Formation of Five-co-ordinate Cations between Copper(II) Polyamine Complexes and Some Inorganic Anions. Standard Thermodynamic Functions in Methanol at 25 °C

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The standard thermodynamic functions for the equilibrium $[CuL]^{2+} + X^- \rightleftharpoons [CuLX]^+$ with L = 2 en, 2 tn, trien, (2,3,2-tet), and (3,3,3-tet) [*i.e.*, ethylenediamine, trimethylenediamine, triethylenetetramine, *NN′*-bis(2-aminoethyl)propane-1,3-diamine, and *NN′*-bis(3-aminopropyl)propane-1,3-diamine respectively] and X^- = iodide, thiocyanate, and azide ions have been studied in methanol at 25 °C. The equilibrium constants have been measured by a spectrophotometric method. The heats of reaction have been determined directly by calorimetric titration. The enthalpies of formation are all positive or only slightly negative, while the entropies are largely positive. For each copper(II) polyamine complex the enthalpy and entropy changes decrease in the order: $N_3^- > I^- > SCN^-$. In the reactions with the same inorganic anion $\Delta H°$ and $\Delta S°$ decrease according to the sequence $[Cu(en)_2]^{2+} > [Cu(trien)]^{2+} \simeq [Cu(2,3,2\text{-}tet)]^{2+} > [Cu(tn)_2]^{2+} > [Cu(3,3,3\text{-}tet)]^{2+}$.

THE polyamine complexes of Cu^{II} ion can co-ordinate a halide or pseudohalide anion to give species of unusual stereochemistries in both the solid and solution state. At present however there is little knowledge of the factors stabilising five-co-ordination.[1] Thermodynamic studies are valuable for understanding changes in properties of the acceptor complex on five-co-ordinate cation formation. For example, in some uncharged copper(II) complexes [2] the spectral and magnetic changes observed on five-co-ordinate adduct formation vary regularly with the thermodynamic functions and suggest an electronic and structural reorganisation of the copper(II)–acceptor complex.

This paper reports a study of the thermodynamics of five-co-ordinate complex formation of copper(II) polyamine aliphatic complexes $[Cu(en)_2]^{2+}$, $[Cu(trien)]^{2+}$, $[Cu(2,3,2\text{-}tet)]^{2+}$, $[Cu(tn)_2]^{2+}$, and $[Cu(3,3,3\text{-}tet)]^{2+}$ [en = ethylenediamine, trien = triethylenetetramine, (2,3,2-tet) = *NN′*-bis-(2-aminoethyl)propane-1,3-diamine, tn = trimethylenediamine, (3,3,3-tet) = *NN′*-bis-(3-aminopropyl)propane-1,3-diamine] with iodide, thiocyanate, and azide ions in methanol at 25 °C. The formation constants were determined spectrophotometrically and the heats of reaction by calorimetric titration. The equilibrium constants (by a spectrophotometric method) and the heat (by the temperature-dependence method) for a formally similar equilibrium of five-co-ordinate $[Pt(diars)_2X]^+$ [diars = *o*-phenylenebis(dimethylarsine)] in methanol have been studied.[3]

The thiocyanate ion can be bonded *via* sulphur or nitrogen to copper(II) polyamine complexes.[4,5] The different bonding mode is related to the polarity of the solvent.[6] We used methanol which belongs to a class with intermediate behaviour between that favouring *N*-bonded and that favouring *S*-bonded co-ordination. It has been predicted that the difference in entropy and in enthalpy between an *N*- and an *S*-bonded thiocyanate can be important in recognising the different bonding modes.[7]

EXPERIMENTAL

Materials.—Ethylenediamine, trimethylenediamine, triethylenetetramine, and *NN′*-bis-(3-aminopropyl)propane-1,3-diamine were commercial. *NN′*-Bis-(2-aminoethyl)-propane-1,3-diamine was prepared as described.[8] Methanol was reagent grade. The compounds $CuL(ClO_4)_2$ were prepared by a method analogous to that of ref. 5.

The inorganic anions used as donor ions were derived from tetra-n-butylammonium iodide, tetra-n-butylammonium thiocyanate, and tetramethylammonium azide Me_4NN_3. Bu_4NI was commercial. Bu_4NSCN was prepared by adding a stoicheiometric quantity of KSCN to Bu_4NClO_4 in hot alcoholic solution. On cooling, $KClO_4$ was precipitated and filtered off. The solution was evaporated under reduced pressure and the white precipitate of Bu_4NSCN was collected by adding ether. Me_4NN_3 was prepared by mixing a hot methanolic solution of Me_4NCl with a saturated solution of NaN_3. The precipitated NaCl was filtered off and the compound Me_4NN_3 was obtained from the alcoholic solution. It was recrystallised several times from methanol. All the compounds gave satisfactory C, H, and N analyses.

Spectrophotometric Measurements.—The spectra were measured at 25 °C by use of a Beckman DK 2A instrument, over the range 1200—400 nm in 1 cm quartz cells. The solutions were prepared immediately before recording u.v. spectra.

The concentration of the copper(II) polyamine complex was fixed, while the amount of the anion was variable. The composition of the solutions was determined by weighing and the concentration of metal complex was 10^{-2}—10^{-3}M. One or two isosbestic points are observed in the visible region. As an example the family of spectra referring to the system $[Cu(3,3,3\text{-}tet)]^{2+}$–$N_3^-$ is reported in the Figure. The stability constants were calculated for the equilibrium (1).

$$[CuL]^{2+} + X^- \rightleftharpoons [CuLX]^+ \qquad (1)$$

Attempts to bring in two equilibrium constants yield unreliable values of *U* or the rejection of one constant (see

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[1] C. Furlani, *Co-ordination Chem. Rev.*, 1968, **3**, 141.

[2] B. L. Libutti, B. B. Wayland, and A. F. Garito, *Inorg. Chem.*, 1969, **8**, 1510.

[3] G. Dolcetti, A. Peloso, and L. Sindellari, *Gazzetta*, 1966, **96**, 1648.

[4] R. Barbucci, G. Cialdi, G. Ponticelli, and P. Paoletti, *J. Chem. Soc.* (*A*), 1969, 1775.

[5] R. Barbucci, P. Paoletti, and G. Ponticelli, *J. Chem. Soc.* (*A*), 1971, 1637.

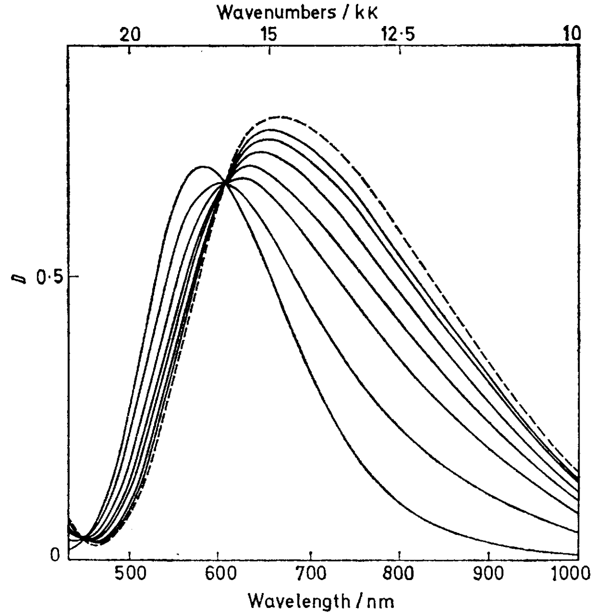
[6] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.*, 1971, **9**, 2032.

[7] A. H. Norbury, *J. Chem. Soc.* (*A*), 1971, 1090; R. D. Gillard and S. H. Lanzie, *J. Inorg. Nuclear Chem.*, 1971, **33**, 947.

[8] J. Van Alphen, *Rec. Trav. chim.*, 1936, **55**, 835.

Calculations section). The number of absorbances used for calculation of the equilibrium constants were 11—15 for each curve over the range 1100—550 nm, and the number of curves for each system was never less than five.

Calorimetric Measurements.—A titration calorimeter LKB 8700/2 was used. The measurements were carried out at 25 °C in a room thermostatted at 25 ± 1 °C. A volume of a standard solution of the salt was added from a Metrohm Multidosimat E 412 burette linked to a Metrohm Dosifix E 442 programmer to a methanolic solution containing the copper(II) polyamine complex.



The set of absorption curves in the system $[Cu(3,3,3\text{-tet})]^{2+}$–$N_3^-$. The concentration of acceptor complex was constant (4×10^{-3}M); the ratio of the reagent to $[Cu(3,3,3\text{-tet})]^{2+}$ for consecutive curves was: 0, 0·33, 0·67, 1·43, 2·00, 3·33, 10·0. The broken line is the calculated limit curve

The heats of the reaction (1) were calculated with an IBM 1130 computer and an appropriate FORTRAN programme. Results are in Table 1.

TABLE 1

Calorimetric data for the reaction $[CuL]^{2+} + X^- \rightleftharpoons [CuLX]^+$ in methanolic solution at 25 °C

$[CuL]^{2+}$	mmol	X^-	mmol	V/ml	$Q_{corr.}$ [a]
$[Cu(en)_2]^{2+}$	0·5071	N_3^-	0·5897	92·68	−0·943
	0·5086		0·5897	92·92	−0·968
	0·4761		0·3866	84·51	−0·733
	0·5120		0·3686	90·49	−0·753
	0·5322	I^-	0·8666	96·87	−0·4857
	0·5392		0·8666	98·24	−0·4945
	0·5344		0·8666	97·13	−0·4899
	0·5385	SCN^-	1·1880	97·95	−0·5432
	0·5619		1·1880	101·86	−0·5432
	0·5484		1·1880	99·47	−0·5430
$[Cu(trien)]^{2+}$	0·2318	N_3^-	0·5897	102·34	−0·5364
	0·2400		0·5897	105·65	−0·5427
	0·2370		0·5897	104·33	−0·5406
	0·2160	I^-	0·7833	95·92	−0·2725
	0·2286		0·7833	101·03	−0·2917
	0·2217		0·7833	98·13	−0·2862
	0·2223	SCN^-	0·7112	98·48	−0·1387
	0·2361		0·7112	104·09	−0·1445
	0·2268		0·7112	100·22	−0·1418
$[Cu(2,3,2\text{-tet})]^{2+}$	0·4562	N_3^-	0·5897	97·68	−0·828
	0·4382		0·5897	94·25	−0·810
	0·3847		0·5897	84·00	−0·822
	0·4573	I^-	0·6939	98·44	−0·3414
	0·4522		0·6939	96·90	−0·3370
	0·4656		0·6939	99·52	−0·3485
	0·4562	SCN^-	1·1880	97·78	−0·3059
	0·4593		1·1880	98·38	−0·3142
	0·4530		1·1880	97·05	−0·3050
$[Cu(tn)_2]^{2+}$	0·5558	N_3^-	0·5897	97·72	−0·7240
	0·5459		0·5897	96·04	−0·7967
	0·4708		0·5897	84·03	−0·6858
	0·4820	I^-	0·8666	101·21	−0·1594
	0·4746		0·8666	99·79	−0·1721
	0·4767		0·8666	100·12	−0·1630
	0·4816	SCN^-	1·1880	101·17	0·0088
	0·4752		1·1880	99·94	0·0068
	0·4582		1·1880	96·55	0·0055
$[Cu(3,3,3\text{-tet})]^{2+}$	0·4780	N_3^-	0·5897	98·10	−0·5574
	0·4458		0·5897	92·03	−0·5517
	0·4038		0·5897	84·13	−0·5502
	0·4671	I^-	0·6939	98·72	0·1442
	0·4646		0·6939	98·24	0·1433
	0·4721		0·6939	99·69	0·1298
	0·4676	SCN^-	1·188	98·82	0·3181
	0·4641		1·188	98·12	0·3131
	0·4616		1·188	97·55	0·3152

[a] Corrected for heat of dilution.

Calculations.—The general equation for the equilibria involved is $ML + nX \rightleftharpoons MLX_n$ where ML is a complex acceptor and X a donor ion (in this case $M = Cu^{2+}$ and $X = N_3^-$, I^-, or SCN^-). The equations are general for any Lewis acid–base reaction. The equilibrium constant expression for this reaction is (2). Consider the mass balance equations (3) and (4) where T_M and T_X are the total concentrations of metal and ligand present. If arbitrary values are assigned to the constants β_n, equations (3) and (4) become two non-linear equations in the unknown [ML] and [X]. Values of [ML] and [X] which satisfy the equations are calculated by the reiterative method of Newton and Raphson.[9] Owing to the fact that the donor atom does not absorb in the region studied, the relationship of the total absorbance D_λ at any given wavelength for a 1 cm cell is (5) where ε is the extinction coefficient for a particular species.

$$\beta_n = \frac{[MLX_n]}{[ML][X]_n} \tag{2}$$

$$T_M = [ML] + \Sigma\beta_n[ML][X]^n \tag{3}$$

$$T_X = [X] + \Sigma n\beta_n[ML][X]^n \tag{4}$$

$$D_\lambda = \varepsilon_{ML}[ML] + \varepsilon_{MLX}[MLX] + \varepsilon_{MLX_2}[MLX_2], \textit{etc.} \tag{5}$$

The unknowns ε_{ML} and ε_{MLX} can be obtained by resolving, with a least-squares method, a set of linear equations where the coefficients are the concentrations of complex and the known terms are the D_λ values. It is evident that the number of curves (number of D_λ at the same wavelength, but of solutions with different concentrations) must be higher than the number of unknowns ε. From values obtained in this way a value of $D_{\lambda,calc}$ is calculated from equation (5). The calculated total absorbance ($D_{\lambda,calc}$) for each curve is compared with the experimental absorbance $D_{\lambda,exp}$ at the same wavelength. If the agreement, for all D_λ, is not satisfactory, the values of β_n can be varied in turn

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[9] H. Margenau and G. M. Murphy, 'The Mathematics of Physics and Chemistry,' 2nd edn., D. Van Nostrand, Princeton, 1956, p. 492.

to minimise the sum of the squares of the residuals U in equation (6) where Σ_i is extended to the number of wavelengths (N) and Σ_j is extended to the number of curves (M).

$$U = f(\beta_n) = \sum_{1}^{N}{}_i \sum_{1}^{M}{}_j (D_{\lambda,\mathrm{exp}} - D_{\lambda,\mathrm{calc}})_{ij}^2 \tag{6}$$

The search of the minimum of the function U is carried out by Sillén's 'pit-mapping' procedure.[10] The calculations were performed on an IBM 1130 computer with a FORTRAN programme. After each cycle, the computer gave the refined values of the constants, the relative standard deviations, and the values of U. In addition, as a measure of the closeness of fit, the standard deviation σ which is calculated from the formula (7) (where n is number of

$$\sigma = \sqrt{[U(N.M. - n)]} \tag{7}$$

unknown stability constants) was also printed by the computer. The programme stops the calculations when the values for the constants calculated in two successive cycles differ by less than a small pre-established amount. The programme gives also the molar absorbance (ε) for all the wavelengths pre-established, both of the acceptor complex and of the adduct formed. From the values of (ε) it is possible to calculate the limiting curve of the ion $[\mathrm{CuLX}]^+$.

TABLE 2

Spectrophotometric data and standard thermodynamic functions (standard state of 1 mol kg^{-1}) of the formation of the five-co-ordinate cation $[\mathrm{CuLX}]^+$ in methanol at 25 °C

$[\mathrm{CuL}]^{2+}$	$\nu_{\mathrm{max.}}$/kK of $[\mathrm{CuL}]^{2+}$ in MeOH [a]	X^-	$\nu_{\mathrm{max.}}$/kK of $[\mathrm{CuLX}]^+$ in MeOH [a]	log K/ kg mol^{-1} [b]	ΔG° [b] / kcal mol^{-1}	ΔH° [b] / kcal mol^{-1}	ΔS° [b] / cal mol^{-1} K^{-1}
$[\mathrm{Cu(en)_2}]^{2+}$	18·5(73)	N_3^-	16·9(85)	2·48(3)	−3·39(4)	3·48(2)	23·0(2)
		I^-	17·5(97)	1·73(5)	−2·36(7)	2·84(2)	17·4(3)
		SCN^-	17·2(89)	2·07(2)	−2·82(3)	1·78(2)	15·4(2)
$[\mathrm{Cu(trien)}]^{2+}$	17·2(163)	N_3^-	15·6(200)	2·79(1)	−3·81(1)	3·09(2)	23·1(1)
		I^-	16·1(215)	2·83(2)	−3·86(3)	1·57(2)	18·2(2)
		SCN^-	15·9(210)	3·22(1)	−4·39(1)	0·70(1)	17·0(1)
$[\mathrm{Cu(2,3,2\text{-}tet)}]^{2+}$	19·1(75)	N_3^-	18·0(105)	2·48(1)	−3·38(1)	3·32(1)	22·4(1)
		I^-	18·3(210)	2·53(4)	−3·45(5)	1·19(1)	15·5(2)
		SCN^-	17·8(117)	2·73(3)	−3·73(4)	0·82(1)	15·2(2)
$[\mathrm{Cu(tn)_2}]^{2+}$	17·9(118)	N_3^-	16·3(136)	2·57(1)	−3·50(1)	2·41(3)	19·8(1)
		I^-	16·5(154)	2·52(1)	−3·43(1)	0·51(2)	13·2(1)
		SCN^-	16·3(140)	2·70(2)	−3·68(3)	−0·02(1)	12·2(1)
$[\mathrm{Cu(3,3,3\text{-}tet)}]^{2+}$	17·1(165)	N_3^-	15·1(188)	3·07(1)	−4·19(1)	1·59(3)	19·9(1)
		I^-	15·2(230)	3·10(1)	−4·23(1)	−0·36(2)	12·9(1)
		SCN^-	15·3(187)	3·44(1)	−4·69(1)	−0·73(1)	13·3(1)

[a] The values in parentheses are the molar extinction coefficients. [b] The values in parentheses are the standard deviations.

RESULTS AND DISCUSSION

The addition of N_3^-, I^-, or SCN^- ion to the copper complexes listed in Table 2 always causes a shift of the maximum to lower frequencies and an increase of the molar absorbtivity. This behaviour is generally observed as a result of the formation of a five-co-ordinate species.[11] Table 2 shows the values of absorption maxima and of molar extinction coefficients obtained from the limiting curves, and the standard thermodynamic functions of reaction (1).

The standard molal enthalpies relative to the formation of the five-co-ordinate cation $[\mathrm{CuLX}]^{2+}$ are all positive or only slightly negative, while the standard molal entropies are largely positive.

Reaction (1) involves (i) the exothermic formation of the Cu–X bond, and (ii) the endothermic desolvation process accompanying the reaction. The desolvation process should be a result of the steric effect of the placing of the anion adjacent to the cation, as well as the decrease in the charge from +2 to +1. The breakdown of the solvent lattice around the reacting ions and the consequent release of solvent molecules accounts for the largely positive entropy changes.

In general the reactions involving the addition of thiocyanate ion are less endothermic and less entropic than those involving the iodide ion which, in turn, are less endothermic and less entropic than those involving the azide ion (Table 2). This trend is in agreement with the fact that, in protic solvents, the solvation sphere of the azide ion is bulkier than that of iodide, which, in turn, is bulkier than that of thiocyanate.[12] This shows that the most important effect in these reactions is probably that concerning the desolvation process.

When the enthalpy change of a reaction is slightly positive, and the entropy change is largely positive, the reaction is ascribed as an A-character (hard) interaction;[13] the bond is due to a predominantly electrostatic interaction. On the contrary, the B-character reactions involving soft species are characterised by negative enthalpy changes; this exothermic effect reflects the increasing covalent interaction.[14]

The reactions of copper(II) polyamine complexes with the anions I^-, N_3^-, and SCN^- are all entropy-stabilised so they should be classified as A-type reactions. The analogous reactions of $[\mathrm{Pt(diars)}]^2$ with I^-, SCN^-, and N_3^- exhibit negative enthalpy changes [3] and should be classified as B-type interactions. In fact the $-\Delta H$

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[11] R. C. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, 1957, **26**, 1165; D. P. Graddon, *J. Inorg. Nuclear Chem.*, 1960, **14**, 161.

[12] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.

[13] S. Ahrland, *Structure and Bonding*, 1968, **5**, 118.

[14] G. H. Nancollas, *Co-ordination Chem. Rev.*, 1970, **5**, 379.

values decrease with the decreasing softness of the anion: $I^- > SCN^- > N_3^-$. The sequence of ΔH° values for the reactions of copper(II) polyamine complexes with the same anion is $[Cu(en)_2]^{2+} > [Cu(trien)]^{2+} \sim [Cu(2,3,2\text{-}tet)]^{2+} > [Cu(tn)_2]^{2+} > [Cu(3,3,3\text{-}tet)]^{2+}$. The complexes containing five-membered chelate rings exhibit a more positive enthalpy change than those containing six-membered rings. $[Cu(2,3,2\text{-}tet)]^{2+}$, which has two external five-membered rings and a central six-membered ring, has an intermediate behaviour. Also the entropy changes follow the same trend (Table 2).

The size of the chelate rings seems to affect the stereochemistry of five-co-ordinate copper(II) complexes. The crystal structure of the five-co-ordinate cation $[Cu(tn)_2(NCS)]^{2+}$, containing six-membered chelate rings, have been reported:[15] the co-ordination polyhedron is a distorted trigonal bipyramid, the co-ordination sites being occupied by ammine and thiocyanate nitrogen atoms. The five-co-ordinate ion $[Cu(trien)(SCN)]^+$, involving all five-membered rings, exhibits a square-pyramidal geometry:[16] the cupric ion is slightly above the plane of the four nitrogen atoms and the apical position is occupied by a sulphur atom.

We suggest that in solution, as in the solid state, the five-co-ordinate cations of type $[CuLX]^+$ are arranged in a different way according to the size of the chelate ring. Then the different thermal effect would be ascribed to a different stereochemistry of the five-co-ordinate cation formed.

The thermodynamic functions show clearly a different behaviour between N_3^- and SCN^-. The latter ion has an entropic and enthalpic value similar to that of the 'softer' iodide in all the series considered (Table 2). This should agree with the hypothesis that in solution all these complexes have the thiocyanate group bonded with the same sulphur atom. This assertion is, however, hazardous, because of the different entropy of desolvation of these anions. Further, hard interaction involves co-ordination *via* the 'hard' nitrogen atom of the ambidentate SCN^- ligand. Spectroscopic data indicate this possibility as the more favourable.

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