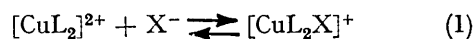


The Thermodynamic and Electronic Properties of Some Copper(II) Five-co-ordinate Cations in Non-aqueous Solution

By R. Barbucci, P. Paoletti,* and L. Fabbrizzi, Istituto di Chimica Generale ed Inorganica dell'Università and Laboratorio del C.N.R., Via I. Nardi, 39, 50132 Florence, Italy

The standard thermodynamic functions for the equilibrium $[\text{CuL}_2]^{2+} + \text{X}^- \rightleftharpoons [\text{CuL}_2\text{X}]^+$ with L = en, meen, dmen, amen (ethylenediamine, *N*-methylethylenediamine, *NN'*-dimethylethylenediamine, and *NN'*-dimethylethylenediamine respectively) and $\text{X}^- = \text{Cl}^-$, Br^- , I^- , or SCN^- have been obtained in methanol at 25 °C. The equilibrium constants were measured spectrophotometrically. The heats of reaction were determined by calorimetric titration. The spectroscopic parameters and thermodynamic functions of the five-co-ordinate cations except for those of $[\text{Cu}(\text{amen})_2\text{I}]^+$ show a regular trend in each series of anions considered. These regularities indicate that the five-co-ordinate cations with a given chelate have the same stereochemistry. The anomalous values for the five-co-ordinate $[\text{Cu}(\text{amen})_2\text{I}]^+$ are probably due to a large distortion of the cation towards a trigonal-bipyramidal configuration. The thermodynamic functions clearly show that the driving force of these reactions is the desolvation process, as all are entropy-stabilized. There is a linear correlation between the enthalpies of reaction and the enthalpies of anion desolvation. The different slope found for each $[\text{CuL}_2]^{2+}$ complex is explained in terms of the steric hindrance of the methyl groups to the introduction of the donor anion into the co-ordination sphere of copper(II).

In a previous paper¹ on the thermodynamics of the formation of five-co-ordinate cations in methanol solutions we were concerned with the interpretation of the CuL-X interaction as manifested by the enthalpy and the entropy of reaction. We now report an investigation on the formation (1) of copper(II) complexes of the formula $[\text{CuL}_2\text{X}]^+$, where L = en, meen, dmen, and amen (ethylenediamine, *N*-methylethylenediamine, *NN'*-dimethylethylenediamine, and *NN'*-dimethylethylenediamine, respectively) and $\text{X}^- = \text{Cl}^-$, Br^- , I^- , and



NCS^- in methanol at 25 °C. Stability constants were measured spectrophotometrically, and the heats of reac-

tion by calorimetric titration. Our purpose was to identify the driving force of the reaction and the factors which stabilize the five-co-ordinate cation. Though it is not easy to derive the configuration of the copper(II) complex just from an analysis of the electronic spectra, it is interesting to see whether a consideration of the spectroscopic and thermodynamic parameters together might lead to more precise information on possible stereochemistries. By combining the ΔH° values with the ΔG° values we have calculated the standard molal ΔS° quantities associated with the formation of the complexes. The entropy data go far towards defining the

¹ R. Barbucci, L. Fabbrizzi, and P. Paoletti, *J.C.S. Dalton*, 1972, 1099.

steric factors which influence the metal-anion interaction and therefore are important for obtaining a reliable understanding of the reaction process, especially in a highly solvating medium such as methanol.

EXPERIMENTAL

All the amines were commercial. Methanol (Baker analysed reagent) (H_2O 0.03%) was used without further purification. The compounds $[\text{CuL}_2](\text{ClO}_4)_2$ were prepared by a method analogous to that of ref. 2 from methanolic solution. In this solvent they are 1:2 electrolytes. The inorganic Cl^- , Br^- , or I^- salts were derived from the commercial tetra-n-butylammonium salts. The preparation of $\text{Bu}_4\text{N}^+\text{SCN}^-$ was described.¹ All compounds gave satisfactory C, H, and N analysis.

Spectra were measured at 25 °C with a Beckman DK-2A spectrophotometer over the range 1200–400 nm in a thermostatted 1 cm quartz cell. The solutions contained *ca.* 10^{-3}M -complex and known amounts of each donor anion. The solution used as a blank contained the same concentration of anion as the sample. One or two isosbestic points are observed in the visible region associated with the equilibrium (1).

Even a 10-fold excess of X^- does not result in complete 1:1 complex formation, but the formation constants and the spectra of the complexes formed can still be derived from a family of spectra. The calculation method has been described.¹ The calculations were performed on an IBM 1130 computer with a Fortran programme. The calorimetric measurements were carried out with a titration calorimeter LKB 8700-2 at 25 °C in a room thermostatted at 25 ± 1 °C. Procedure and calculation methods have been reported.¹ Results are in Table 1. The ionic strength of the experimental solutions was maintained at 0.05M by addition of $\text{Bu}_4\text{N}^+\text{ClO}_4^-$. Some calorimetric measurements were performed without the added salt, and the heats agreed well with those obtained at constant ionic strength.

RESULTS AND DISCUSSION

The addition of Cl^- , Br^- , I^- , and SCN^- to the copper(II) complexes listed in Table 2 always causes a shift of the electronic absorption maximum to lower frequencies and an increase of the molar absorptivity. The pronounced spectral changes obtained indicate the formation of new species that are not merely ion pairs but probably five-co-ordinate cations.³ Sharp isosbestic points are observed with a ratio $\text{X}^- : [\text{CuL}_2]^{2+}$ up to 10:1 and are consistent with the single equilibrium (1). These results lead to the conclusion that there are only two absorbing species in solution, $[\text{CuL}_2]^{2+}$ and $[\text{CuL}_2\text{X}]^+$, and no six-co-ordinate chelates $[\text{CuL}_2\text{X}_2]$. The spectrophotometric values of the five-co-ordinate cations, obtained from the limiting spectra, are in Table 2. The spectra of our five-co-ordinate cations $[\text{CuL}_2\text{X}]^+$ are very similar in shape, exhibiting a maximum and a tail at lower wavenumbers (Table 2). The complex

$[\text{Cu}(\text{amen})_2\text{I}]^+$ is the only one to show two maxima of equal intensity at 16.0 and at 13.8 kk (Figure 1). For a given ligand, the band maxima shift towards higher energies as a function of X^- in the order $\text{NCS}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. This trend, already observed in other five-co-ordinate copper chelates,⁴ is contrary to the spectrochemical series. The position of the maxima in the $[\text{CuL}_2\text{NCS}]^+$ complexes at lower frequency than the corresponding Cl^- complexes (Table 2) seems to indicate that the SCN group is bonded through the nitrogen atom. The band maxima for a sulphur-bonded thiocyanate are expected to occur at about the same energies as those of

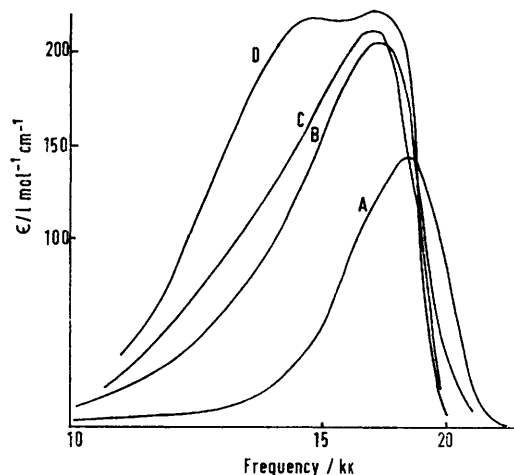


FIGURE 1 Absorption spectra of the complexes: A, $[\text{Cu}(\text{amen})_2]^{2+}$; B, $[\text{Cu}(\text{amen})_2\text{Cl}]^+$; C, $[\text{Cu}(\text{amen})_2\text{Br}]^+$; and D, $[\text{Cu}(\text{amen})_2\text{I}]^+$

the bromo-compounds. The reactions of formation of the five-co-ordinate complexes show positive standard molal entropies and positive or only slightly negative standard molal enthalpies (Table 2). Thus these complexes are entropy-stabilized, dominated by the desolvation process. The heat change for the formation of the 1:1 complex can be expressed by equation (2) where ΔH_g

$$\Delta H = \Delta H_g + \Delta H(\text{CuL}_2\text{X})_{\text{soln}} - \Delta H(\text{X})_{\text{soln}} - \Delta H(\text{CuL}_2)_{\text{soln}} \quad (2)$$

is the enthalpy of reaction (1) in the gaseous state (bond energy (Cu-X) and $\Delta H(\text{CuL}_2\text{X})_{\text{soln}}$, $\Delta H(\text{X})_{\text{soln}}$, and $\Delta H(\text{CuL}_2)_{\text{soln}}$ are the enthalpy of solvation of the given co-ordinate cation, anion, and acceptor complex respectively. As $\Delta H(\text{CuL}_2)_{\text{soln}}$ is constant in a series in which there is a common $[\text{CuL}_2]^{2+}$ and various X^- , the variable quantities are ΔH_g , $\Delta H(\text{CuL}_2\text{X})_{\text{soln}}$, and $\Delta H(\text{X})_{\text{soln}}$. In the gas phase the M-X bond energies decrease in the sequence: $\text{M-Cl} > \text{M-Br} > \text{M-I}$;⁵ in our reaction the exothermic process of formation of a new bond is over-

² R. Barbucci, P. Paoletti, and G. Ponticelli, *J. Chem. Soc. (A)*, 1971, 1637.

³ R. C. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, 1957, **26**, 1165; D. P. Graddon, *J. Inorg. Nuclear Chem.*, 1960, **16**, 163.

⁴ C. M. Harris and E. D. McKenzie, *J. Chem. Soc. (A)*, 1969, 746; S. Utsuno and K. Sone, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2647.

⁵ S. J. Ashcroft and C. T. Mortimer, 'Thermochemistry of Transition-metal Complexes,' Academic Press Inc., London, 1970, p. 303.

come by the more endothermic heat of desolvation, and the ΔH° values therefore follow the order of desolvation energy of the anion ⁶ (Figure 2). The bulkier the solvation sphere of the anion, the greater the loss of energy

the corresponding lines are different for each series. The line of $[\text{Cu}(\text{amen})_2\text{X}]^+$ has been drawn through the points of the chloride and bromide complexes. The monotonic sequence of the enthalpies of reactions suggests that there

TABLE I
Calorimetric data for reaction (1) in methanol at 25 °C

$[\text{CuL}_2]^{2+}$	mmol	X ⁻	mmol	$V_{\text{tot.}}/\text{ml}$	Q/cal^a	$[\text{CuL}_2\text{X}]^{2+}$ formed mmol	ΔH° kcal mol ⁻¹
$[\text{Cu}(\text{en})_2]^{2+}$	0.4483	Cl ⁻	0.8102	99.02	-0.776	0.2646	2.93
	0.4578		0.8102	98.76	-0.775	0.2696	2.87
	0.4487		0.8102	96.95	-0.759	0.2668	2.84
	0.4564	Br ⁻	0.8048	98.48	-0.513	0.1766	2.91
	0.4477		0.8048	96.75	-0.513	0.1753	2.93
	0.4468		0.8048	96.56	-0.481	0.1751	2.75
$[\text{Cu}(\text{meen})_2]^{2+}$	0.5338	Cl ⁻	0.7984	95.28	-0.900	0.3826	2.35
	0.5899		0.7984	104.45	-0.847	0.4047	2.09
	0.5209		0.8104	93.18	-0.817	0.3794	2.15
	0.5389	Br ⁻	0.8048	96.11	-0.639	0.3918	1.63
	0.5266		0.8048	94.10	-0.604	0.3864	1.56
	0.5276		0.8048	94.27	-0.639	0.3868	1.65
	0.5498	I ⁻	0.8002	97.90	-0.382	0.3808	1.00
	0.5514		0.8002	98.15	-0.390	0.3814	1.02
	0.5500		0.8002	98.00	-0.388	0.3808	1.02
	0.5214	SCN ⁻	0.6655	96.94	-0.2085	0.3682	0.566
	0.5279		0.6655	98.05	-0.2120	0.3707	0.572
	0.5255		0.6655	97.60	-0.2100	0.3698	0.568
$[\text{Cu}(\text{dmen})_2]^{2+}$	0.2345	Cl ⁻	0.8104	94.94	-0.419	0.2093	2.00
	0.2323		0.8104	94.12	-0.454	0.2076	2.19
	0.2234		0.8104	90.83	-0.413	0.2006	2.06
	0.3173	Br ⁻	0.8048	99.79	-0.399	0.2853	1.40
	0.2992		0.8048	94.55	-0.369	0.2711	1.36
	0.3100		0.8048	96.30	-0.385	0.2799	1.38
	0.3094	I ⁻	0.8002	97.51	-0.183	0.2757	0.66
	0.3399		0.8002	98.35	-0.182	0.3009	0.60
	0.3094		0.8002	97.51	-0.187	0.2757	0.68
	0.3110	SCN ⁻	0.6655	97.99	0.258	0.3033	-0.85
	0.3091		0.6655	97.42	0.242	0.3016	-0.80
	0.3098		0.6655	97.30	0.249	0.3022	-0.82
$[\text{Cu}(\text{amen})_2]^{2+}$	0.5424	Cl ⁻	0.8104	97.54	-0.769	0.4542	1.69
	0.5567		0.8104	98.37	-0.753	0.4635	1.62
	0.5828		0.8104	99.85	-0.756	0.4799	1.57
	0.5416	Br ⁻	0.8048	96.51	-0.329	0.4524	0.73
	0.5427		0.8048	96.69	-0.394	0.4531	0.87
	0.5448		0.8048	97.05	-0.400	0.4543	0.88
	0.5507	I ⁻	0.8002	98.01	-0.535	0.4333	1.23
	0.5396		0.8002	96.18	-0.558	0.4276	1.30
	0.4448		0.8002	94.24	-0.491	0.3647	1.35
	0.4654	SCN ⁻	0.8002	97.33	-0.491	0.3773	1.30
	0.5224		0.6655	93.39	0.352	0.3649	-0.96
	0.5142		0.6655	92.04	0.304	0.3618	-0.84
	0.5464	0.6655	97.30	0.369	0.3735	-0.99	

^a Corrected for the heat of dilution.

due to 1:1 complex formation. The ΔS values also follow the same trend (Table 2).

In Figure 2 there appears to be good evidence of a linear relation for each series between the ΔH values and the energies of desolvation of the anions. The slopes of

⁶ G. Choux and R. L. Benoit, *J. Amer. Chem. Soc.*, 1969, **91**, 6221.

is no change of stereochemistry along a series. The slopes of the regression lines increase in the order $\text{en} < \text{meen} < \text{dmen} < \text{amen}$. This may be related to the greater hindrance of the complex ⁷ to the introduction of another atom into the co-ordination sphere. The

⁷ R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J.C.S. Dalton*, 1972, 740.

TABLE 2

Spectrophotometric data and standard thermodynamic functions (standard state of 1 mol kg⁻¹) of the formation of the five-co-ordinate cation [CuL₂X]⁺_n in methanol at 25 °C

[CuL ₂] ²⁺	$\nu_{\max.}/\text{kK}$ of [CuL ₂] ²⁺ in MeOH ^a	X ⁻	$\nu_{\max.}/\text{kK}$ of [CuL ₂ X] ⁺ in MeOH ^a	$-\Delta G^\circ$ ^b kcal mol ⁻¹	ΔH° ^b kcal mol ⁻¹	ΔS° ^b cal mol ⁻¹ K ⁻¹
[Cu(en) ₂] ²⁺	18.5 (73)	Cl ⁻	17.5 (83)	2.91 (3)	2.88 (2)	19.4 (2)
		Br ⁻	17.5 (91)	2.60 (3)	2.86 (6)	18.3 (3)
		I ⁻	17.5 (97) ^e	2.36 (7) ^e	2.84 (2) ^e	17.4 (3) ^e
		SCN ⁻	17.2 (89) ^e	2.82 (3) ^e	1.78 (2) ^e	15.4 (2) ^e
[Cu(meen) ₂] ²⁺	18.6 (82)	Cl ⁻	17.2 (108)	3.62 (3)	2.19 (8)	19.5 (4)
		Br ⁻	17.5 (110)	3.65 (1)	1.61 (3)	17.6 (1)
		I ⁻	17.9 (111)	3.57 (3)	1.01 (1)	15.3 (1)
		SCN ⁻	16.3 (113)	3.81 (4)	0.57 (1)	14.7 (1)
[Cu(dmen) ₂] ²⁺	18.2 (107)	Cl ⁻	16.1 (148)	4.11 (1)	2.08 (5)	20.7 (2)
		Br ⁻	16.2 (153)	4.27 (1)	1.38 (1)	18.9 (1)
		I ⁻	16.3 (165)	4.16 (1)	0.64 (2)	16.1 (1)
		SCN ⁻	15.9 (155)	5.36 (5)	-0.83 (1)	15.2 (2)
[Cu(amen) ₂] ²⁺	18.0 (146)	Cl ⁻	16.3 (196)	4.15 (3)	1.63 (3)	19.4 (2)
		Br ⁻	16.4 (216)	4.15 (2)	0.83 (4)	16.7 (2)
		I ⁻	16.0 (224), 13.8 (219)	3.94 (1)	1.29 (2)	17.5 (1)
		SCN ⁻	15.8 (219)	3.76 (1)	-0.93(4)	9.5 (2)

^a Values in parentheses are molar extinction coefficients/l mol⁻¹ cm⁻¹. ^b The values in parentheses are the standard deviations. Ref. 1.

enthalpies of the [Cu(en)₂X]⁺ cations are independent of the type of co-ordinating anion. The lines with different slopes meet at a point with a $\Delta H(X)_{\text{solv}}$ value corresponding to a hypothetical anion. The radius of this hypothetical anion would be so small as to leave it unaffected by the steric hindrance of the *N*-methyl groups

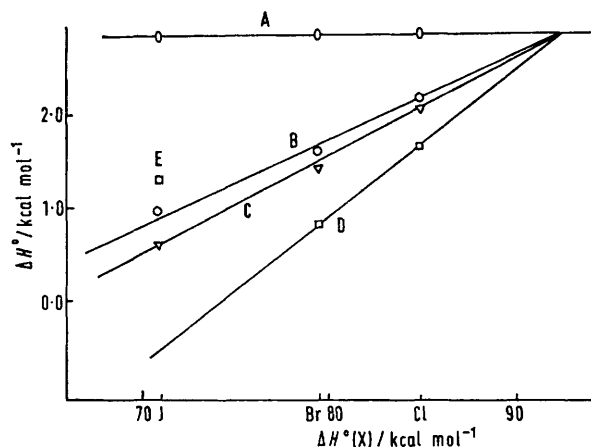


FIGURE 2 The relationship between enthalpy of reaction and enthalpy of anion desolvation for [CuL₂-X]⁺ systems: A, [Cu(en)₂X]⁺; B, [Cu(meen)₂X]⁺; C, [Cu(dmen)₂X]⁺; D, [Cu(amen)₂X]⁺; and E, (single point), [Cu(amen)₂I]⁺

to formation of the [CuL₂X]⁺ complex. The absence of [Cu(amen)₂I]⁺ from the line for amen complexes also emphasizes the importance of the steric factors in these reactions. The interaction here is between the most sterically hindered complex [Cu(amen)₂]²⁺ and the biggest anion I⁻. It is likely that steric effects force this five-

co-ordinate cation more towards a trigonal-bipyramidal than a square-pyramidal configuration. Its spectrum correlates reasonably well with the spectra of various five-co-ordinate Cu^{II} complexes to which a trigonal-bipyramidal configuration has been assigned⁸ and its thermodynamic data seem to indicate that the reaction [Cu(amen)₂]²⁺ + I⁻ ⇌ [Cu(amen)₂I]⁺ liberates more solvent molecules (and therefore has a greater ΔH and ΔS) than the other reactions. Since the dipole moment of the square-pyramidal structure is higher than that of a trigonal bipyramidal one, the [Cu(amen)₂I]⁺ ion will be able to orient fewer solvent molecules than the other ions. In all the series considered, the reactions with NCS⁻ are the most exothermic while the entropies are the lowest (Table 2). This behaviour can be explained by the fact that the co-ordination of this group occurs only through one atom (probably N) so that the rest may keep the bonds with the solvent. Thus the anion is incompletely desolvated.

In the literature there are few data concerning the entropies of solvation of these anions in methanol, so we cannot know whether a linear reaction exists between the entropies of solvation and those of reaction, as shown for the enthalpies. Nevertheless we can observe that the entropies decrease in the order Cl⁻ > Br⁻ > I⁻ > NCS⁻.

We thank Mr. C. Bianchi for experimental assistance and the Italian C.N.R. for financial help.

[2/730 Received, 28th March, 1972]

⁸ B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. (A)*, 1969, 2219; R. Barbucci, M. Campbell, and P. Paoletti, unpublished results.