1013. *Thermochemical Studies. Part VI.*[1] *Heats and Entropies of Reaction of Transition-metal Ions with Triethylenetetramine.*

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The heats of reaction of 3*d* bivalent metal ions with triethylenetetramine 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 stabilities of these complexes are nearly equal to those of the corresponding bisethylenediamine complexes. This arises from a balance between their lower heats of formation and their higher entropy changes. The chelate effect for the replacement of ammonia by triethylenetetramine appears to be mainly due to the higher entropy of the ammonia molecules than that of triethylenetetramine. The heat of formation as well as the spectrum of the protonated ion [Cu Htrien]$^{3+}$ have been measured and compared with those of the analogous [Cu den]$^{2+}$ ion. The magnetic moment of [Co trien]$^{2+}$ was found to be 4·8 B.M., thus indicating a high-spin configuration.

IN previous studies the heats of stepwise formation of the chelate complexes of bivalent transition ions from manganese to zinc with the bidentate ligand ethylenediamine[2] and the terdentate ligand diethylenetriamine[3] were measured. This research has now been extended to the tetradentate ligand triethylenetetramine (trien), $H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$. For this purpose direct calorimetric measurements of the heats of formation of the 1 : 1 complexes of this base with the above cations were carried out in 0·1M-potassium chloride and the results are reported in the present paper. Jonassen and his co-workers[4] have reported some values of the heat of formation of triethylenetetramine complexes calculated from the isobar equation. However, their values do not appear to be reliable, owing to the narrow temperature range of ten degrees investigated.

EXPERIMENTAL

Materials.—Technical triethylenetetramine containing a large proportion of 2,2′,2″-triaminotriethylamine (tren) was purified by fractional crystallization of the hydrochlorides (tren,3HCl and trien,4HCl) from ethanol–water.[5] To the saturated solution of the pure triethylenetetramine hydrochloride a concentrated solution of sodium hydroxide was added, and the precipitate of sodium chloride filtered off and washed with ethanol. The solution of amine was concentrated and then distilled *in vacuo*. The triethylenetetramine was titrated potentiometrically against hydrochloric acid and proved to be 99·8% pure. It was dissolved in carbon dioxide-free 0·1M-potassium chloride and its concentration was determined potentiometrically against hydrochloric acid.

The preparation and standardization of the solutions of the different metal sulphates have already been described.[3] The nitrogen was purified by passage through copper gauze at 400°.

Calorimetric Measurements.—The calorimeter and the general procedure used were described in previous reports.[2,3] With manganese, iron, and cobalt, oxidation was avoided by bubbling a slow stream of nitrogen into the calorimetric solution. For each run the bottle was filled with *ca.* 24 ml. of a 0·4M-metal sulphate. A weighed amount of the base and, when necessary, of hydrochloric acid was placed in the Dewar flask and the volume made up to about 930 ml. with carbon dioxide-free 0·1M-potassium chloride. The final concentration of the metal complexes was about 0·01M.

The base was in slight excess (1—2%) on the 1 : 1 base–metal ratio. Under these conditions the metal ions were wholly present as [M trien]$^{2+}$ complexes. A larger excess of the base

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[1] Part V, Ciampolini and Paoletti, *J. Phys. Chem.*, 1961, **65**, 1224.
[2] Ciampolini, Paoletti, and Sacconi, *J.*, 1960, 4553.
[3] Ciampolini, Paoletti, and Sacconi, *J.*, 1961, 2994.
[4] Jonassen, Hurst, LeBlanc, and Meibohm, *J. Phys. Chem.*, 1952, **56**, 16.
[5] Jonassen, LeBlanc, Meibohm, and Rogan, *J. Amer. Chem. Soc.*, 1950, **72**, 2430.

was avoided in order to prevent the formation of the $[M_2\ trien_3]^{4+}$ complexes.[4] For manganese, a 4—30% excess of the base was used. According to the values of the relevant stability constants, manganese is present as 97—99% of $[M\ trien]^{2+}$ and 3—1% of aquo-ion. In the calculations of the molar heat of reaction, allowance was made for the amount of unreacted manganese(II) ions.

The heat evolved was corrected for the thermal effect arising from the dissociation of the base in water.

For each metal–base system two independent sets of three runs were carried out with different solutions of the reactants.

In the experimental determination of the heat of formation of the $[Cu\ Htrien]^{3+}$ ion the distribution of the ionic species present in the various systems before and after the reaction was calculated by using the known values of the equilibrium constants determined in 0·1M-potassium chloride.[6] As these constants are given at 20°, they were corrected to 25° by using the values of ΔH obtained in this work, the method of successive approximations being employed.

TABLE 1.

The system $CuSO_4$ + HCl + trien in 0·1M-potassium chloride.

Copper (10^{-5} mole)	HCl (10^{-5} mole)	trien (10^{-5} mole)	Q (cal.)	Q_{cz} (cal.)	$-\Delta H$ (kcal. mole^{-1})
983	1398	1145	152·4	16·8	15,860
906	1291	1056	140·9	14·7	15,810
891	4596	1790	78·7	54·7	15,680
916	4723	1840	82·0	56·2	15,830
				Mean =	15,800.

$\Delta G = -18{\cdot}80 \pm 0{\cdot}3$ (kcal. mole^{-1})
$\Delta H = -15{\cdot}80 \pm 0{\cdot}1$ (kcal. mole^{-1})
$\Delta S = 10{\cdot}0 \pm 1{\cdot}3$ (cal. deg.$^{-1}$ mole^{-1})

TABLE 2.

Thermodynamic functions for metal(II)–triethylenetetramine systems in 0·1M-potassium chloride at 25°.

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$-\Delta G$ (kcal. mole^{-1}) [a]	6·70 ± 0·07	10·50 ± 0·07	14·90 ± 0·14	18·80 ± 0·28	27·40 ± 0·14	16·40 ± 0·07
$-\Delta H$ (kcal. mole^{-1}) [b]	2·30 ± 0·05	6·05 ± 0·05	10·65 ± 0·15	14·00 ± 0·10	21·55 ± 0·10	8·90 ± 0·15
ΔS (cal. deg.$^{-1}$ mole^{-1})	15·0 ± 0·5	15·0 ± 0·5	14·5 ± 1·0	16·0 ± 1·5	19·5 ± 1·0	25·0 ± 0·5

[a] Cf. ref. 6; corrected to 25° by using the enthalpy values obtained in this work. [b] Jonassen's values (ref. 4) for $-\Delta H$, in kcal. mole^{-1}, are: Mn 4; Fe 9; Co 9; Ni 13; Cu 22; Zn 4.

Magnetic Measurements.—The magnetic susceptibility of the solution of the $[Co\ trien]^{2+}$ ion was determined by using a Gouy-type magnetic balance.[7]

In order to prevent oxidation, the solution of the complex ion was prepared as follows. Weighed amounts of standardized solutions of cobalt(II) sulphate and triethylenetetramine in the molar ratio 1 : 1 were separately freed from dissolved oxygen by passage of nitrogen for 20 min. The two solutions were then mixed and stoppered. All the above operations were performed in an atmosphere of pure nitrogen.

The susceptibility of the $[Co\ trien]SO_4$ complex was determined according to the formula:

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

where x = fraction by weight of $[Co\ trien]SO_4$ in the solution. Diamagnetic corrections for the organic ligand were calculated from the Pascal constants.[8] The diamagnetic susceptibility of the sulphate ion was taken as $-40{\cdot}10^{-6}$.[9]

Spectrophotometric Measurements.—The spectra of the copper complexes were measured with a Beckman DU spectrophotometer with 1 cm. stoppered silica cells. With the diethylenetriamine–copper(II) complex, buffering at *ca.* pH 6·3 was necessary to avoid the formation of $[Cu\ den(OH)]^+$. The spectrum of $[Cu\ trien]^{2+}$ was recorded for a 1 : 1 solution of copper sulphate and triethylenetetramine.

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[6] Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 974.

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

[8] Cf. Selwood, "Magnetochemistry," Interscience Publ. Inc., New York, 1956, p. 92.

[9] Klemm, *Z. anorg. Chem.*, 1941, **246**, 347; cf. ref. 8, p. 78.

The solutions used to measure the spectrum of the [Cu Htrien]$^{3+}$ ion were 10·00mM in copper sulphate, 46·80mM in hydrochloric acid, 19·44mM in triethylenetetramine (test solution); and 2·20mM in copper sulphate, 1·63mM in triethylenetetramine (control). The composition of the test solution, calculated from the equilibrium constants,[6] was: Cu Htrien^{3+}, 7·81; Cu trien^{2+}, 1·63; Cu^{2+}, 0·56; H$_3$trien^{3+}, 2·41; H$_4$trien^{4+}, 7·59; H$^+$, 1·50 mmoles l.$^{-1}$. The only cations contained in the control solutions were Cu^{2+} and [Cu trien]$^{2+}$; their concentrations were the same as in the test solution. Another spectrum was recorded in a similar way for a solution of the composition: Cu Htrien^{3+}, 6·20; Cu trien^{2+}, 0·65; Cu^{2+}, 3·15; H$_3$trien^{3+}, 1·37; H$_4$trien^{4+}, 8·63; H$^+$, 3·00 mmoles l.$^{-1}$. The value of $\lambda_{\text{max.}}$ and the shape of the spectra were the same in both cases, only the height of the maximum differing by about 7%. The mean of the two spectra is recorded in Fig. 1. This procedure was followed as it is impossible to prepare a solution containing copper entirely as the [Cu Htrien]$^{3+}$ ion.

RESULTS

The calorimetric details for the formation of the [Cu Htrien]$^{3+}$ complex ion are recorded in Table 1. The heat (Q) evolved in each experiment was corrected for the heat of dilution of the metal salt. The heat effects (Q_{cz}) due to the change in the concentration of the various protonated forms of the base on complex formation were calculated by using the values of the heats of stepwise neutralization.[10] The thermodynamic functions for the formation of [Cu Htrien]$^{3+}$ ion are also recorded.

Table 2 reports the values for the thermodynamic functions ΔG, ΔH, and ΔS relative to the reaction between bivalent metal ions from manganese to zinc and triethylenetetramine in 0·1M-potassium chloride at 25°. The values of ΔG were obtained by using the stability constants of Schwarzenbach at 20°,[6] corrected at 25° by using our values of ΔH.

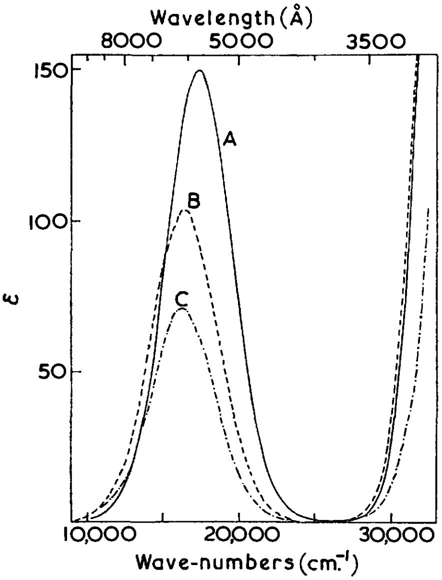

FIG. 1. Absorption spectra of complexes of copper and polyamines: A, [Cu trien]$^{2+}$; B, [Cu Htrien]$^{3+}$; C, [Cu den]$^{2+}$.

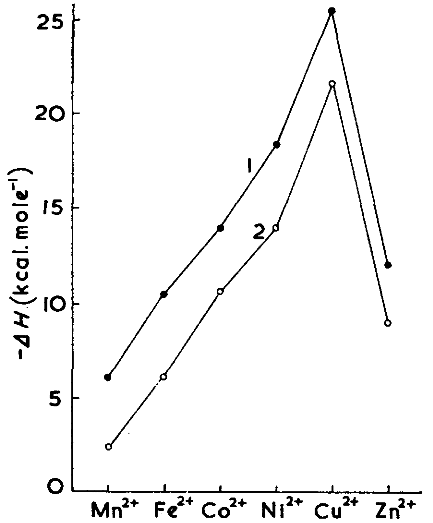

FIG. 2. Heats of formation of: (1) [M en$_2$]$^{2+}$ ions; (2) [M trien]$^{2+}$ ions.

The results of the magnetic measurements carried out at 24° were: $x = 5{\cdot}87 \times 10^{-2}$; $\chi_{g(\text{solution})} = 1{\cdot}19 \times 10^{-6}$; $\chi_{g(\text{complex})} = 31{\cdot}85 \times 10^{-6}$; $\chi_{\text{M}} = 9594 \times 10^{-6}$; $\delta = 151 \times 10^{-6}$; $\chi_{\text{Co}^{2+}} = 9745 \times 10^{-6}$; $\mu_{\text{eff.}} = 4{\cdot}83$ B.M.

The results of the spectrophotometric measurements are: [Cu trien]$^{2+}$, $\lambda_{\text{max.}} = 575$ mμ, $\varepsilon = 150$; [Cu den]$^{2+}$, $\lambda_{\text{max.}} = 610$ mμ, $\varepsilon = 71$; [Cu Htrien]$^{3+}$, $\lambda_{\text{max.}} = 610$ mμ, $\varepsilon = 104$. Fig. 2

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[10] Our unpublished results.

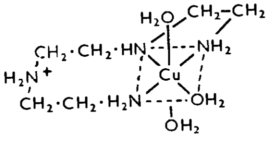
shows the absorption spectra of the [Cu trien]$^{2+}$, [Cu den]$^{2+}$ and [Cu Htrien]$^{3+}$ complex ions over the wavelength range 300—1000 mμ. The spectra of the first two complexes were already recorded for the ranges 430—670 [11] and 490—830 mμ [12] respectively.

DISCUSSION

The values of ΔH, plotted against the atomic number of the metals in Fig. 2, increase monotonically from manganese to copper and then diminish to zinc for which the value falls between that of iron and cobalt. In this Figure the heats of formation of the [M en$_2$]$^{2+}$ complexes [2] are also shown. The fact that the two curves run parallel seems to indicate that the two series of complexes have the same structure, namely, diaquo-octahedral for the metals from manganese to copper and tetrahedral for zinc.[2] The heat changes for the [M trien]$^{2+}$ ions are 3—4 kcal. mole^{-1} lower than for the corresponding [M en$_2$]$^{2+}$ complexes. An equal lowering was also found on going from [M en$_3$]$^{2+}$ to the corresponding [M den$_2$]$^{2+}$ complexes.[3] Both the [M den$_2$]$^{2+}$ and [M trien]$^{2+}$ complexes differ from the [M en$_3$]$^{2+}$ and [M en$_2$]$^{2+}$ complexes, respectively, in that they contain one chelate ring more and have two secondary nitrogen atoms in place of two primary ones. Both these factors probably lead to a lowering of the heat of reaction: the first as a result of the increased internal strain within the chelate rings; [13] the second as a result of the probable lower strength of the metal–secondary nitrogen bond as compared with the metal–primary one.[3] The latter hypothesis is supported by a comparison of the heats of formation of the [Cu den]$^{2+}$ and [Cu Htrien]$^{3+}$ complexes. The first complex ion which contains two primary and one secondary nitrogen atom bound to the copper(II) ion has a heat of formation of 18·00 kcal. mole^{-1}: [3] the second, in which the nitrogen donor atoms are one primary and two secondary,* has a heat of formation of only 15·80 kcal. mole^{-1}. This difference of 2·20 kcal. mole^{-1} need not, in fact, be taken as the difference between the strength of the copper–primary nitrogen and copper–secondary nitrogen bonds. It is likely that some inductive and electrostatic effects as well as those arising from the hydration of the terminal $-NH_3^+$ group may affect the strength of the bond between copper and secondary nitrogen adjacent to the free chain.

No spectrophotometric evidence for the [Cu Htrien]$^{3+}$ complex ion, whose stability constant was reported by Schwarzenbach,[6] was found by Jonassen *et al.*[4] The absorption spectrum we obtained shows a maximum at 610 mμ (curve 2 in Fig. 1). This value differs by *ca.* 35 mμ from $\lambda_{max.}$ of [Cu trien]$^{2+}$ but coincides with $\lambda_{max.}$ of the [Cu den]$^{2+}$ which also has a group of three nitrogen donor atoms.

The entropy changes for the formation of triethylenetetramine complexes of bivalent manganese, iron, cobalt, and nickel ions are essentially constant, ranging from 14·5 to 16·0 cal. deg.$^{-1}$ mole^{-1}, while with copper and zinc they are distinctly higher than the preceding ones. A similar trend has already been found with the [M en$_2$]$^{2+}$ and [M den]$^{2+}$ complex ions,[2, 3] and the same explanation probably holds here. Thus, for copper, the high value of the entropy can be ascribed to a planar arrangement of the triethylenetetramine molecule around the ion with a concomittant higher crystal field stabilization energy.[14] Thus the configuration of the [Cu trien(H$_2$O)$_2$]$^{2+}$ complex ion will mainly be *trans*-octahedral, while for the other metal ions from manganese to nickel the prevailing structure



* The other possible form (annexed) with an eight-membered ring is very improbable. It may be noted, in this connection, that the diamines tetramethylenediamine and hexamethylenediamine seem to act as non-chelating ligands.[13]

[11] Kirson, *Bull. Soc. chim. France*, 1957, 1178.
[12] Haendler, *J. Amer. Chem. Soc.*, 1942, **64**, 686.
[13] Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2344.
[14] Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

attributable to the complex ions on statistical and steric grounds[15] is *cis*-diaquaoctahedral. Since the dipole moment of the *trans*-octahedral structure is lower than that of the two possible *cis*-octahedral ones, the $[\text{Cu trien}(H_2O)_2]^{2+}$ ion will be able to orient fewer water molecules than the other ions, the entropy of the final state thus being higher.[16]

The value of ΔS for zinc, which is even higher than that for copper, leads to the hypothesis that more than four water molecules are released from the first co-ordination sphere of the aquo-ion with the consequent formation of a tetrahedral $[\text{Zn trien}]^{2+}$ ion. Such an ion, however, should have a larger second-sphere hydration since the spatial geometry should allow more water molecules to pack close to the metal ion. It may be noted, in this connection, that a tetrahedral structure was also postulated for other tri- and tetra-amine complexes of zinc.[2,3,17]

Let us now consider the displacement of ammonia and ethylenediamine respectively by triethylenetetramine:

$$[ML_n]^{2+} + \text{trien} \rightleftharpoons [\text{M trien}]^{2+} + n\text{L} \quad . \; . \; . \; . \; . \quad (1)$$

($L = NH_3$ or en; $n = 4$ or 2). The corresponding functions are recorded in Table 3.

The enthalpy term for the replacement of ammonia by triethylenetetramine does not favour the formation of the $[\text{M trien}]^{2+}$ ions. The higher stability of these complexes arises from the larger value of the entropy term. Contrary to the free-energy and enthalpy changes, the entropy changes are roughly constant for every metal, but the results recorded in Table 3 are too scanty to allow definite conclusions to be drawn.

The chelate effect for the replacement of ethylenediamine by triethylenetetramine is negligible. In this case, too, the ΔH values do not favour the formation of the $[\text{M trien}]^{2+}$ complexes but this effect is compensated by the positive ΔS values.

The entropy changes accompanying the processes of type (1) may be expressed by the equation:

$$\Delta S = [\bar{S}^0(\text{M trien}) - \bar{S}^0(\text{M L}_n)] + [n\bar{S}^0(\text{L}) - \bar{S}^0(\text{trien})] \quad . \; . \; . \quad (2)$$

where the terms $\bar{S}^0$ indicate partial molal entropies. The values of $\bar{S}_0(NH_3)$ in water at 25° is 26·3 cal. deg.$^{-1}$ mole^{-1}.[18] No experimental values have been reported for the partial molal entropies of ethylenediamine and triethylenetetramine. The values, calculated according to the Cobble equation[19] are: $\bar{S}^0(\text{en}) = 44$; $\bar{S}^0(\text{trien}) = 84$ cal. deg.$^{-1}$ mole^{-1}. Then $[4\bar{S}^0(NH_3) - \bar{S}^0(\text{trien})] = 21 \pm 2$; $[2\bar{S}^0(\text{en}) - \bar{S}^0(\text{trien})] = 4 \pm 4$ cal. deg.$^{-1}$ mole^{-1}. By substituting these values, together with the experimental values of ΔS in equation (2) we obtain:

$[\bar{S}^0(\text{M trien}) - \bar{S}^0(\text{M}(NH_3)_4)]$: Ni, 12; Cu, 14; Zn, 10 cal. deg.$^{-1}$ mole^{-1},
$[\bar{S}^0(\text{M trien}) - \bar{S}^0(\text{M en}_2)]$: Mn, 8·5; Fe, 10·5; Co, 8·5; Ni, 9·0; Cu, 9·5; Zn, 10·5 cal. deg.$^{-1}$ mole^{-1},

with an estimated uncertainty of ±6 cal. deg.$^{-1}$ mole^{-1}. These differences are positive and roughly constant. For the metathetic systems ethylenediamine–ammonia and trimethylenediamine–ammonia, Rasmussen[20] found values of these differences ranging from 0 to 8 cal. deg.$^{-1}$ mole^{-1}, with an indeterminacy of about ±10 cal. deg.$^{-1}$ mole^{-1} and concluded that the entropy change is mainly due to the entropy difference between the ligands. For the triethylenetetramine–ammonia and triethylenetetramine–ethylenediamine systems the difference between the entropies of the complexes contributes in a

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[15] Basolo, *J. Amer. Chem. Soc.*, 1948, **70**, 2634; Sarma and Bailar, *ibid.*, 1955, **77**, 5480.

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

[17] Yatsimirskii and Milyukov, *Zhur. fiz. Khim.*, 1957, **31**, 842.

[18] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Washington, D.C., Circular 500.

[19] Cobble, *J. Chem. Phys.*, 1953, **21**, 1446.

[20] Rasmussen, *Acta Chem. Scand.*, 1956, **10**, 1279.

TABLE 3.

Thermodynamic functions for the replacements (1).

	*n*L	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
ΔG (kcal.)	$4NH_3$				−7·85	−10·00	−3·35
	2en	−0·05	−0·05	−0·35	0·40	−0·10	−1·30
ΔH (kcal.)	$4NH_3$				2·00	0·45	5·90
	2en	3·70	4·35	3·30	4·35	3·85	3·00
ΔS (cal. deg.$^{-1}$)	$4NH_3$				33·0	35·00	31·0
	2en	12·5	14·5	12·5	13·0	13·5	14·5

comparable degree to the ΔS of replacement. When the replaced ligand is ammonia, the largest contribution to the entropy changes is given by the difference between the entropies of the ligands.

Concerning the stereochemistry of the complexes with triethylenetetramine, particular attention has been given to those of nickel(II) and cobalt(II). On the basis of magnetic measurements made on solutions of the [Ni trien]$^{2+}$ and [Co trien]$^{2+}$ ions, Jonassen *et al.*[21] stated that they are " low-spin " complexes. These workers have not, however, reported the values of either the magnetic susceptibility or, in the case of nickel, the ionic strength used. From spectrophotometric measurements on the [Ni trien]$^{2+}$ complex Jørgensen [22] showed that, at high temperature or strong salt concentrations, a yellow form, probably planar diamagnetic, does exist. Thus, under the conditions used for our calorimetric measurements, only a few percent of this form should occur. On the other hand, the magnetic moment of 4·8 B.M. we obtained for the triethylenetetramine–cobalt(II) complex in 0·2M-solution, indicates that this ion is " high spin."

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[21] Jonassen and Strickland, *J. Amer. Chem. Soc.*, 1958, **80**, 312; Jonassen and Ramanujam, *J. Phys. Chem.*, 1959, **63**, 411.

[22] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 399.