. This was done by placing in the Dewar vessel the proper amount of ca. 1.5N-hydrochloric acid (see Table 1, column 3). Distilled water necessary to give an ionic strength of 0.1 was added and the volume made up to about 930 ml. with 0.1M-potassium chloride.

Spectrophotometric Measurements.—The spectra of the complexes [Fe den₂]²⁺, [Co den₂]²⁺, [Ni den₂]²⁺ were measured with a Beckman DU spectrophotometer with 1 cm. stoppered silica cells. The spectrum of the nickel complex has already been recorded⁵ and our results are in good agreement. The oxidisable solution containing the complex ion [Fe den₂]²⁺ was prepared and transferred to the cell in the manner already described¹ for the preparation of solutions of [Fe en₃]²⁺. The solution of bisdiethylenetriaminocobalt(II) was prepared, as well as transferred to the cell, under nitrogen. The solutions of the metal chlorides were 0.4M for iron and cobalt and 0.06M for nickel. The concentration of free base (always present in excess) was 0.4M in every case.

RESULTS

The calorimetric data are shown in Table 1. The distribution of ionic species present in the various systems before and after the reaction was calculated by using the known values of the stability constants determined in 0.1M-potassium chloride,² and correcting these to 25° with the values of ΔH obtained in this work. The heat evolved was corrected for the thermal effect arising from the side reaction in unbuffered systems:



With buffered systems containing iron- and copper-diethylenetriamine, changes in the concentration of the various protonated forms of the base were taken into account in calculating the heat of reaction. For this purpose previously determined values of the molar heat of neutralisation were used.⁶ Column 5 of Table 1 gives the heat (Q) evolved in each experiment, corrected for the heat of dilution of the metal salt. The heat effects due to the reactions which take place in buffered or in unbuffered systems are reported in column 6. The last column gives the values of ΔH_a , the average heat of reaction per mole of diethylenetriamine bound to the metal ion. The values of ΔH_a for adjacent values of \bar{n} (\bar{n} = average number of ligands attached to one metal ion) give an indication of the reproducibility of the measurements.

The heat of stepwise complex-formation for the separate complexes was obtained by combining the results of two runs carried out at different \bar{n} and solving the set of two simultaneous equations:

$$Q_m = \alpha_1 \Delta H_1 + \alpha_2 \Delta H_{1-2}$$

where Q_m is the heat evolved per g.-ion of metal added and α_1, α_2 are the degrees of formation of the two complexes in the reaction mixture.

The estimated errors are: ± 200 cal. mole⁻¹ for ΔH_1 and ± 100 cal. mole⁻¹ for ΔH_{1-2} .

Table 2 shows the values of the thermodynamic functions ΔG , ΔH , and ΔS of the two

⁵ Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

⁶ Unpublished results.

TABLE 1. Systems $\text{MSO}_4 + \text{den}$ in 0.1M-potassium chloride.

Metal	Metal (10^{-5} mole)	HCl (10^{-5} mole)	den (10^{-5} mole)	Q (cal.)	Q_{cs} (cal.)	\bar{n}	$-\Delta H_s$ (kcal. mole $^{-1}$)
Mn $^{2+}$ (932 ml.)	930		28,600	65.0	0	2.00	3.5
	930		31,100	64.0	0	2.00	3.4
	888		31,700	61.6	0	2.00	3.5
	915		31,300	63.1	0	2.00	3.5
	926		32,500	64.4	0	2.00	3.5
Fe $^{2+}$ (933 ml.)...	1024	15 *	3719	131.7	0.6	2.00	6.4
	963	14 *	3719	126.4	0.6	2.00	6.5
	965	14 *	3725	125.8	0.6	2.00	6.5
Co $^{2+}$ (932 ml.)...	984		3730	182.5	0.7	2.00	9.2
	985		3721	181.9	0.7	2.00	9.2
	994		3726	183.7	0.7	2.00	9.2
	983		987	83.2	1.1	1.00	8.4
	962		969	81.7	1.1	1.01	8.4
	989		990	83.1	1.1	1.00	8.3
	986		3732	250.1	0.7	2.00	12.6
	992		3733	247.3	0.7	2.00	12.6
Ni $^{2+}$ (933 ml.)...	992		3725	253.1	0.7	2.00	12.7
	995		997	121.3	1.1	1.00	12.1
	987		987	119.3	1.1	1.00	12.0
	966		966	114.4	1.1	1.00	11.8
	981	6103	6030	258.4	1.4	2.00	13.1
	978	6104	6021	258.1	1.5	2.00	13.0
	967	6106	6005	255.3	2.0	2.00	13.1
	971	508	1223	175.4	-0.3	1.00	18.0
	976	516	1232	175.9	-0.2	1.00	18.0
	969	510	1217	173.5	0.2	1.00	17.9
Zn $^{2+}$ (941 ml.)...	972		3742	126.6	0.7	2.00	8.3
	985		3719	164.5	0.7	2.00	8.3
	987		3726	164.7	0.7	2.00	8.3
	986		989	68.8	1.1	1.00	6.9
	983		984	67.3	1.1	1.00	6.7
	963		963	64.2	1.1	1.00	6.6

* In the ferrous sulphate solution.

TABLE 2. Thermodynamic and spectrophotometric data for the equilibria between diethylenetriamine and some metal(II) ions in 0.1M-potassium chloride at 25°.

	Mn $^{2+}$	Fe $^{2+}$	Co $^{2+}$	Ni $^{2+}$	Cu $^{2+}$	Zn $^{2+}$
$-\Delta H_1^a$ (kcal. mole $^{-1}$)			8.15	11.85	18.00	6.45
$-\Delta H_2$ "			10.25	13.45	8.15	10.15
$-\Delta H_{1-2}^a$ "	6.95	12.95	18.40	25.30	26.15	16.60
$-\Delta G_1^b$ (kcal. mole $^{-1}$)			10.90	14.45	21.55	12.00
$-\Delta G_2^b$ "			8.00	10.90	7.10	7.50
$-\Delta G_{1-2}^b$ "			18.90	25.35	28.65	19.50
ΔS_1 (cal. deg $^{-1}$ mole $^{-1}$)			9.0	8.5	12.0	18.5
ΔS_2 "			-7.5	-8.5	-3.5	-9.0
ΔS_{1-2} "			1.5	0.0	8.5	9.5
Dq [$\text{M}(\text{H}_2\text{O})_6$] $^{2+}$ (cm $^{-1}$)		1040 ^c	900 ^d	850 ^e		
Dq [$\text{M} \text{den}_2$] $^{2+}$ (cm $^{-1}$)		1140	1100	1160		
$-\Delta H_{\text{cryst.}}$ (kcal. mole $^{-1}$)	0	1.15	4.55	10.60		0
$-\Delta H_{1-2} \text{ corr.}$ "	6.95	11.80	13.85	14.70		16.60

^a Jonassen's thermodynamic values (ref. 3) for $-\Delta H_1$, $-\Delta H_{1-2}$, in kcal. mole $^{-1}$, are, respectively: Mn 4, 9; Fe 9, 17; Co 9, 19; Ni 12, 25; Cu 20, —; Zn 8, —. McIntyre's values (ref. 4) are, respectively: Cu 18.9, 25.2; Zn 6.4, —. ^b Calculated from data for 20° and $\mu = 0.1\text{M}$ -potassium chloride (ref. 2) by using the enthalpy values obtained in the present work. ^c Cf. ref. 7. ^d Ballhausen and Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 397.

successive steps of the reaction. Values of ΔG and ΔS could not be calculated for manganese and iron, as values of the formation constants in 0.1M-potassium chloride are not available. Nevertheless, in these two cases as well, the values of the ΔH_{1-2} could be determined. For this purpose a sufficient excess of base was used to allow complete formation of the $[\text{M} \text{den}_2]^{2+}$ ions. To make a rough estimate of the desired amount of this excess, the constants β_2 in (M-potassium chloride + potassium nitrate) by Jonassen *et al.*³ were used. On the other hand, with manganese, which has the lowest constant of all, measurements made with different base: metal ratios from 307 to 357, gave the same value of ΔH_{1-2} . Table 2 also shows the

values of Dq for the ions $[M(H_2O)_6]^{2+}$ and $[M(den_2)]^{2+}$, which are needed for calculating $\Delta H_{1-2 \text{ cryst.}}$.

DISCUSSION

The spectra of the $[M(den_2)]^{2+}$ complex ions [$M = Fe(II), Co(II), Ni(II)$; den = diethylenetriamine] are found to resemble closely those of the corresponding hexa-coordinate complexes $[M(en_3)]^{2+}$ and $[M(NH_3)_6]^{2+}$. This shows that, for the diethylenetriamine complexes, too, the symmetry of the ligand field is essentially octahedral. In particular, the wavelengths of the "first" absorption band coincide, within experimental error, with those of the corresponding band of the complexes with three molecules of ethylenediamine.⁷ The crystal-field stabilisation energy calculated from the spectroscopic values of Dq is therefore the same for complexes of types $[M(den_2)]^{2+}$ and $[M(en_3)]^{2+}$.

In the Figure the heats of formation ΔH_{1-2} are plotted against the atomic number: the upper curve refers to the experimental values; the lower one was obtained by applying the correction $\Delta H_{1-2 \text{ cryst.}}$ for the crystal-field stabilisation energy

$$\Delta H_{1-2 \text{ cryst.}} = (4n_e - 6n_v)(Dq_{6H_2O} - Dq_{2den}).$$

For copper the crystal-field stabilisation energy was not calculated because of the pronounced tetragonal distortion due to the Jahn-Teller effect and also, as will be shown below, because it is doubtful how many copper-nitrogen bonds exist in the complex $[Cu(den_2)]^{2+}$.

The trend of the two curves is about the same as that of the corresponding curves for the heats of formation ΔH_{1-3} of the ethylenediamine complexes.¹ In particular the points representing the corrected heats for iron, cobalt, and nickel lie above the line joining manganese to zinc. This provides further evidence that the proposed linear interpolation between manganese and zinc⁸ cannot be considered correct in every case.

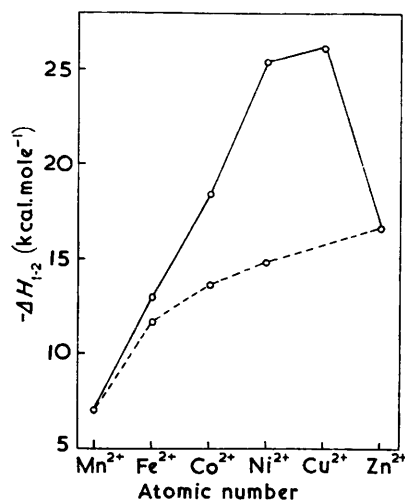
The overall heats of formation of the diethylenetriamine complexes are all about 3–4 kcal. lower than the heats of the corresponding trisethylenediamine complexes.

This could be due either to strain within the chelate rings or to the fact that the bonds between the metal and the secondary nitrogen atoms of the amines are weaker than those between the metal and the primary nitrogen atoms. The latter hypothesis is supported by the fact that the heats of formation for the compounds of alkylamines with different acceptors such as trimethylboron,⁹ (diacetyl bis-benzoylhydrazono)nickel(II),¹⁰ and the hydrogen ion,¹¹ show that dialkylamines are more weakly bound than monoalkylamines.

Table 2 shows that, except for copper, the heat changes for the second step, ΔH_2 , are larger than those for the first step, ΔH_1 . The tendency of the successive heat changes to increase has already been noted among metal complexes with ethylenediamine. In the complexes with diethylenetriamine this increase is even more marked, particularly with zinc.

In the copper-diethylenetriamine system, the heat of reaction of the first ligand molecule is $-18.00 \text{ kcal. mole}^{-1}$, while that of the second molecule is only $-8.15 \text{ kcal. mole}^{-1}$.

⁷ Jørgensen, Reports 10th Solvay Conf., Brussels, 1956.
⁸ Orgel, Reports 10th Solvay Conf., Brussels, 1956.
⁹ Brown, McDaniel, and Häfliger, in Braude and Nachod's "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, 1955, p. 642.
¹⁰ Sacconi, Lombardo, and Ciofalo, *J. Amer. Chem. Soc.*, 1960, **82**, 4182; Sacconi and Lombardo, *ibid.*, 6266.
¹¹ Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.



The value of the copper–nitrogen bond energy, taken as equal to half the heat of formation of the complex $[\text{Cu en}]^{2+}$, determined by various authors,^{4,12} is about -6.5 kcal. mole⁻¹. Copper, therefore, behaves normally on the addition of the first molecule of diethylenetriamine, since the value of the heat of reaction ΔH_1 , -18.00 kcal. mole⁻¹, is roughly equal to the heat of formation of three copper–nitrogen bonds, *viz.* -19.5 kcal. mole⁻¹. The difference of 1.5 kcal. mole⁻¹ is, in effect, exactly half of what we found to be the difference between a trisethylenediamine complex and the corresponding bis-diethylenetriamine complex. McIntyre *et al.*,⁴ on the other hand, found a value of -6.3 kcal. mole⁻¹ for the heat of binding of a second diethylenetriamine molecule and concluded that only a fourth metal–nitrogen bond had been formed. On the contrary, we regard our calorimetric ΔH_2 value of -8.15 kcal. mole⁻¹ as more reliable and therefore believe that it indicates the formation of more than one bond between copper and the second molecule of ligand. The fact that this value is less than expected for the formation of two copper–nitrogen bonds is probably due to the crystal-field stabilisation energy which is less for the complex $[\text{Cu den}_2]^{2+}$ than for $[\text{Cu en}]^{2+}$. In fact, the three nitrogen atoms in the latter ion very probably lie in one plane,¹³ the remaining three co-ordination positions being occupied by three water molecules. If this is so, the resulting octahedral configuration will be tetragonally distorted and the ground state of the complex stabilised by a gain in the energy due to the removal of the degeneracy of the d_e and d_o orbitals caused by the tetragonal component of the electric field acting on the copper ion. In the complex $[\text{Cu den}_2]^{2+}$, on the contrary, this tetragonal distortion is considerably smaller. This is shown by the spectra in which, contrary to the rule of average environment, the absorption maximum of the "first" band of the $[\text{Cu den}_2]^{2+}$ ion is shifted towards the lowest frequencies (penta-amino-effect), as compared to that of $[\text{Cu en}]^{2+}$.⁵ Consequently the crystal-field stabilisation energy decreases, so causing a lower heat of formation of the ion $[\text{Cu den}_2]^{2+}$. It should be remembered in this connection that the tetra-amino-configuration is already excluded by Jørgensen's study of the spectra of $[\text{Cu en}]^{2+}$ and $[\text{Cu den}_2]^{2+}$, which made him postulate⁵ a penta- or hexa-co-ordination of the complex ion $[\text{Cu den}_2]^{2+}$.

The heat of formation of the complex $[\text{Zn den}]^{2+}$ is particularly low, even lower than the heat of formation of the $[\text{Zn en}]^{2+}$ ion¹ in which only two metal–nitrogen bonds are present. In this case, as well as for the $[\text{Zn en}_2]^{2+}$ ion,¹ we are forced to admit that the low heat change is due to the additional endothermic effect arising from the displacement of more than three water molecules from the first co-ordination sphere. As a consequence a tetrahedral ion of the type $[\text{Zn}(\text{H}_2\text{O})\text{den}]^{2+}$ could be formed.¹⁴

The heat of formation of the complex $[\text{Zn den}_2]^{2+}$ is -16.60 kcal. mole⁻¹. Taking half the heat of formation of the $[\text{Zn en}]^{2+}$ complex,¹ *i.e.*, -3.5 kcal., as the strength of the zinc–nitrogen bond, one may conclude that at least five zinc–nitrogen bonds exist in the $[\text{Zn den}_2]^{2+}$ complex.

The entropy changes ΔS_1 and ΔS_{1-2} are all positive; the ΔS_1 values for cobalt and nickel are equal within experimental error. The higher value for copper agrees with the above-mentioned hypothesis¹³ that the first molecule of diethylenetriamine is not bound on an octahedral face, as is probably the case with cobalt and nickel,¹⁵ but is instead so disposed that the three bonds are co-planar. With copper, this planar configuration, though strained, is doubtless preferred because of the increased crystal-field stabilisation energy so obtained. The dipole moment of the non-planar configuration is roughly $\sqrt{3}$ times greater than that of the planar one. The $[\text{Cu den}]^{2+}$ ion will therefore be able to

¹² Poulsen and Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 1407.

¹³ Courtney, Gustafson, Chaberek, jun., and Martell, *J. Amer. Chem. Soc.*, 1959, **81**, 519.

¹⁴ Martell and Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, 1953, p. 146.

¹⁵ Barclay, *Rev. Pure Appl. Chem.*, 1954, **4**, 77.

orientate fewer water molecules than the corresponding ions $[\text{Ni den}]^{2+}$ and $[\text{Co den}]^{2+}$, and the entropy of the final state will thus be higher.¹⁶

The value of ΔS_1 for zinc is even higher than that for copper. This seems to indicate that the introduction of a molecule of diethylenetriamine in the first co-ordination sphere of a zinc aquo-ion detaches more water molecules than it does from other aquo-cations, with a consequent increase in translational entropy.¹⁷ This corroborates the above hypothesis of the formation of a tetrahedral $[\text{Zn den}]^{2+}$ ion.

The values of ΔS_{1-2} (which are all positive) can be divided into two groups: the first includes cobalt and nickel (1.5 and 0.0 cal. deg.⁻¹ mole⁻¹, respectively), and the second includes copper and zinc (8.5 and 9.5 cal. deg.⁻¹ mole⁻¹). For the last two ions the higher value of the overall entropy change can be explained by assuming that the complexes formed are less rigid than the corresponding complexes of the first group. This could agree with the hypothesis put forward by Jonassen *et al.*³ that in the $[\text{Cu den}_2]^{2+}$ and $[\text{Zn den}_2]^{2+}$ ions the number of the co-ordinated nitrogen atoms is less than six. In this case, freedom of movement of the non-co-ordinated portions of the ligand molecules would contribute to the increase of the entropy. If the number of the co-ordinated nitrogen atoms were really less than six, the value of ΔH_{1-2} for the ion $[\text{Zn den}_2]^{2+}$ could not constitute a reference point in the Figure.

The changes of free energy during the formation of bisdiethylenetriamine complexes that have been reported in the literature¹⁸ are roughly equal to those of the corresponding trisethylenediamine complexes. Nevertheless, as shown by the measured heats of formation, the nitrogen-metal bonds are stronger in the ethylenediamine complexes than in those of diethylenetriamine. The latter are, however, stabilised by the positive entropy term, whereas in the ethylenediamine complexes the entropy change is negative and varies from -13.0 to -8.5 cal. deg.⁻¹ mole⁻¹.

The entropy of formation of the hexamminometal(II) ions is known only for the nickel complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$. For nickel, then, it is possible to compare the entropy changes for the hexa-co-ordinated complexes with ammonia, ethylenediamine, and diethylenetriamine severally, which contain an increasing number of chelate rings. The overall ΔS values are: $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $\Delta S_{1-6} -42$; ¹⁹ $[\text{Ni en}_3]^{2+}$, $\Delta S_{1-3} -11$; $[\text{Ni den}_2]^{2+}$, $\Delta S_{1-2} = 0$ cal. deg.⁻¹ mole⁻¹. This marked increase in the entropy change, which stabilises the complexes having a greater number of chelate rings, must be ascribed, at least in part, to the increase in the number of free particles which takes place on complex formation, with a consequent increase in translational entropy.

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¹⁶ Chatt and Wilkins, *J.*, 1952, 4300; 1956, 525.

¹⁷ Calvin and Bailes, *J. Amer. Chem. Soc.*, 1946, 68, 949.

¹⁸ Bjerrum, Schwarzenbach, and Sillén, "Stability Constants," Part I, *Chem. Soc. Special Publ. No. 6*, 1957.

¹⁹ Yatsimirskii and Milyukov, *Zhur. fiz. Khim.*, 1957, 31, 842.