

1033. *Thermodynamics of the Formation of Complexes of Nitrilotriacetic Acid and Bivalent Cations.*

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Calorimetric measurements have been made at 20° and at an ionic strength of 0.1 of the heats of formation of the 1 : 1 complexes of nitrilotriacetic acid with the bivalent cations of manganese, cobalt, nickel, copper, zinc, calcium, and strontium. For copper, the heat of formation of the 1 : 2 complex has also been determined. The heats of formation are small and do not vary much from one metal to another, the considerable variation in stability of the complexes depending more on differences in entropies of formation than on differences in heats of formation. The 1 : 1 copper complex has a particularly high entropy of formation, and perhaps in this complex, the metal ion only uses three of the four-co-ordinating centres of the nitrilotriacetic acid.

WE have determined, by direct calorimetry, the heats of formation, ΔH_f , of the 1 : 1 complexes of nitrilotriacetic acid (NTA) with the bivalent cations of manganese, cobalt, nickel, copper, zinc, calcium, and strontium. We have also measured ΔH_f for the 1 : 2 complex of copper with NTA, *i.e.*, for the formation of CuY_2^{4-} , where Y^{3-} is the anion of NTA. Our measurements of ΔH_f have been made under the same conditions as those used by Schwarzenbach *et al.*¹ for the determination of the corresponding stability constants, namely, 20° and an ionic strength, μ , of 0.1, so that our values of ΔH_f can be combined with their stability constants to give ΔS° , the standard entropy of formation of the complexes.

EXPERIMENTAL

The calorimeter used was that described by Davies, Singer, and Staveley,² and the procedure followed was very similar to that of Care and Staveley³ in experiments on complexes of ethylenediaminetetra-acetic acid (EDTA). The complex was formed at a concentration of *ca.* 0.01M in the presence of sufficient potassium nitrate to make the final ionic strength 0.1. Control of the pH was necessary to avoid formation of a hydrogen or a hydroxyl complex, and to ensure that complexing was as complete as possible (the stability constants for some of the systems studied were rather low). If necessary, a small amount of nitric acid was added to the solution of the metal salt in order to give an acceptable final pH. The molar ratio of NTA to metal ion exceeded unity, but generally by not more than 5%, so that a high degree of formation of the 1 : 1 complex was achieved without a significant amount of the 1 : 2 complex being formed. For copper, some experiments were carried out in which this ratio was varied more widely, to give ΔH_f for the 1 : 2 complex also.

¹ Schwarzenbach, Anderegg, Schneider, and Senn, *Helv. Chim. Acta*, 1955, **38**, 1147.

² Davies, Singer, and Staveley, *J.*, 1954, 2304.

³ Care and Staveley, *J.*, 1956, 4571.

The metals were always used in the form of their nitrates. The concentrated solutions, from which the dilute solutions used in the calorimeter were prepared, were analysed gravimetrically for their metal content as follows: copper, electrolytically; nickel, as the dimethylglyoxime complex; cobalt and manganese, as the pyrophosphates; zinc, as the oxinate; calcium, as the carbonate (by heating the oxalate); and strontium, as the sulphate.

NTA was purified by twice recrystallizing it from water, followed by drying *in vacuo* over phosphorus pentoxide at 100°. Analysis, by means of titration with alkali, gave a purity of 99.9%. A stock solution (*ca.* 0.5M) of the tripotassium salt was prepared by adding the acid in stoichiometric proportions to a solution of carbonate-free potassium hydroxide. This stock solution was kept in a Polythene bottle. The ultimate standard for the determination of the strengths of the solutions of acid and alkali used in this work was a standard sodium carbonate solution prepared from the anhydrous salt.

Measurements of pH were made with a glass electrode which was calibrated in N/500 hydrochloric acid at 20° and at an ionic strength of 0.1. These measurements could then be combined with values of K_W and of the ionization constants of NTA (determined with a glass electrode calibrated in the same way and under the same conditions) to estimate the concentrations of ionic species in the solutions studied. In calculating ΔH_f from the calorimetric results, it was necessary to have values for the following quantities: (a) pK_3 for NTA, for which we used Schwarzenbach, Ackermann, and Ruckstuhl's value⁴ of 9.73, which is in good agreement with the figure of 9.80 obtained by Moeller and Ferrus,⁵ (b) pK_W , for which a direct determination, under the appropriate conditions, gave 13.95; and (c) the heat-content change for the process $HY^{2-} \longrightarrow H^+ + Y^{3-}$ —this was determined by adding a solution of K_3Y to *ca.* 0.01M-nitric acid in a 1 : 1 molar ratio, and measuring, in a separate experiment, the heat of dilution of the K_3Y solution. Two concordant experiments gave $\Delta H = 4.56$ kcal./mole for the third heat of ionization of NTA, in good agreement with a value of 4.58 kcal./mole subsequently obtained in

TABLE 1.

Type	M	pH	Q	ΔH
D	0	10.66	1.47	
D	0	10.66	1.76	
D	0	10.66	1.68	
C	8.513 Cu ²⁺	4.53	-17.89	
C	8.511 Cu ²⁺	4.77	-17.51	
C	8.077 Cu ²⁺	7.13	-19.02	-1.84 (1 : 1)
C	8.077 Cu ²⁺	7.13	-19.37	-8.3 (1 : 2)
C	7.273 Cu ²⁺	7.78	-25.10	
C	7.277 Cu ²⁺	7.88	-25.37	
C	8.685 Ni ²⁺	3.81	-23.56	-2.53
C	8.399 Ni ²⁺	5.67	-23.49	
C	8.402 Zn ²⁺	4.59	-9.69	-0.84
C	8.408 Zn ²⁺	4.53	-9.61	
C	8.403 Mn ²⁺	6.41	+7.20	+1.135
C	8.404 Mn ²⁺	6.43	+6.94	
C	8.398 Co ²⁺	5.21	-3.90	-0.15
C	8.400 Co ²⁺	5.62	-3.76	
D	0	10.76	5.54	
D	0	10.77	5.58	
C	8.404 Ca ²⁺	8.58	-11.49	-1.36
C	8.406 Ca ²⁺	8.73	-11.28	
C	8.400 Sr ²⁺	9.75	-4.02	-0.54
C	8.404 Sr ²⁺	9.73	-3.77	

C denotes an experiment involving the formation of a complex-ion; D denotes a dilution experiment. The final volume of the solution was always 935.6 ml. In every experiment recorded above the line, the system at the start of the experiment contained 8.83 mmoles of K_3Y and the dilute solution to which it was added contained 0.504 mmoles of nitric acid. In the six experiments recorded below the line, the no. of mmoles of K_3Y was 8.464, and no nitric acid was added. M = no. of mg-ions of metal; pH = that of the final solution; Q = heat absorbed, in cal., on forming the solution C or D. ΔH_f is the average heat of formation of the 1 : 1 complex, in kcal./mole (1 cal. = 4.1840 abs. joules), *i.e.*, ΔH_f is ΔH for the process $M^{2+} + Y^{3-} \longrightarrow MY^-$ at 20° and an ionic strength of 0.1.

⁴ Schwarzenbach, Ackermann, and Ruckstuhl, *Helv. Chim. Acta*, 1949, **32**, 1175.

⁵ Moeller and Ferrus, *Inorg. Chem.*, 1962, **1**, 49.

this laboratory by Mr. Edelin de la Praudiere using a different calorimeter, and also in agreement with the result of 4.68 ± 0.22 kcal./mole derived by Moeller and Ferrus⁵ from the temperature coefficient of the third ionization constant.

Our experimental results are recorded in Table 1, in the same form as were those for the EDTA work given by Care and Staveley.³ Experiments in which the complex was actually formed (by adding, in the calorimeter, the concentrated K_3Y solution to a large amount of the dilute metal-nitrate solution, sometimes with added nitric acid) are denoted by C; the necessary dilution experiments, in which the K_3Y was diluted to give the same final volume at the same final ionic strength of 0.1, are denoted by D. The values of ΔH_f given in the last column are based on the mean values of the pH and of the observed heat absorbed, Q , for duplicate experiments. From the experiments on the copper complex, it was possible to evaluate not only ΔH_f for the 1:2 complex, but also an approximate value (4×10^4) for $[CuY_2^{4-}]/[CuY^-][Y^{3-}]$. For the corresponding nickel complex, Schwarzenbach and Biedermann⁶ reported a value of *ca.* 5×10^4 , and rather lower values for zinc, manganese, cobalt, and calcium.

DISCUSSION

Table 2 gives the thermodynamic parameters for the formation of the 1:1 NTA complexes of the metal ions we have studied. The values of ΔG° , the increase in standard free energy for the process $M^{2+} + Y^{3-} \longrightarrow MY^-$, are derived from the stability constants of Schwarzenbach *et al.*¹ For manganese, the value of S_M° , the standard partial molar entropy of the metal ion, is that estimated by Walkley,⁷ while that for nickel is based on measurements in this laboratory, as yet unpublished, of the heat capacity and heat of solution of nickel chloride hexahydrate (used in conjunction with published solubility and activity-coefficient data for nickel chloride). The value of S_M° for cobalt has been assessed from the value for nickel and from Heymann and Jellinek's data⁸ for the equilibrium between the two ions and metallic nickel and cobalt.

Moeller and Ferrus⁵ have estimated ΔH_f for the 1:1 calcium and copper complexes from the temperature-coefficients of the stability constants, obtaining values of -0.81 ± 0.22 and -1.1 ± 1.1 kcal./mole, respectively, in reasonable agreement with our own results.

It is perhaps surprising that there is so little variation in ΔH_f for the complexes of the seven ions studied. The considerable differences in stability constant, amounting to a factor of *ca.* 10^8 for the ratio of that of the most stable complex (copper) to that of the least stable (strontium), depend more on differences in the entropies of formation than on differences in ΔH_f . The quantity $\Delta S^\circ + S_M^\circ$, effectively a measure of the standard partial

TABLE 2.
Thermodynamic parameters for the formation of the 1:1 NTA complexes
at 20° and $\mu = 0.1$.

Metal ion	ΔH_f	ΔG°	ΔS°	S_M°	$\Delta S^\circ + S_M^\circ$
Mn ²⁺	+1.14	-9.98	37.9	-18	20
Co ²⁺	-0.15	-13.95	47.1	-22	25
Ni ²⁺	-2.53	-15.47	44.1	-23	21
Cu ²⁺	-1.84	-17.39	53.0	-23.6	29.4
Zn ²⁺	-0.84	-14.32	46.0	-25.5	20.5
Ca ²⁺	-1.36	-8.60	24.7	-13.2	11.5
Sr ²⁺	-0.54	-6.68	20.9	-9.4	11.5

The units of ΔH_f and ΔG° (the standard free energy of formation) are kcal./mole, and those of ΔS° (the standard entropy increase in the reaction) and S_M° (the standard entropy of the metal ion) are cal./mole deg.

molar entropy of the complex in solution, is not even approximately constant, which implies that there are structural differences between complexes which affect their relation with the solvent environment and hence their relative entropies. The same applies to EDTA complexes.³

⁶ Schwarzenbach and Biedermann, *Helv. Chim. Acta*, 1948, **31**, 331.

⁷ Walkley, *J. Electrochem. Soc.*, 1948, **93**, 316.

⁸ Heymann and Jellinek, *Z. phys. Chem.*, 1932, **160**, 34.

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For the 1 : 1 rare-earth NTA complexes, ΔS° for the process $\text{Ln}^{3+} + \text{Y}^{3-} \longrightarrow \text{LnY}$ falls between 48 and 58 cal./mole deg.⁹ We might expect the corresponding quantity to be smaller for bivalent ions, partly because the cation is less highly charged and less powerfully hydrated, and partly because the complex of the bivalent ion still carries a residual charge. This expectation is fulfilled for the calcium and strontium complexes, but ΔS° values for the complexes of transition-metal ions do not differ much from those for the rare earths.

It has been known for some time that, in a series of complexes of metal ions of the same charge with a given ligand, ΔS° decreases with increasing ionic radius. For the 1 : 1 NTA complexes, the largest ions (of calcium and strontium) are indeed associated with the smallest ΔS° values, and of the five transition-metal ions, that normally regarded as the largest (manganese) forms its complex with the smallest value of ΔS° . The correlation of ΔS° with ionic size breaks down, however, for the remaining four transition-metal ions, notably for copper with its particularly high value of ΔS° . Abnormality of the copper-NTA complex (which may take the form of a relation between the ligands and the metal atom in the complex different from that for the other transition metals) is also suggested by a comparison of the NTA and EDTA complexes. Care and Staveley³ evaluated ΔS° for the EDTA complexes, and the following are the values of $\delta(\Delta S^\circ) = [\Delta S^\circ(\text{EDTA}) - \Delta S^\circ(\text{NTA})]$:

Metal	Mn	Co	Ni	Cu	Zn	Ca	Sr
$\delta(\Delta S^\circ)$	6.6	12.6	12.6	3.4	10.3	2.2	4.5

The value of $\delta(\Delta S^\circ)$ is, of course, independent of the value of S_M° .

While more data for a variety of ligands must be accumulated before the finer details of the pattern can be understood, it may be noted that the four co-ordinating centres of an NTA anion cannot lie in a plane, but they could either approach a tetrahedral disposition round the metal ion or alternatively provide four corners of a crude octahedron in a 1 : 1 complex, with water molecules filling the remaining sites. However, the cupric ion only rarely forms tetrahedral complexes and prefers the well-known distorted octahedral configuration, and it may be, therefore, that in the 1 : 1 NTA-copper complex, only three of the four co-ordinating centres of the NTA anion are used by the copper, giving relatively strong binding to the cation, but causing the complex with, perhaps, one "free" $-\text{CH}_2\text{CO}_2^-$ group to have a relatively large entropy.

For the rare earths, the ratio K_1/K_2 , where K_1 and K_2 are, respectively, the equilibrium constants for the reactions



falls between 10^2 and 10^3 . For the reaction (2), ΔS° is still considerable, being between 22 and 39 cal./mole deg.⁵ Whereas for calcium the ratio K_1/K_2 is also about 10^3 , for the bivalent transition-metal ions it is much greater, being between 10^6 and 10^8 . Our value of ΔH of ca. -6.5 kcal./mole for reaction (2) for copper, combined with our estimate of K_2 of ca. 4×10^4 , shows that the entropy change for the second stage of the formation of CuY_2^{4-} is almost zero. For the overall formation of the 1 : 2 complex of copper with NTA from Cu^{2+} and 2Y^{3-} , the values of ΔH_f° and ΔS° of -8.3 kcal./mole and 55 e.u., respectively, are quite close to the corresponding values for the EDTA complex of -8.7 kcal./mole and 57 e.u.

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⁹ Edelin de la Praudiere and Staveley, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1713.