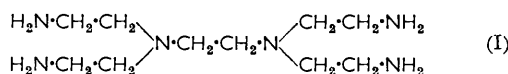**970.** *Thermochemical Studies. Part XII.*[1] *Heats and Entropies of Reaction of Transition-metal Ions with* NNN'N'-tetra-(2-aminoethyl)-ethylenediamine.

By L. Sacconi, P. Paoletti, and M. Ciampolini.

The heats of reaction of some bivalent ions of the $3d$ transition metal series with $NNN'N'$-tetra-(2-aminoethyl)ethylenediamine (penten) and with [penten H]$^+$ in 0·1M-potassium chloride have been measured calorimetrically at 25°. The corresponding entropies have been calculated by combining these values with the published values of the free energy changes. In the complexes [Cu penten]$^{2+}$ and [Zn penten]$^{2+}$ the ligand is pentaco-ordinating while in the complexes [Co penten]$^{2+}$ and [Ni penten]$^{2+}$ the sixth amine group appears to be bonded, but only weakly. The enthalpy and entropy of formation of the manganese complex appear to indicate that the ligand is hexaco-ordinating but the resulting manganese ion is also aquated. The entropies of protonation of the complexes [M penten]$^{2+}$ have been obtained and are compared with the entropies of stepwise nautralization of the free ligand. The spectra of some [M penten]$^{2+}$ and [M penten H]$^{3+}$ complexes have been measured and are discussed.

Continuing our investigations of the thermochemistry of complexes formed by bivalent transition metal ions with multidentate amines we now report the results of a study of the complexes formed by the bivalent metal ions of manganese through zinc with $NNN'N'$-tetra-(2-aminoethyl)ethylenediamine, penten (I). Penten has six amino-groups available

$$\text{H}_2\text{N·CH}_2\text{·CH}_2 \diagdown \quad \diagup \text{CH}_2\text{·CH}_2\text{·NH}_2$$
$$\qquad\qquad\qquad \text{N·CH}_2\text{·CH}_2\text{·N} \qquad\qquad\qquad (I)$$
$$\text{H}_2\text{N·CH}_2\text{·CH}_2 \diagup \quad \diagdown \text{CH}_2\text{·CH}_2\text{·NH}_2$$

for co-ordination; it forms 1 : 1 metal complexes and some of these can be protonated. Schwarzenbach and Moser have determined the formation constants of these penten–metal complexes.[2] They postulated that the ligand is quinquedentate in the copper and zinc complexes but sexidentate in the other complexes of this series.

We have measured the heats of formation of the complexes [M penten]$^{2+}$ and [M penten H]$^{3+}$. The entropies of formation have been calculated from these values, using the values of the free energies obtained from the formation constants. Together with the spectra these results shed light on the stereochemistry of the complexes.

<center>Experimental</center>

Materials.—$NNN'N'$-Tetra-(2-aminoethyl)ethylenediamine was prepared by the method of Gauss *et al.*[3] Addition of ethanolic concentrated hydrochloric acid to a saturated aqueous solution of the base gave iridescent plates of penten, 6 HCl,2H$_2$O (Found: N, 17·65; Cl, 43·7. C$_{10}$H$_{38}$Cl$_6$N$_6$O$_2$ requires N, 17·25; Cl, 43·7%). The primary amine content of the base, as liberated from the hydrochloride, was estimated by titration against hydrochloric acid (Found: 1·727. C$_{10}$H$_{28}$N$_6$ requires 1·721 eq. %). Penten was dissolved in 0·1M-aqueous potassium chloride and standardized potentiometrically against hydrochloric acid. The metal sulphate solutions were prepared and standardized as before.[4] Solutions of oxidizable metal salts were made up in oxygen-free solvents and were handled under nitrogen; solutions of penten were prepared in carbon dioxide-free solvents. Nitrogen was deoxygenated by passage over copper gauze at 400°.

Calorimetry.—The calorimeter and general procedure have been described.[5] Oxidation

[1] Part XI, Paoletti and Vacca, *Trans. Faraday Soc.*, 1964, **60**, 50.
[2] Schwarzenbach and Moser, *Helv. Chim. Acta*, 1953 **36**, 581.
[3] Gauss, Moser, and Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2359.
[4] Ciampolini, Paoletti, and Sacconi, *J.*, 1960, 4553.
[5] Sacconi, Paoletti, and Ciampolini, *J. Amer. Chem. Soc.*, 1960, **82**, 3828.

was avoided by bubbling a slow stream of nitrogen through the calorimetric solutions where necessary. In each run the bottle was filled with *ca.* 24 ml. of 0·4M-metal sulphate solution. A weighed amount of base was placed in the Dewar flask. In the measurement of the heats of formation of [M penten]$^{2+}$ sufficient potassium hydroxide was added to the calorimetric solution to suppress the formation of [M penten H]$^{3+}$, but in the measurements of the heats of formation of the latter complex, hydrochloric acid was added. The volume was made up to *ca.* 930 ml. with 0·1M-potassium chloride, the final concentration of the metal complex being *ca.* 0·01M. With nickel, however, the heats of formation were determined indirectly because the complexes are formed slowly. The complexes were prepared in solution by keeping the appropriate mixtures overnight at 45°. The heats of reaction of these solutions with 25 ml. of 3·3N-hydrochloric acid (placed in the calorimetric bottle) were measured. The complexes are destroyed rapidly under these conditions, as shown by spectral observations. Blank runs using potassium sulphate in place of the nickel sulphate were also performed.

Spectrophotometry.—The absorption spectra of the complexes were recorded with a Beckman DK2 spectrophotometer using 1 cm. stoppered silica cells. The solution of [Fe penten]$^{2+}$ was prepared by adding a solution of penten in *ca.* 10% excess to a solution of ferrous chloride obtained by a reduction method [4] and removing a very slight precipitate by filtration. The final concentration of [Fe penten]$^{2+}$ was *ca.* 0·236M. A 0·170M solution of [Co penten]$^{2+}$ was prepared by mixing together solutions of penten and cobaltous chloride in mole ratio 1·02 : 1. In order to measure the spectrum of [Co penten H]$^{3+}$ a solution of cobaltous chloride, penten, and hydrochloric acid was prepared which had the calculated composition (mmole l.$^{-1}$): [Co penten H]$^{3+}$, 111; [Co penten]$^{2+}$, 31; [Co penten H$_3$]$^{5+}$, 3; [Co]$^{2+}$, 4. A 1 : 1 solution of cupric chloride and penten was used for measuring the spectrum of [Cu penten]$^{2+}$. For the protonated complex [Cu penten H]$^{3+}$ hydrochloric acid was added to give the calculated composition: [Cu penten H]$^{3+}$, 4·55 mmole l.$^{-1}$; [Cu penten]$^{2+}$, 0·45 mmole l.$^{-1}$. Concentrations were calculated by means of the stability constants of the complex compounds and the basicity constants of the amine.[2]

RESULTS

The calorimetric data are in Table 1. The heat developed during each experiment, corrected for the experimentally measured heat of dilution of the liquid contained in the bottle (for the nickel system see below) is reported in the column headed Q. The number of moles of [M penten]$^{2+}$ and [M penten H]$^{3+}$ which were formed, given in the two following columns, were calculated from the formation constants. The latter were calculated for 25° from Schwarzenbach and Moser's data,[2] which were obtained at 20°; our ΔH values obtained at 25° and the formation constants were mutually adjusted until self consistent. These final values of the formation constants were: log $K^M_{M penten}$: Mn, 9·30; Fe, 11·05; Co, 11·55; Ni, 19·05; Cu, 22·15; Zn, 16·05; and log $K^M_{M penten H}$: Co, 12·40; Ni, 15·65; Cu, 20·15; Zn, 14·00. In the experiments concerned with [Zn penten H]$^{3+}$ an appreciable proportion of the metal was not involved in complex formation.

The heat liberated on complex formation due to changes in the concentrations of hydroxyl ion and protonated species of penten are given in the column headed Q_{cz}. These were calculated using the values of 13·800 kcal. mole^{-1} for the heat of formation of water and the heats of stepwise neutralization of penten which have been measured previously:[6] $\Delta H_1 = -11·30$, $\Delta H_{1-2} = -22·75$, $\Delta H_{1-3} = -35·90$, $\Delta H_{1-4} = -47·00$ kcal. mole.$^{-1}$ The molar enthalpy changes given in Table 2 are calculated according to the formulæ

$$-\Delta H = \frac{Q - Q_{cz}}{\text{moles [M penten]}^{2+}}$$

and
$$-\Delta H = \frac{Q - Q_{cz} + \Delta H[\text{M penten}]^{2+} \times \text{moles [M penten]}^{2+}}{\text{moles [M penten H]}^{3+}}$$

For the nickel system, Q in the above formula should be replaced by the difference between the heats measured as outlined in the experimental section.

Allowance for the presence of not negligible concentrations of [Co penten H$_3$]$^{5+}$ and [Ni penten H$_2$]$^{4+}$ was made in the calculation of the heats of formation of the respective monoprotonated complexes. The values of $-8·15$ and $-14·00$ kcal. mole^{-1} were taken for the

[6] Paoletti and Ciampolini, *Ricerca sci.*, 1963, **33** (II-*A*), 405.

Sacconi, Paoletti, and Ciampolini:

TABLE 1.

Calorimetric data for metal (II)–*NNN'N'*-tetra-(2-aminoethyl)ethylenediamine systems in 0·1M-potassium chloride at 25°.

Metal	Penten	KOH	HCl	pH	Q	[M penten]$^{2+}$	[M penten H]$^{3+}$	Q_{cz}
(10^{-5} mole)	(10^{-5} mole)	(10^{-6} mole)	(10^{-5} mole)		(cal.)	(10^{-5} mole)	(10^{-5} mole)	(cal.)
Manganese 938	947	25		9·6	85·5	938		2·3
942	951	25		—	85·9	942		2·4
Iron 918 [a]	923	327		9·9	93·4	918		4·8
1000 [a]	1006	345			101·6	1000		4·8
Cobalt 951	955	145		9·8	141·8	951		2·2
940	947	145		9·8	141·5	940		2·2
895	955		1065		121·5	185	664 [b]	0·0
899	988		916		129·9	354	537 [c]	1·0
Nickel [d] 900	900	108			340·6	900		−1·4
900	900	108			339·3	900		−1·4
	900 [e]	108			518·9			
	900 [e]	108			517·1			
823	908		1058		246·8	126	679 [f]	1·0
823	908		1058		246·5	126	679 [f]	1·0
	908 [g]		1058		399·1			
	908 [g]		1058		400·3			
Copper 932	939	272		10·1	229·3	932		1·9
923	930	181		10·1	230·0	923		2·2
925	932	182		10·1	228·5	925		2·2
926	1033		1295	7·0	230·5	59	867	1·3
975	1083		1315	7·2	242·7	88	887	1·1
Zinc 925	930	182		10·1	136·2	925		2·2
929	932	182		10·0	136·4	929		2·2
955	1025		1303	6·1	136·7	7	922 [h]	1·2
927	996		1251	6·1	134·3	7	904 [i]	−0·1

[a] This solution contains also 0·022 mole of sulphuric acid per mole of ferrous sulphate.   [b] 19 × 10^{-5} moles of [Co penten H$_3$]$^{5+}$ are also formed.   [c] 4 × 10^{-5} mole of [Co penten H$_3$]$^{5+}$ are also formed   [d] The complexes contained in these solutions were decomposed with 24·5 ml. of 3·3M-HCl.   [e] These solutions contain 900 × 10^{-5} mole of K$_2$SO$_4$.   [f] 18 × 10^{-5} mole of [Ni penten H$_2$]$^{4+}$ are also formed.   [g] These solutions contain 823 × 10^{-5} mole of K$_2$SO$_4$.   [h] This solution contains 26 × 10^{-5} mole of unbound zinc ion.   [i] This solution contains 16 × 10^{-5} mole of unbound zinc ion.

TABLE 2.

Thermodynamic data for the reaction between metal(II) ions and penten or [penten H]$^+$ in 0·1M-potassium chloride at 25°.

Metal	Ligand	ΔH * (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})
Mn	penten	8·85 ± 0·00	12·5 ± 0·2
Fe	penten	9·65 ± 0·02	18·5 ± 1·2
Co	penten	14·75 ± 0·06	21·5 ± 0·4
	penten H$^+$	14·00 ± 0·09	10·0 ± 0·5
Ni	penten	19·65 ± 0·15	21·5 ± 1·4
	penten H$^+$	18·35 ± 0·10	10·0 ± 1·2
Cu	penten	24·50 ± 0·12	19·0 ± 1·3
	penten H$^+$	24·80 ± 0·03	9·0 ± 1·0
Zn	penten	14·50 ± 0·02	25·0 ± 0·3
	penten H$^+$	14·65 ± 0·07	15·0 ± 0·5

* Mean of observed values to the nearest 0·05 kcal. mole^{-1} ± experimental scatter.

enthalpies of formation of these two complexes, that is, the values found for the complexes [7,8] [Co den]$^{2+}$ and [Ni trien]$^{2+}$ in which there are a number of bound nitrogen atoms and chelate rings equal to those in the corresponding penten complexes. This choice is not critical how-ever, since an error of ±10% in the estimate of these heats gives rise to an error of only *ca.* ±0·04 kcal. mole^{-1} (0·3%) in the molar enthalpies of formation of the mono-protonated complexes.

DISCUSSION

The heats developed during the formation of the complexes [M penten]$^{2+}$ in 0·1M-potassium chloride vary from 8·85 kcal. mole^{-1} with manganese to 24·5 kcal. mole^{-1} with

[7] Ciampolini, Paoletti, and Sacconi, *J.*, 1961, 2994.
[8] Sacconi, Paoletti, and Ciampolini, *J.*, 1961, 5115.

copper. These values are the largest that have been observed so far for one-step reactions between polyamines and bivalent transition metal ions. In Fig. 1 the enthalpies of formation of the complexes [M penten]$^{2+}$, [M den$_2$]$^{2+}$,[7] and [M Y]$^{2-}$ [9] (Y = EDTA), in all of which the ligands provide a set of six donor atoms, are plotted against the atomic number of the metal. The curves of [M penten]$^{2+}$ and [M Y]$^{2-}$ are similar to each other in some respects and to the curve of [M den$_2$]$^{2+}$ except for the positions of the manganese and copper complexes. This behaviour can be understood in terms of the effective number of nitrogen atoms bound to the metal in the penten complexes, and a comparison of the heats of reaction of the metal ions with penten as ligand or with [penten H]$^+$ (which obviously has only five nitrogen atoms available for co-ordination) gives useful informations about this number. As has already been postulated by Schwarzenbach and Moser,[2] penten acts as a quinquedentate ligand with Cu^{2+} and Zn^{2+} ions. This point of view receives confirmation from the fact that the revelant heats of reaction are not greater than those with

Fig. 1.   Heats of formation.

○, [M penten]$^{2+}$ ions; ●, [M den$_2$]$^{2+}$ ions (values taken from ref. 7); ◓, [MY]$^{2-}$ ions (values taken from ref. 9).
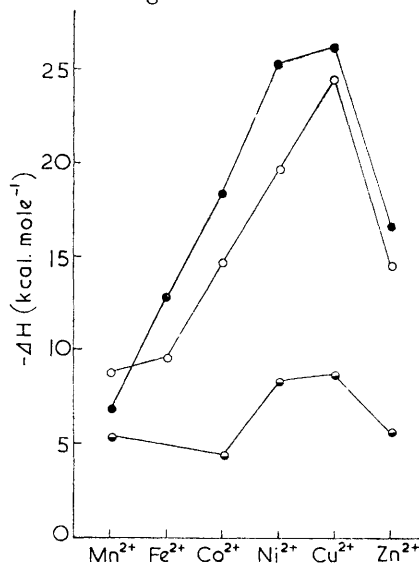
[penten H]$^+$, the difference being perhaps within the experimental error. The absence of any shift in the spectrum of [Cu penten H]$^{3+}$ (Fig. 2) with respect to that of [Cu penten]$^{2+}$ further confirms the pentaco-ordination in the copper complex.

The heats of formation of the complexes [M penten]$^{2+}$ in the cases of cobalt and nickel are higher than the corresponding heats of formation of [M penten H]$^{3+}$. In order to interpret these results it is useful to compare the enthalpies of formation of cobalt and nickel complexes with polyethylenepolyamines as a function of increasing number of co-ordinating nitrogen atoms and chelate rings. For the series [M en]$^{2+}$,[4] [M den]$^{2+}$,[7] [M tren]$^{2+}$,[10] [M penten H]$^{3+}$ and [M penten]$^{2+}$ the respective values of $-\Delta H$ for the cobalt complexes are: 6·90; 8·15; 10·65; 14·00; 14·75 and for the nickel complexes: 8·90; 11·85; 15·15; 18·35; 19·75 kcal. mole^{-1}. It will be seen that the increment in $-\Delta H$ on passing from [M penten H]$^{3+}$ to [M penten]$^{2+}$ is small compared with the other increments in the series. One can deduce, therefore, either that six atoms are bonded, but only weakly or that five and hexaco-ordinated species exist in equilibrium in the complexes [Co penten]$^{2+}$ and [Ni penten]$^{2+}$. In the case of the cobalt complex, the greater complexity of the spectrum compared with that of [Co penten H]$^{3+}$ argues for the latter hypothesis. In the spectrum of the nickel complex there is only a slight blue shift compared with the spectrum of [Ni penten H]$^{3+}$.

⁹ Charles, *J. Amer. Chem. Soc.*, 1954, **76**, 5854; Care and Staveley, *J.*, 1956, 4571; Staveley and Randall, *Discuss. Faraday Soc.*, 1958, **26**, 157.
  ¹⁰ Paoletti, Ciampolini, and Sacconi, *J.*, 1963, 3589.

No conclusions about the co-ordination number in the iron complex [Fe penten]$^{2+}$ can be drawn owing to the impossibility of measuring the heat of formation of the ion [Fe penten H]$^{3+}$.

Inspection of the curves in Fig. 1 shows the unusual position of manganese. Whereas in all the analogous curves for polyamine complexes the heats of formation of the manganese, iron, cobalt, and nickel complexes lie more or less on a straight line, in the case of the penten complex of manganese the value is much above the extrapolated line; the heat of formation is in fact greater than that of [Mn den$_2$]$^{2+}$ [7] in which there are six nitrogen atoms co-ordinated and less internal strain since there is one fewer chelate ring.* Thus one is led to suppose that the actual co-ordination number in the complex [Mn penten]$^{2+}$ is
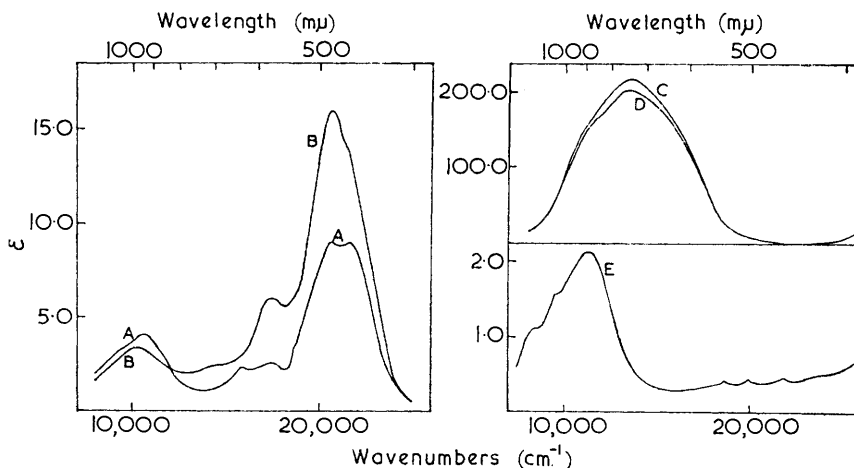

FIG. 2.   Absorption spectra of:

A [Co penten]$^{2+}$, *B* [Co penten H]$^{3+}$, *C* [Cu penten]$^{2+}$, *D* [Cu penten H]$^{3+}$, *E* [Fe penten]$^{2+}$ in aqueous solution.

greater than six and that there are water molecules in the primary co-ordination sphere in addition to the six nitrogen atoms of penten. This hypothesis receives support from the *X*-ray structural investigation of the manganese complex with EDTA, Mn[Mn(H$_2$O)H Y]$_2$,8H$_2$O.[13] In this complex two out of three manganese atoms have a co-ordination number of seven, achieved through the co-ordination of an extra water molecule. The exceptionally large heat of formation of the manganese complex in the series [M Y]$^{2-}$ [9] shown in Fig. 1 indicates that [M Y]$^{2-}$ is probably heptaco-ordinate also in solution. Considering the structural similarity of the two ligands penten and Y^{4-}, then, the large heat of reaction between Mn^{2+} and penten in solution suggests the formation of an ion of the type [Mn(H$_2$O)penten]$^{2+}$ containing co-ordinated water. The entropy of formation of [Mn penten]$^{2+}$ ($\Delta S = 12.5$ cal. deg.$^{-1}$ mole^{-1}) is much smaller than that of the other complexes of this series. This is to be expected when a more hydrated complex is formed and gives further support to the heptaco-ordination hypothesis.

The values of ΔS for the other metal–penten complexes vary from 18.5 to 21.5 cal.

* It has been shown that the strain associated with the formation of a chelate ring is *ca.* 3—4 kcal. mole^{-1},[7,8,10,11] Melson and Wilkins [12] found that the energy of activation for the opening of one chelate ring, as a result of protonation of an amine group, decreases by *ca.* 3 kcal. mole^{-1} with each chelate ring present in the complex.

[11] Ciampolini, Paoletti, and Sacconi, " Advances in the Chemistry of the Co-ordination Compounds," Proc. Sixth International Conference on Co-ordination Chemistry, Detroit 1961, The MacMillan Company, New York, 1961, p. 303.

[12] Melson and Wilkins, *J.*, 1963, 2662.

[13] Hoard, Pedersen, Richards, and Silverton, *J. Amer. Chem. Soc.*, 1961, **83**, 3533.

deg.$^{-1}$ mole^{-1} except that of zinc which is rather higher. This phenomenon is not unusual in zinc complexes with polyamines and has been attributed to the displacement of a greater number of co-ordinated water molecules from the Zn^{2+} ion and a smaller degree of hydration of the polyamine complex.[4,7,8,11] The entropies of formation of the protonated complexes [M penten H]$^{3+}$ are 10·0—11·5 cal. deg.$^{-1}$ mole^{-1} less than those of the corresponding non-protonated complexes. It will be recalled that the entropy of formation of the complex [Cu trien H]$^{3+}$ was also found to be 9·6 cal. deg.$^{-1}$ mole^{-1} less than the complex [Cu trien]$^{2+}$.[8] Taking the entropy of the first neutralization, penten + H$^+$ ⟶ penten H$^+$ (ΔS = 8·0 cal. deg.$^{-1}$ mole^{-1})[6] into account, we find the entropy of protonation of the complexes, [M penten]$^{2+}$ + H$^+$ ⟶ [M penten H]$^{3+}$, becomes Co, −3·5; Ni, −3·5; Cu, −2·0; Zn, −2·0 cal. deg.$^{-1}$ mole^{-1}. For trien the entropy of neutralisation of the ligand[14] is 7·8 cal. deg.$^{-1}$ mole^{-1} and that of the copper complex is −1·7 cal. deg.$^{-1}$ mole^{-1}. Thus, protonation of the complex is accompanied by a much smaller entropy change than with the free base, actually a negative one. This entropy change is about equal to that which accompanies the third stage of neutralization of the free base (−3·1 and −2·0 cal. deg.$^{-1}$ mole^{-1} for penten[6] and trien,[14] respectively). Perhaps it is a consequence of the fact that in both processes [M amine]$^{2+}$ + H$^+$ ⟶ [M amine H]$^{3+}$ and Amine H$_2^{2+}$ + H$^+$ ⟶ Amine H$_3^{3+}$ the proton is reacting with a doubly-charged moiety.

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[14] Paoletti, Ciampolini, and Vacca, *J. Phys. Chem.*, 1963, **67**, 1065.