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The Preparation of Copper(II) Complexes of N,N′, N″, N‴-tetra(2-cyanoethyl)-1,4,8,11-tetraazacyclotetradecane and Studies of the Acid Dissociation Kinetics

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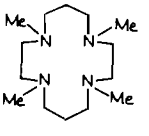
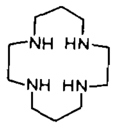
Since the discovery of 1,4,8,11-N-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) (I) it was realised [1, 2] that its metal complexes do not show the usual square planar or octahedral coordination geometry as do the analogous complexes with the unsubstituted ligand, 1,4,8,11-tetraazacyclotetradecane (cyclam = (II)) [3]. Instead the complexes exhibit either square pyramidal or trigonal bipyramidal structures.



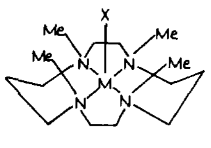
(I)



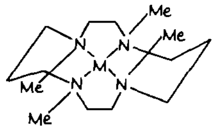
(II)

The X-ray structures of $[Ni(TMC)N_3]^+$ [4] and $[Zn(TMD)Cl]^+$ [5] establish that the four nitrogen donors of the macrocycle occupy the base of the square pyramid with the fifth ligand in the axial site. However, in solution, ^{13}C nmr and ^{1}H nmr spectra of the nickel(II) and zinc(II) complexes indicate fluxional behaviour of a species with a trigonal bipyramidal structure [5, 6].

The nickel(II) complex prepared by reacting TMC with nickel(II) has the *trans* I (R,S,R,S) structure (III) [7], while the *trans* III (R,S,SR) (IV) diastereoisomer is formed when $[Ni(cyclam)]^{2+}$ is alkylated directly with methyl iodide in DMSO [8]. The interaction of various solvents and unidentate ligands (N_3^-, SCN^-, OCN^- and OH^-) with copper(II), nickel(II) and cobalt(II) complexes of TMC has recently been studied [9].

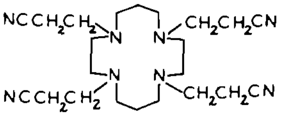


(III)
(RSRS)



(IV)
(RSSR)

The present paper deals with the preparation of the copper(II) complex of the TMC analogue N,N′, N″, N‴-tetra(2-cyanoethyl–1,4,8,11-tetraazacyclotetradecane (V), and detailed kinetic studies of the dissociation of the complex in acidic solution. Nickel(II) complexes of (V) have previously been characterised [10].



(V)·L

Experimental

Cyclam was prepared as described by Barefield and Wagner [11], and N,N′,N″,N‴-tetra(2-cyanoethyl)-1,4,8,11-tetraazacyclotetradecane essentially as described by Wainwright [10]. The latter compound was twice recrystallised from ethanol–chloroform (9:1) yielding white prisms, m.p. 127–128 °C.

The copper(II) complex of the tetracyanoethyl derivative was prepared as follows. The ligand (0.41 g, 0.001 mol) was dissolved in boiling ethanol (20 cm^3) and treated dropwise with a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 0.001 mol) in ethanol (5 cm^3). A blue product was obtained on heating the solution for about 15 min. The solution was cooled and the complex filtered off and washed with ethanol. The crude complex was dissolved in the minimum volume of hot acetonitrile and an excess of ethanol added. The mixture was heated on a water bath for 10–15 min and the complex filtered off on cooling. It was washed with ethanol, then ether and dried *in vacuo*. *Anal.* Calc. for $C_{22}H_{36}N_8Cl_2O_8Cu$; C, 39.1; H, 5.4; N, 16.6. Found: C, 39.2; H, 5.6; N, 16.6%. The complex is a 2:1 electrolyte in CH_3CN with Λ_M = 250 ohm^{-1} cm^2 mol^{-1} (1 × 10^{-3} *M* solution). The i.r. spectrum has $\nu C{\equiv}N$ at 2250 cm^{-1} which may be compared with 2248 cm^{-1} in the free ligand (KBr disc).

[CuL(NCS)]NCS

The complex $CuL(ClO_4)_2$ (0.3 g) was suspended in a solution of potassium thiocyanate (0.15 g) in methanol (50 cm^3) and the mixture heated on a steam bath for *ca.* 0.5 hr. During this period the light blue complex dissolved and a fine crystalline dark greenish-blue precipitate appeared which was filtered off, washed with methanol, then ether and dried *in vacuo*. *Anal.* Calc. for $C_{24}H_{36}N_{10}S_2Cu$: C, 48.7;

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TABLE I. Absorption Spectra of $CuL(ClO_4)_2$ in Various Solvents.

Solvent	λ_{max} (nm)	ϵ^a (M^{-1} cm^{-1})
Acetonitrile	655	310
DMSO	660	244
Water	670	236
DMF	675	238
Nitromethane	760	288
Solid State	600	–

[a] Values of ϵ calculated using a molecular weight of 675.06, *i.e.* assuming a monomeric complex.

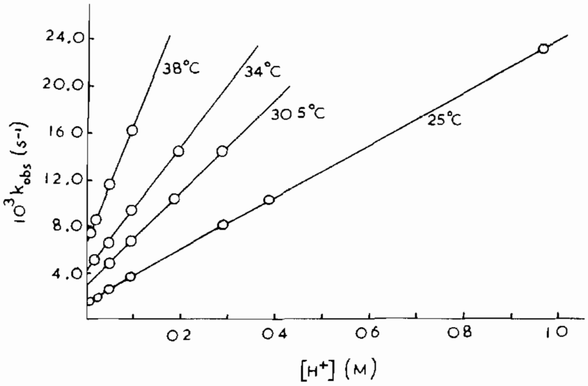


Fig. 1. The acid catalysed dissociation of $CuL(ClO_4)_2$ in $HClO_4$ solutions at various temperatures and I = 0.98 *M* ($NaClO_4$).

H, 6.1; N, 23.65. Found: C, 48.5; H, 6.2; N, 23.8%. The complex is a 1.1 electrolyte in water with Λ_M = 130 ohm^{-1} cm^2 mol^{-1} (1 × 10^{-3} *M* solution at 25 °C). Bands due to νCN occur at 2243 cm^{-1} (nitrile) and strong bands at 2052 and 2070 (sh) assigned to two non-equivalent thiocyanate groups.

The acid dissociation kinetics were studied using perchloric acid solutions adjusted to I = 0.98 *M* with $NaClO_4$. Reactions were monitored at 325 nm where an absorbance decrease occurs. Plots of log(A_t – A_∞) *versus* time were linear for several half lives. Values of k_{obs}, the observed first order rate constant at constant hydrogen ion concentration, were determined from such plots using a microcomputer.

Visible spectra were determined using a Perkin Elmer 402 instrument. Conductivity measurements were made with a Portland Electronics Model P310 conductivity meter using 10^{-3} *M* solutions at 25 °C. I.r. spectra were obtained on a Perkin Elmer 457 instrument using KBr discs.

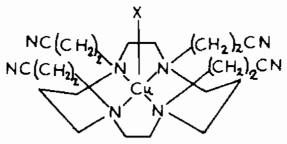
Results and Discussion

The complex $CuL(ClO_4)_2$ (L = N,N′, N″,N‴-tetra(2-cyanoethyl)1,4,8,11-tetraazacyclotetradecane) is readily prepared by the reaction of L with $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol. The complex has a single sharp νC≡N band at 2250 cm^{-1} which may be compared with 2248 cm^{-1} in the free ligand. The constancy of this band position indicates that there is no interaction between copper(II) and the nitrile groups. Such an interaction would be expected to lead to a marked lowering of the C≡N stretching frequency. The i.r. spectrum also provides some evidence for coordinated perchlorate. The normally broad ν(O–Cl) band at *ca.* 1100 cm^{-1} is split into well defined bands at 1080, 1110 and 1192 cm^{-1}, and in addition to the δClO_4 band at 623 cm^{-1}, there are sharp bands at 938 and 960 cm^{-1} either of which could be ν_4 in C_{3v}. In the coordinating solvent CH_3CN the complex is a 2:1 electrolyte with Λ_M = 250 ohm^{-1} cm^2 mol^{-1} at 25 °C, while in water Λ_M = 182 ohm^{-1} cm^2 mol^{-1} at 25 °C.

The visible spectra of copper(II) complexes are generally not very diagnostic of stereochemistry. However, the visible spectrum of $CuL(ClO_4)_2$ is very solvent dependent (Table I). In a coordinating nitrogen donor solvent such as acetonitrile, λ_{max} occurs at 655 nm, while in oxygen donor solvents (DMSO, H_2O, DMF) λ_{max} falls in the range 660–675 nm. In the poorly coordinating solvent nitromethane λ_{max} occurs at 760 nm. The shift to shorter wavelengths is indicative of solvent interaction with copper(II) in the axial sites.

Reaction of $CuL(ClO_4)_2$ with KNCS in methanol gives a dark greenish blue complex, $CuL(NCS)_2$ which is a 1:1 electrolyte in water and displays two νCN bands due to thiocyanate at 2052 and 2070 cm^{-1}, which can be assigned to non-equivalent thiocyanates.

Although definitive structural information is lacking it appears likely that the copper(II) complex, in the presence of a further donor ligand, is pentacoordinate. Similar behaviour is observed with $Cu(TMC)^{2+}$ [9]. By analogy with TMC complexes a structure of type (VI) with an RSRS arrangement of the chiral nitrogen centres is possible.



(VI)

A further novel feature of the complex is its marked lability in acid solution. Thus the complex

TABLE II. Acid Catalysed Dissociation of $CuL(ClO_4)_2$ at Various Temperatures and I = 0.98 *M* ($NaClO_4$).

Temp. (°C)	10^3 [H^+] (*M*)	k_{obs} (s^{-1})
25	9.66	1.45
	19.33	1.80
	38.00	2.70
	48.33	2.40
	96.67	3.45
	290.00	7.85
	386.66	10.12
	966.66	23.14
30.5	48.33	4.60
	96.67	6.39
	193.33	10.00
	290.00	14.08
34	19.33	4.82
	48.33	6.08
	96.67	9.00
	193.11	13.11
38	9.66	7.38
	19.33	8.22
	48.33	11.13
	96.67	15.81

TABLE III. Values of k_o and k_H for the Acid Catalysed Dissociation and the Appropriate Activation Parameters.

Temp. (°C)	10^3 k_o (s^{-1})	10^2 k_H (M^{-1} s^{-1})
25	1.40	2.24
30.5	2.64	3.93
34	4.02	5.31
38	6.10	10.28

For k_o $\Delta H^{\ddagger} = 85.3$ kJ mol^{-1}; $\Delta S^{\ddagger} = -13.6$ J K^{-1} mol^{-1}
For k_H $\Delta H^{\ddagger} = 85.2$ kJ mol^{-1}; $\Delta S^{\ddagger} = +8.8$ J K^{-1} mol^{-1}

dissociates readily in acid solutions (10^{-2} *M* to 1 *M*) at 25 °C. At constant hydrogen ion concentrations the reaction is first order in the complex. Values of k_{obs} at various acidities and temperatures are listed in Table II. Plots of k_{obs} *versus* [H^+] are linear with a positive intercept, Fig.1, so that the rate expression takes the form

$$k_{obs} = k_o + k_H[H^+]$$

The k_o term can be assigned to non-catalysed solvolytic displacement of the ligand and the k_H term to the acid catalysed pathway. This type of behaviour has been noted previously for the dissociation of a number of macrocyclic complexes in acidic solution [12, 13]. Values of k_H and k_o were determined from the least squares slope and intercept of the plots shown in the Figure. The temperature dependence of k_o gives $\Delta H^{\ddagger} = 85.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -13.6$ J K^{-1} mol^{-1} while for k_H, $\Delta H^{\ddagger} = 85.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = +8.8$ J K^{-1} mol^{-1}. The acid catalysed reaction can be rationalised in terms of the scheme,

$$CuL^{2+} + H^+ \overset{K}{\rightleftharpoons} CuLH^{3+} \qquad (1)$$

$$CuLH^{3+} \xrightarrow[\text{slow}]{k} Cu^{2+}(aq) + LH^+ \qquad (2)$$

where there is a rapid pre-equilibrium protonation of the complex followed by slow dissociation of the protonated species.

For such a scheme,

$$(k_{obs} - k_o)([CuLH^{3+}] + [CuL^{2+}]) = k[CuLH^{3+}] \qquad (3)$$

and

$$k_{obs} = k_o + \frac{kK[H^+]}{(1 + K[H^+])} \qquad (4)$$

Under the conditions of the present experiments $K[H^+] \ll 1$ so that equation (4) can be simplified to

$$k_{obs} = k_o + kK[H^+] \qquad (5)$$

The activation parameters for k_H thus refer to the kK term and involve both rate and equilibrium constants. The activation parameters indicate that acid catalysis is primarily associated with a much more positive $\Delta S^{\ddagger}$ term compared with the solvolytic pathway. Detailed mechanisms for reactions of this type have previously been presented [13].

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References

1 E. K. Barefield and F. Wagner, *Inorg Chem.*, *12*, 2435 (1973).
2 R. Buxtorf, W. Steinmann and T. A. Kaden, *Chimia*, *28*, 15 1035 (1974).

3 See for example, N F. Curtis, in 'Coordination Chemistry of Macrocyclic Compounds', (Ed. G. A. Melson), Plenum Press, New York, 1979, p. 219.

4 M. J. d'Aniello, M. T. Mocella, F. Wagner, E. K. Barefield and J. C. Paul, *J Am Chem. Soc., 97,* 192 (1975).

5 N. W. Alcock, N. Herron and P. Moore, *J. Chem. Soc. Dalton Trans.,* 1282 (1978).

6 N. Herron and P. Moore, *Inorg Chim. Acta, 36,* 89 (1979).

7 B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg Chem., 4,* 1106 (1965).

8 F. Wagner and E. K. Barefield, *Inorg Chem, 15,* 408 (1976).

9 M. Micheloni, P. Paoletti, S. Burki and T. A. Kaden, *Helv. Chim. Acta, 65,* 587 (1982).

10 K. P. Wainwright, *J Chem. Soc Dalton Trans.,* 2117 (1980)

11 E. K. Barefield and F. Wagner, *Inorg Syn, 16,* 220 (1976).

12 See for example, L J. Murphy and L. J. Zompa, *Inorg Chem., 18,* 3271 (1979),
P. G. Graham and D. C. Weatherburn, *Aust J Chem., 34,* 291 (1981).

13 R. W. Hay and R. Bembi, *Inorg Chim. Acta, 62,* 89 (1982).