

Synthetic, Thermodynamic and Crystallographic Studies of Pentacoordinated Copper(II) Complexes with [2⁴.3¹]Adamanzane, 1,4,7,10-Tetraazabicyclo[5.5.3]pentadecane, and Bromide, Iodide, Hydroxide, Water or Ammonia

Johan Springborg^{a,*} and Inger Søjtofte^b

^aChemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark and ^bDepartment of Chemistry, Technical University of Denmark, DTU 207, DK-2800 Lyngby, Denmark

Springborg, J. and Søjtofte, I., 1997. Synthetic, Thermodynamic and Crystallographic Studies of Pentacoordinated Copper(II) Complexes with [2⁴.3¹]Adamanzane, 1,4,7,10-Tetraazabicyclo[5.5.3]pentadecane, and Bromide, Iodide, Hydroxide, Water or Ammonia. – Acta Chem. Scand. 51: 357–366. © Acta Chemica Scandinavica 1997.

The copper(II) complex with the bicyclic tetraamine L=[2⁴.3¹]adamanzane (1,4,7,10-tetraazabicyclo[5.5.3]pentadecane) and bromide as the fifth ligand has been synthesized and isolated as the perchlorate salt, [Cu(L)Br]ClO₄, in a yield of 87%. This complex reacts with aqueous NaI to form the corresponding iodide complex, which has been isolated as the iodide salt, [Cu(L)I]I, in a yield of 72%. The complexes Cu(L)(H₂O)²⁺, Cu(L)(OH)⁺ and Cu(L)(NH₃)²⁺ have been characterized in solution. The equilibria between Cu(L)(H₂O)²⁺ and X^{z-} to give Cu(L)(X)^{(2-z)+} have been studied spectrophotometrically (X^{z-} = Br⁻, I⁻ or NH₃) and potentiometrically (X^{z-} = OH⁻) at 25 and 40 °C and at an ionic strength of 1 M (NaClO₄). The concentration equilibrium constants at 25 °C are: K(Br⁻) = 8.3(2) M⁻¹, K(I⁻) = 12.4(6) M⁻¹, K(NH₃) = 2.5(11) × 10³ M⁻¹ and K(OH⁻) = 5.0(1) × 10⁴ M⁻¹. The latter value corresponds to pK_a = 9.10(2) for Cu(L)(H₂O)²⁺. For each equilibrium the thermodynamic parameters ΔH° and ΔS° have been estimated. The structures of [Cu(L)Br]ClO₄ and [Cu(L)I]I have been determined by X-ray diffraction techniques at T = 120 K; For [Cu(L)Br]ClO₄: M_r = 455.24, monoclinic, P2₁/n, a = 8.097(3), b = 22.750(9), c = 8.983(3) Å, β = 94.21(3)°, Z = 4, D_x = 1.83 g cm⁻³, MoKα = 0.710 73 Å, μ = 39.3 cm⁻¹, F(000) = 924, R(F) = 0.0764 for 1761 reflections with I > 2σ(I) and wR(F²) = 0.1828 for 3599 unique reflections. For [Cu(L)I]I: M_r = 529.68, orthorhombic Pmn2, a = 13.678(4), b = 13.359(4), c = 9.219(3) Å, Z = 4, D_x = 2.09 g cm⁻³, CuKα = 1.5418 Å, μ = 305.3 cm⁻¹, F(000) = 1012, R(F) = 0.1296 for 1302 reflections with I > 2σ(I) and wR(F²) = 0.3261 for 1822 unique reflections. The coordination geometry about the copper(II) ions is for [Cu(L)Br]ClO₄ best described as being halfway between trigonal bipyramidal and square pyramidal, whereas in [Cu(L)I]I it is approximately trigonal bipyramidal.

Coordination compounds of macrocyclic and macrobicyclic polyamines are of current interest because of their importance as model systems within bioinorganic chemistry, their applications in medicine and as catalysts.^{1–8} Structural modifications of the important macrocyclic ligands cyclam and cyclen involving ethylene or trimethylene bridging of the non-adjacent nitrogens have been reported and represent a new class of macrocyclic ligands (Fig. 1).^{9–13} These bowl-shaped ligands may adopt conformations having all four nitrogen lone pairs

pointing inside the cavity for complexation of metal ions. They all have a relatively fixed geometry with respect to coordination and are expected to force the metal ion into a configuration where the four nitrogen atoms form a distorted tetrahedron close to C_{2v} geometry. Complexation of Li⁺ and Cu²⁺ with these ligands has been observed, but no detailed studies have been reported.^{9,12} In this paper we present the syntheses and crystal structures of some pentacoordinated copper(II) complexes with the bowl amine [2⁴.3¹]adamanzane (L in Fig. 1) and with Br⁻, I⁻, OH⁻, H₂O and NH₃, respectively, as the fifth ligand (donor group). Abbreviations used for the amine ligands are given below.

* To whom correspondence should be addressed.
Dedicated to Professor R. G. Wilkins on the occasion of his 70th birthday.

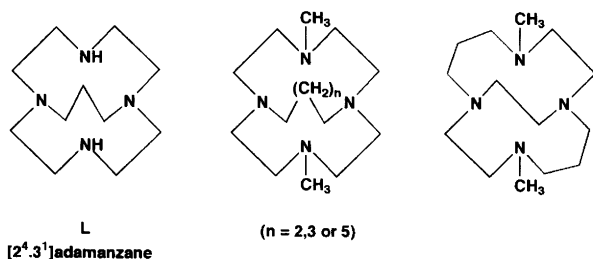


Fig. 1. Cross-bridged derivatives of cyclen and cyclam. In this work copper(II) coordination compounds with the bowl amine [2⁴.3¹]adamanzane (L) have been investigated.

Experimental

Abbreviations. cyclen, 1,4,7,10-tetraazacyclododecane; cyclam, 1,4,8,11-tetraazacyclotetradecane; tet a, meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; tet b, racemic-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; (*R,S,R,S*)-tbtcyclen, (2*R*,5*S*,8*R*,11*S*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane; (*R,R,R,S*)/(*S,S,S,R*)-tbtcyclen, (2*R*,5*R*,8*R*,11*S*)/(2*S*,5*S*,8*S*,11*R*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane; L, [2⁴.3¹]adz = 1,4,7,10-tetraazabicyclo[5.5.3]pentadecane = [2⁴.3¹]adamanzane. The name [2⁴.3¹]adamanzane is obtained by an extension of the simplified nomenclature¹⁴ used for the tricyclic tetraaza cage derivatives as discussed in the Appendix.

Materials and instruments. L.3HBr and [Cu(cyclen)]ClO₄ were synthesized by previously published methods.^{13,15} All other chemicals were of analytical grade and CO₂-free doubly deionized water was used for all measurements. A Cary 3 spectrophotometer was used for spectral measurements in the region 400–800 nm, and a Zeiss DMR 21 spectrophotometer for the region 800–1200 nm. Stopped-flow measurements were made using equipment from Applied Photophysics. A temperature of 25 °C at the time of mixing was achieved by cooling the reactant solutions to 14.8 °C in order to compensate for the heat production caused by mixing 10 M HCl with water. Potentiometric pH measurements were performed using Radiometer equipment as described previously¹⁶ using a constant flow of nitrogen in order to exclude contamination with carbon dioxide.

Calculations. Non-linear least-squares calculations for the determinations of the equilibrium constants were performed using the program PROC NLIN (DUD method) from the SAS Institute INC, Cary, NC. Kinetic data were calculated using programs written by one of the authors (J.S.).¹⁷

Analyses. Bromide analysis was made potentiometrically using standard procedures. C, H and N analyses were made at the Microanalytical Laboratory, the H.C. Ørsted Institute, Copenhagen.

Caution. Mechanical handling or heating of perchlor-

ates represents a potential danger. However, we have never experienced an explosion with the present compound.

Syntheses. [Cu(L)Br]ClO₄. The salt L.3HBr (1.15 g, 2.53 mmol) was dissolved in 0.5 M CuSO₄ (6 ml, 3 mmol), and 2 M NH₃ (10 ml, 20 mmol) was added. The blue solution was refluxed for 10 min. The colour changed to a deeper blue colour. The solution was cooled in ice and 2 M HClO₄ (25 ml, 50 mmol) was added. This immediately gave a blue precipitate, and after cooling for a further 5 min the crystals were filtered off, washed with ice-cold water (4 ml), four times with 5-ml portions of 96% ethanol and dried in the air. Yield 1.00 g (87%). Calculated for C₁₁H₂₄N₄BrClO₄Cu: Br, 17.55. Found: Br, 17.51. The product is soluble in water, acetonitrile and dimethylformamide. Crystals suitable for X-ray diffraction studies were made by slow cooling to 0 °C of a hot (90–100 °C) solution of the perchlorate salt (115 mg) in water (1.8 ml). The crystals were washed with 96% ethanol and dried in the air.

[Cu(L)I]I. The blue salt [Cu(L)Br]ClO₄ (184 mg, 0.404 mmol) was dissolved in 10 ml 5 M KI at 100 °C. The solution was slowly cooled to 0 °C and kept at this temperature for some hours. The green crystals were filtered off, washed with ice-cold water (5 ml), 96% ethanol (10 ml) and dried in the air. Yield 154 mg (72%). Calculated for C₁₁H₂₄N₄I₂Cu: C, 24.94; H, 4.57; N, 10.58. Found: C, 25.14; H, 4.42; N, 10.41. The product is soluble in water, acetonitrile and dimethylformamide. The crystals obtained by this procedure were used for the X-ray diffraction studies.

X-Ray techniques. Crystal and experimental data for the compounds are listed in Table 1. The possible space groups were established from rotation and Weissenberg photographs using Cu radiation. The crystals were cooled to 120 K using the Cryostream nitrogen gas cooler system.¹⁸ The unit cells were derived from a least-squares fit of refined diffractometer setting angles for 25 reflections. Four standards were measured for intensity and orientation control after every 4 h. A loss of intensity of about 30% and 27% for [Cu(L)Br]ClO₄ and [Cu(L)I]I, respectively, was observed. Therefore, a linear decay correction was applied. Afterwards, the intensities were corrected for Lorentz, polarization and (only in the case of [Cu(L)Br]ClO₄) absorption (Gaussian integration) effects.¹⁹ Because of a breakdown during the collection of the psi-scans the data for [Cu(L)I]I were not corrected for absorption. The structures were solved by the Patterson method with partial structure expansion and refined by a full-matrix least-squares technique. In [Cu(L)Br]ClO₄ the ClO₄⁻ ions are disordered, the population of the two positions being 0.60(1) and 0.40(1), respectively. Unfortunately it was not possible to get good single crystals of [Cu(L)I]I, and furthermore the reflecting power was rather poor. Therefore, in [Cu(L)I]I only the I atoms were refined anisotropically, whereas in

Table 1. Crystal and experimental data.

Formula	$[\text{C}_{11}\text{H}_{24}\text{N}_4, \text{Cu}(\text{II})\text{Br}]^+, \text{ClO}_4^-$	$[\text{C}_{11}\text{H}_{24}\text{N}_4, \text{Cu}(\text{II})\text{I}]^+, \text{I}^-$
Formula weight	455.24	529.68
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pnn2$
Unit-cell dimensions:		
<i>a</i> /Å	8.097(3)	13.678(4)
<i>b</i> /Å	22.750(9)	13.359(4)
<i>c</i> /Å	8.983(3)	9.219(3)
β/°	94.21(3)	
Unit-cell volume <i>V</i> /Å ³	1650(1)	1684.5(9)
Formula units per unit cell, <i>Z</i>	4	4
<i>F</i> (000)	924	1012
Calculated density <i>D_x</i> /g cm ⁻³	1.83	2.09
Radiation	MoKα	CuKα
Wavelength, λ/Å	0.710 73	1.5418
Linear absorption coefficient/cm ⁻¹	39.3	305.3
Temperature, <i>T</i> /K	120	120
Crystal description	Blue	Green
Crystal size/mm	0.15 × 0.13 × 0.02	0.27 × 0.15 × 0.04
Diffractometer	Enraf-Nonius CAD-4F	Enraf-Nonius CAD-4F
Unit-cell determination:		
No. of reflections used	25	25
θ-range/°	10.7–14.5	6.4–17.8
Intensity data collection:		
θ _{max} /°	27	74
Range of <i>h</i>	–10–10	–17–0
Range of <i>k</i>	0–29	0–16
Range of <i>l</i>	0–11	–11–0
Scan mode	ω	ω
Scan range, Δω	1.50 + 0.35 tan θ	2.00 + 0.14 tan θ
Total number of unique reflections	3599	1822
No. of independent reflections, [<i>I</i> > 2σ(<i>I</i>)]	1761	1302
Corrections	Decay, Lorentz-polarization absorption	Decay, Lorentz-polarization
Transmission factors	0.8021–0.9614	
Structure refinement:		
Minimization of	$\sum w(F_o ^2 - F_c ^2)^2$	$\sum w(F_o ^2 - F_c ^2)^2$
Anisotropic thermal parameters	All non-hydrogen atoms	1 atoms
Isotropic thermal parameters	Hydrogen atoms	Cu, N and H atoms
No. of refined parameters	200	84
Weighting scheme	$[\sigma^2(F_o^2) + (0.0718P)^2 + 3.80P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$	$[\sigma^2(F_o^2) + (0.1P)^2]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$
<i>R</i> = $\sum F_o - F_c / \sum F_o $	0.0764 (1761 reflections)	0.1296 (1302 reflections)
<i>wR</i> ² = $[\sum w F_o^2 - F_c^2 ^2 / \sum wF_o^4]^{1/2}$	0.1828 (3599 reflections)	0.3261 (1822 reflections)
<i>S</i> = $[\sum w(F_o ^2 - F_c ^2)^2 / (N_{\text{obs}} - N_{\text{var}})]^{1/2}$	1.00	2.20
Final (Δ/σ) _{max}	0.17	0.69
Final Δρ _{min} and Δρ _{max} /e Å ⁻³	–0.69 and 1.33	–7.75 and 4.46

[Cu(L)Br]ClO₄ all the non-hydrogen atoms were refined anisotropically. In both [Cu(L)Br]ClO₄ and [Cu(L)I]I the hydrogen atoms were at calculated positions using a riding model with C–H = 0.99 Å, N–H = 0.93 Å and fixed thermal parameters [*U*(H) = 1.2 × *U* and 1.4 × *U* for attached C or N for [Cu(L)Br]ClO₄ and [Cu(L)I]I, respectively]. The origin for [Cu(L)I]I was fixed by use of least-squares restraints.²⁰ The Flack *x*-parameter is 0.08(7), indicating that this is the correct structure.²¹ In the centrosymmetric space group *Pnmm* the cation should contain a mirror plane, which is not the case. Attempts

to solve the structure in a space group with lower symmetry than *Pnn2* failed. Therefore, *Pnn2* seems to be the right space group. The crystallographic computations were performed with SHELXS86²² and SHELXL93.²³ The atomic scattering factors were taken from the literature.²⁴ The PLUTO program²⁵ was used for illustrations and PLATON²⁶ for molecular geometry calculations.

The final positional parameters are listed in Table 2. Anisotropic thermal parameters, positional parameters for the hydrogen atoms, bond lengths and bond angles for [Cu(L)I]I and lists of observed and calculated

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters (in Å²).

Atom	x	y	z	U_{eq}^a
[Cu(L)Br]ClO ₄				
Br	0.62884(12)	0.02592(5)	0.31120(13)	0.0328(4)
Cu	0.38526(14)	0.08698(5)	0.31564(14)	0.0201(4)
N(1)	0.2375(9)	0.0305(4)	0.2023(9)	0.023(3)
N(2)	0.1805(10)	0.1175(4)	0.4098(9)	0.024(3)
N(3)	0.5053(10)	0.1537(4)	0.4192(10)	0.031(3)
N(4)	0.3719(10)	0.1397(4)	0.1208(10)	0.027(3)
C(1)	0.0742(12)	0.0308(5)	0.2700(13)	0.031(3)
C(2)	0.0852(12)	0.0626(5)	0.4171(12)	0.028(3)
C(3)	0.2550(12)	0.1357(4)	0.5557(11)	0.023(3)
C(4)	0.3972(13)	0.1778(5)	0.5317(11)	0.030(3)
C(5)	0.5516(15)	0.1961(5)	0.3023(14)	0.046(5)
C(6)	0.5326(15)	0.1698(5)	0.1469(14)	0.044(4)
C(7)	0.3674(14)	0.0920(5)	0.0094(13)	0.039(4)
C(8)	0.2357(14)	0.0463(5)	0.0416(12)	0.031(4)
C(9)	0.0838(12)	0.1656(5)	0.3358(12)	0.030(3)
C(10)	0.0745(13)	0.1685(5)	0.1701(14)	0.040(4)
C(11)	0.2372(16)	0.1829(5)	0.0970(14)	0.046(5)
Cl	0.3044(3)	0.35939(11)	0.2751(3)	0.0351(10)
O(1) ^b	0.2538(17)	0.3108(6)	0.3539(17)	0.039(3)
O(2) ^b	0.3318(15)	0.3332(6)	0.1206(14)	0.039(3)
O(3) ^b	0.1733(15)	0.3998(5)	0.2379(16)	0.039(3)
O(4) ^b	0.4509(15)	0.3856(6)	0.3226(16)	0.039(3)
O(1') ^b	0.194(3)	0.3137(11)	0.319(3)	0.055(5)
O(2') ^b	0.297(3)	0.4008(9)	0.408(2)	0.055(5)
O(3') ^b	0.264(3)	0.3925(10)	0.153(2)	0.055(5)
O(4') ^b	0.474(2)	0.3426(11)	0.298(3)	0.055(5)
[Cu(L)]I				
I(2)	0	0	0.5873(2)	0.0235(13)
I(3)	0	1/2	0.4300(4)	0.0347(14)
I(1)	-0.07763(17)	0.2547(3)	0.0145(6)	0.0323(6)
Cu	0.1114(3)	0.2480(5)	0.0132(11)	0.0160(9)
N(1)	0.121(3)	0.345(3)	0.170(4)	0.016(7)
N(2)	0.192(3)	0.152(3)	0.140(4)	0.033(8)
N(3)	0.126(3)	0.144(3)	-0.145(4)	0.024(9)
N(4)	0.219(3)	0.327(3)	-0.100(4)	0.034(8)
C(1)	0.160(3)	0.299(3)	0.302(4)	0.020(8)
C(2)	0.157(4)	0.180(4)	0.285(5)	0.035(10)
C(3)	0.156(4)	0.058(4)	0.078(5)	0.038(10)
C(4)	0.165(3)	0.047(4)	-0.079(5)	0.028(9)
C(5)	0.187(3)	0.193(3)	-0.272(5)	0.027(9)
C(6)	0.193(3)	0.299(3)	-0.251(4)	0.026(8)
C(7)	0.200(3)	0.425(3)	-0.054(4)	0.022(7)
C(8)	0.178(4)	0.434(4)	0.123(6)	0.037(12)
C(9)	0.302(3)	0.152(3)	0.127(4)	0.026(8)
C(10)	0.345(3)	0.249(3)	0.079(4)	0.021(7)
C(11)	0.326(3)	0.290(3)	-0.074(4)	0.021(7)

^a $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. ^bThe population factors for O(x) and O(x') are 0.60(1) and 0.40(1), respectively.

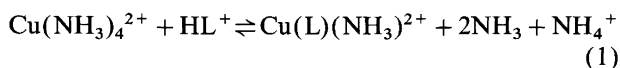
structure factors may be obtained from one of the authors (I.S.) on request.

Results and discussion

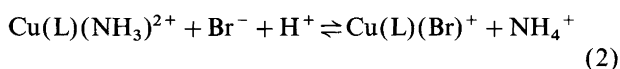
Syntheses. The synthesis of the bowl tetraamine L = [2⁴.3¹]adamanzane (1,4,7,10-tetraazabicyclo[5.5.3]penta-decane) was reported recently and isolated as the triprotonated bromide salt, L · 3HBr.¹³ The tetraprotonated species H₄L⁴⁺ is a very strong acid (pK_{a1} < -1), while the monoprotated form HL⁺ is an extremely weak

acid (pK_{a4} > 15); [2⁴.3¹]adamanzane is a so-called proton sponge. It was therefore anticipated that it would form very stable coordination compounds with metal ions of a suitable size, but also that the formation of such compounds might be hindered kinetically or thermodynamically by the presence of the strongly bound proton in HL⁺. Following these lines it was not surprising that the reaction of Cu²⁺ aqua ions with HL⁺ is prevented due to the strongly bound proton. Hours of heating (100 °C) of neutral solutions containing an equimolar mixture of the amine HL⁺ and Cu²⁺ aqua ions did not

result in any detectable formation of the $\text{Cu}(\text{L})^{2+}$ ion. Similar experiments in basic solutions resulted in precipitation of copper(II) hydroxide (room temperature) or conversion to black copper(II) oxide (when heated) with no further reaction. Finally, it was found that heating of tetraamminecopper(II) ions (19% excess) with HL^+ in an ammonia/ammonium buffer solution ($\text{pH} \sim \text{p}K_a(\text{NH}_4^+) = 9.5$) resulted in formation of a blue copper(II) complex with L [eqn. (1)]



From the acidified product solution the blue compound $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ was isolated in a yield of 87% [eqn. (2)]



The ammonia/ammonium buffer serves two purposes: It keeps the solution basic, which is necessary from a thermodynamic point of view (uptake of the proton from HL^+), and it prevents precipitation of copper(II) hydroxide. The description of the products as ammine and bromo complexes, respectively, in eqn. (1) and (2) is based upon the thermodynamic and crystallographic results given below. In the acidified product solution a significant part of the product is present as the aqua complex, but the less soluble perchlorate salt of the bromo complex precipitates as a pure sample.

Addition of a large excess of iodide to an aqueous solution of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ results in an instantaneous shift in colour from blue to green, and the green salt $[\text{Cu}(\text{L})\text{I}]\text{I}$ was isolated in a yield of 72%.

Crystal structures of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{L})\text{I}]\text{I}$. Bond lengths and bond angles of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ are listed in Table 3. The labelling of the atoms in the cation is shown in Fig. 2. The compound $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ consists of $[\text{C}_{11}\text{H}_{24}\text{N}_4\text{CuBr}]^+$ and ClO_4^- ions and $[\text{Cu}(\text{L})\text{I}]\text{I}$ of $[\text{C}_{11}\text{H}_{24}\text{N}_4\text{CuI}]^+$ and I^- ions. For pentacoordinated compounds two basic idealized geometric forms, the D_{3h} trigonal bipyramid (TBP) and the C_{4v} square pyramid (SP) appear. These two forms are most simply and symmetrically related by the Berry intramolecular ligand exchange process with the trigonal bipyramid as reference. Associated with the Berry exchange is the dihedral angle δ_{24} ($\delta_{\text{BrN}(2)}$ or $\delta_{\text{IN}(4)}$), which is the angle between the normals to the trigonal bipyramidal faces 124 [N(1)BrN(2) or N(1)IN(4)] and 245 [BrN(2)N(3) or IN(4)N(3)]. For TBP the value of δ_{24} is 53.1° and for SP it is 0° . For $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{L})\text{I}]\text{I}$, respectively, the δ_{24} value is 31.0 and 47.7° . Methods of describing the distortion from the idealized geometries (TBP and SP) of crystal structures have been surveyed by Holmes.²⁷ A comparison between the coordination geometry about the copper ions of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{L})\text{I}]\text{I}$ is shown in Table 4 and Fig. 3. The coordination geometry of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ is best described as being about halfway between the two idealized structures,

whereas in $[\text{Cu}(\text{L})\text{I}]\text{I}$ the geometry is approximately trigonal bipyramidal. In the trigonal bipyramidal geometry the N(1) and N(3) in both structures are occupying the axial positions. In $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ the Cu–N(1) and the Cu–N(3) bonds are somewhat shorter than the other two Cu–N bonds. The Cu atom lies $0.014(1)$ Å out of the trigonal plane towards N(1) [In $[\text{Cu}(\text{L})\text{I}]\text{I}$ the Cu atom lies in the plane]. In the square pyramidal arrangement N(4) and N(2), respectively, are occupying the apical position for $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{L})\text{I}]\text{I}$.

Coordination compounds of Cu^{II} have numerous examples of five-coordinated structures and great variation of $\%(\text{TBP}-\text{SP})$ are reported in the literature. In the chloro[(*R,S,R,S*)-tbtecyclen]copper(II) ion²⁸ and in the chloro[(*R,R,R,S*)/(*S,S,S,R*)-tbtecyclen]copper(II) ion²⁹ the Cu^{II} ion is coordinated to four N atoms and one Cl^- ion in a distorted trigonal bipyramid [$\%(\text{TBP}-\text{SP}) = 30$] and in a distorted square pyramid [$\%(\text{TBP}-\text{SP}) = 59$], respectively. In the copper(II) complex with 4,10-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane³⁰ the Cu^{II} ion is coordinated to five N atoms, adopting a trigonal bipyramidal coordination geometry.

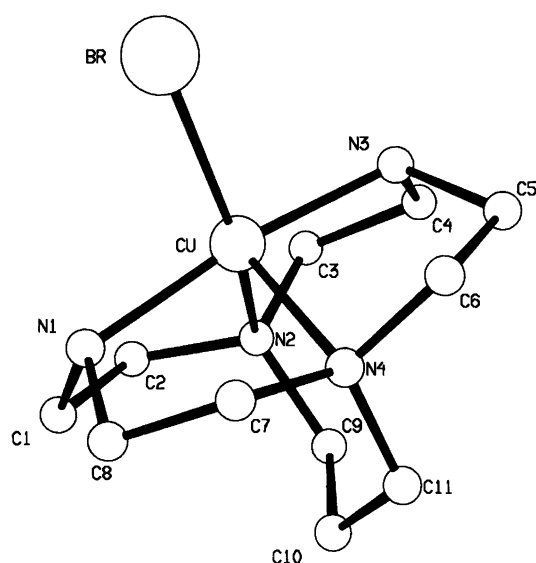
The conformations of the ligand L in $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{L})\text{I}]\text{I}$ are exactly the same. In the 12-membered ring the eight carbon atoms are nearly coplanar, with N(1) and N(3) about 0.7 Å above and N(2) and N(4) about 0.5 Å below the plane. The ring has an approximate *mm* symmetry with respect to the two planes through Cu, N(1), N(3) and Cu, N(2), N(4). In the H_3L^{3+} ion¹³ the 12-membered ring only has *m* symmetry, N(1) and N(3) being positioned on a crystallographic mirror plane, whereas in the (*R,S,R,S*)-tbtecyclen Cu^{II} complex²⁸ the ring has approximate *mm* symmetry.

In the present structures the N(2)–N(4) distance between the bridgehead nitrogen atoms is $3.16(1)$ and $3.24(6)$ Å and the N(1)–N(3) distance is $3.97(1)$ and $3.96(4)$ Å for $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{L})\text{I}]\text{I}$, respectively. The N(2)–N(4) distances are longer and the N(1)–N(3) distances are shorter than the corresponding distances of $2.567(4)$ and $5.194(7)$ Å, found in the H_3L^{3+} ion.¹³ The two 10-membered rings in the ligand both have approximately *m* symmetry with respect to the plane through N(1), Cu, C(10) and through N(3), Cu, C(10), respectively. In the H_3L^{3+} ion¹³ the two rings also have *m* symmetry, the N(1), N(3) and C(6) atoms being positioned on a crystallographic mirror plane. The six-membered ring has an envelope conformation and all the five-membered rings are in a twist form. In the (*R,S,R,S*)-tbtecyclen Cu^{II} complex²⁸ the five-membered rings are all in the envelope form, whereas in the (*R,R,R,S*)/(*S,S,S,R*)-tbtecyclen Cu^{II} complex²⁹ two of the rings have an envelope form and the other two rings a twist conformation. The Cu–Br bond of $2.415(2)$ Å is in agreement with those found in other analogous compounds,^{31,32} whereas the Cu–I bond is somewhat shorter than found in similar compounds.³³

The crystal packings of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{L})\text{I}]\text{I}$ are influenced by hydrogen bonds. In $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$

Table 3. Bond lengths (in Å) and bond angles (in °) for [Cu(L)Br]ClO₄.

Br–Cu	2.4151(18)	Cu–N(1)	1.985(8)
Cu–N(2)	2.038(8)	Cu–N(3)	1.995(9)
Cu–N(4)	2.118(9)	N(1)–C(1)	1.495(13)
N(1)–C(8)	1.487(14)	N(2)–C(2)	1.472(14)
N(2)–C(3)	1.462(13)	N(2)–C(9)	1.475(14)
N(3)–C(4)	1.489(13)	N(3)–C(5)	1.494(15)
N(4)–C(6)	1.474(15)	N(4)–C(7)	1.475(15)
N(4)–C(11)	1.472(15)	C(1)–C(2)	1.503(16)
C(3)–C(4)	1.525(14)	C(5)–C(6)	1.516(17)
C(7)–C(8)	1.532(16)	C(9)–C(10)	1.486(17)
C(10)–C(11)	1.550(17)		
Cl–O(1)	1.390(14)	Cl–O(2)	1.541(13)
Cl–O(3)	1.425(12)	Cl–O(4)	1.368(13)
Cl–O(1')	1.44(3)	Cl–O(2')	1.525(19)
Cl–O(3')	1.35(2)	Cl–O(4')	1.426(18)
Br–Cu–N(1)	94.7(2)	Br–Cu–N(2)	153.3(2)
Br–Cu–N(3)	94.3(2)	Br–Cu–N(4)	107.7(2)
N(1)–Cu–N(2)	87.4(3)	N(1)–Cu–N(3)	170.5(4)
N(1)–Cu–N(4)	87.2(3)	N(2)–Cu–N(3)	86.0(3)
N(2)–Cu–N(4)	99.0(3)	N(3)–Cu–N(4)	87.0(4)
Cu–N(1)–C(1)	107.8(6)	Cu–N(1)–C(8)	107.7(6)
C(1)–N(1)–C(8)	116.6(8)	Cu–N(2)–C(2)	100.1(6)
Cu–N(2)–C(3)	100.0(6)	Cu–N(2)–C(9)	119.1(6)
C(2)–N(2)–C(3)	112.6(8)	C(2)–N(2)–C(9)	112.8(8)
C(3)–N(2)–C(9)	111.4(8)	Cu–N(3)–C(4)	107.8(6)
Cu–N(3)–C(5)	107.6(7)	C(4)–N(3)–C(5)	115.4(9)
Cu–N(4)–C(6)	98.1(6)	Cu–N(4)–C(7)	98.1(6)
Cu–N(4)–C(11)	119.4(7)	C(6)–N(4)–C(7)	115.3(8)
C(6)–N(4)–C(11)	110.4(9)	C(7)–N(4)–C(11)	114.3(9)
N(1)–C(1)–C(2)	111.3(8)	N(2)–C(2)–C(1)	111.5(9)
N(2)–C(3)–C(4)	108.5(8)	N(3)–C(4)–C(3)	110.6(8)
N(3)–C(5)–C(6)	112.3(9)	N(4)–C(6)–C(5)	111.0(10)
N(4)–C(7)–C(8)	110.7(9)	N(1)–C(8)–C(7)	113.0(9)
N(2)–C(9)–C(10)	118.1(9)	C(9)–C(10)–C(11)	116.8(9)
N(4)–C(11)–C(10)	116.2(9)		
O(1)–Cl–O(2)	102.6(8)	O(1)–Cl–O(3)	112.9(8)
O(1)–Cl–O(4)	118.0(9)	O(2)–Cl–O(3)	101.1(8)
O(2)–Cl–O(4)	105.7(8)	O(3)–Cl–O(4)	113.9(8)
O(1')–Cl–O(2')	99.8(13)	O(1')–Cl–O(3')	120.3(15)
O(1')–Cl–O(4')	112.1(14)	O(2')–Cl–O(3')	105.7(12)
O(2')–Cl–O(4')	98.4(14)	O(3')–Cl–O(4')	116.1(15)

Fig. 2. View of the cation Cu(L)Br⁺.Table 4. Coordination around Cu^{II}.

	[Cu(L)Br]ClO ₄	[Cu(L)]I
Cu–N(1)	1.985(8)	1.95(4)
Cu–N(3)	1.995(9)	2.02(4)
Cu–Br, I ^a	2.415(2)	2.587(5)
Cu–N(2,4) ^a	2.038(8)	2.09(4)
Cu–N(4,2) ^a	2.118(9)	2.06(4)
N(1)–Cu–N(3)	170.5(4)	170(2)
Br, I–Cu–N(2,4) ^a	153.3(2)	134(1)
Br, I–Cu–N(4,2) ^a	107.7(2)	124(1)
N(4)–Cu–N(2)	99.0(3)	103(2)
%(TBP-SP) ^b	52.3	16.9

^aAtom 1, atom 2=atom in [Cu(L)Br]ClO₄, atom in [Cu(L)]I.

^bIn the SP configuration the pivot atom is N(4) and N(2) for [Cu(L)Br]ClO₄ and [Cu(L)]I, respectively.

N(1) is hydrogen bonded to O(3) and O(2'), the N–H···O[½–x, –½+y, ½–z] bonds being 3.10(2) and 3.12(2) Å, respectively. N(3) is also hydrogen bonded to the ClO₄[–]-ions, the N–H···O[½+x, ½–y,

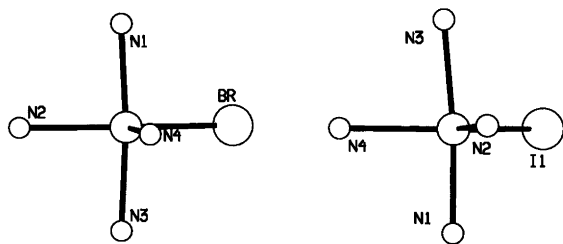
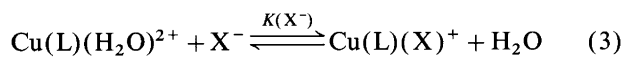


Fig. 3. The coordination spheres of the copper ions in $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ (left) and $[\text{Cu}(\text{L})\text{I}]$ (right).

$\frac{1}{2} + z]$ bonds being 3.11(2) and 3.04(2) Å to O(2) and O(3'), respectively. In $[\text{Cu}(\text{L})\text{I}]\text{I}$ N(1) and N(3) are involved in weak hydrogen bonds, the N(1)–H...I(3)[x, y, z] and the N(3)–H...I(2)[$x, y, -1 + z$] distances both being 3.57(4) Å.

Determination of the equilibrium constants $K_1(\text{Br}^-)$ and $K_1(\text{I}^-)$. Aqueous solutions of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ or $[\text{Cu}(\text{L})\text{I}]\text{I}$ form a fast equilibrium with the corresponding blue aqua complex [eqn. (3)]



These equilibria were studied spectrophotometrically in the region 450–750 nm for solutions with X^- (Br^- or I^-) ranging from 1×10^{-3} to 1.0 M in 1 M Na(X, ClO_4), as illustrated in Fig. 4 for the wavelength 600 nm. The spectral changes for the entire wavelength region could unambiguously be interpreted in terms of the equilibrium shown above, with no indications of the presence of other species. The measurements were made at two temperatures (25 and 40 °C) and non-linear least-squares

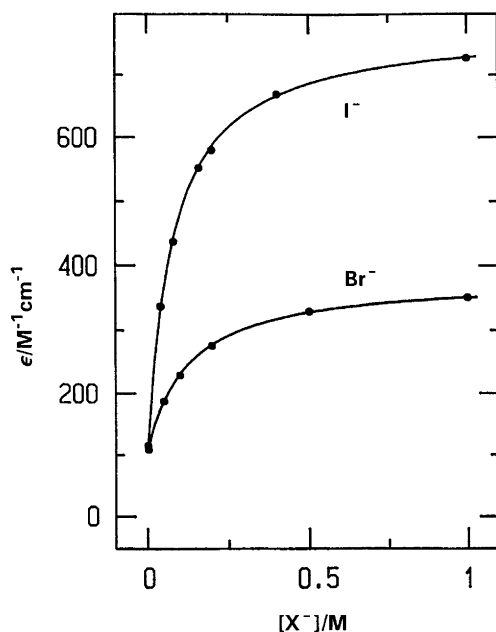


Fig. 4. Change of the molar absorbance as a function of the concentration of Br^- or I^- , respectively, for solutions of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ at 25 °C.

calculations gave the following values: $K(\text{Br}^-) = 8.33(18) \text{ M}^{-1}$ and $K(\text{I}^-) = 12.35(55) \text{ M}^{-1}$ at 25 °C and $K(\text{Br}^-) = 7.08(20) \text{ M}^{-1}$ and $K(\text{I}^-) = 9.57(45)$ at 40 °C. The calculated ΔH° and ΔS° values are listed later in Table 7. The spectra of $\text{Cu}(\text{L})(\text{X})^+$ ($\text{X}^- = \text{Br}^-$ and I^-) and $\text{Cu}(\text{L})(\text{H}_2\text{O})^{2+}$ are shown in Figs. 5 and 6, respectively. It was found that the calculated spectrum of $\text{Cu}(\text{L})(\text{X})^+$ was identical to that of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ in 4 M NaX for $\text{X} = \text{Br}^-$ or I^- , respectively.

The formation constants for the present bromo and iodo complexes are very similar to those reported for copper(II) complexes with other macrocyclic tetraamines, all having values of $K(\text{X}^-)$ in the region $2\text{--}20 \text{ M}^{-1}$.^{34–37} The thermodynamic aspects of

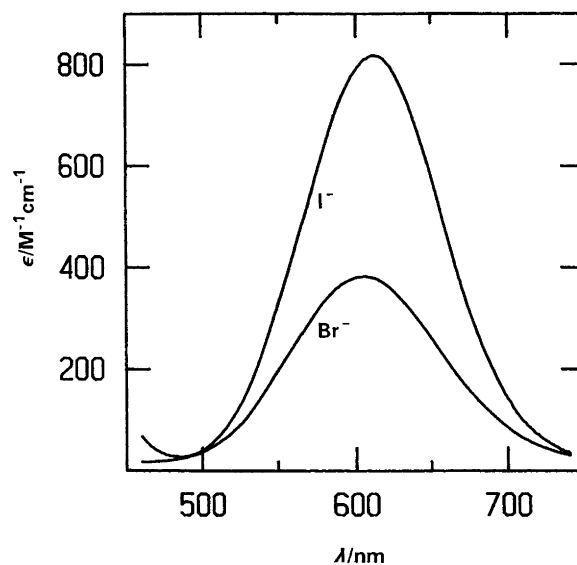


Fig. 5. Visible absorption spectra of $\text{Cu}(\text{L})\text{Br}^+$ and $\text{Cu}(\text{L})\text{I}^+$.

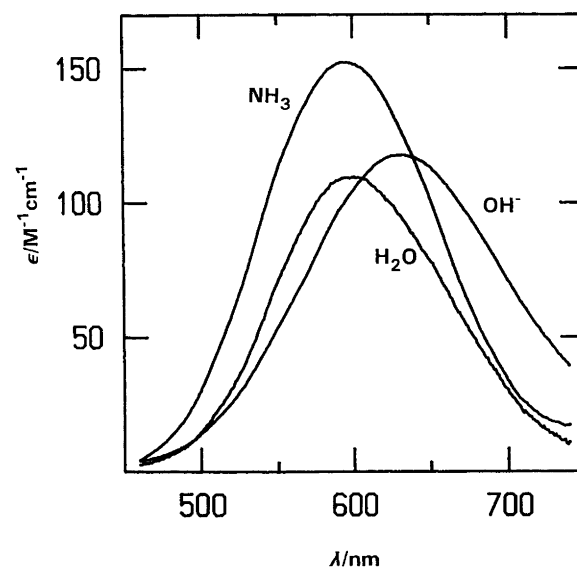


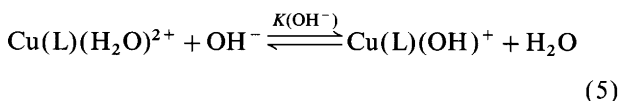
Fig. 6. Visible absorption spectra of $\text{Cu}(\text{L})(\text{H}_2\text{O})^{2+}$, $\text{Cu}(\text{L})(\text{NH}_3)^{2+}$ and $\text{Cu}(\text{L})(\text{OH})^+$.

coordination of anions to macrocyclic tetraamine complexes of copper(II) have been discussed in detail.³⁴⁻³⁷

Determination of the acid dissociation constant K_a . The acid dissociation constant of Cu(L)(OH)^+ was determined by titration of solutions of $[\text{Cu(L)Br}]\text{ClO}_4$. The data were interpreted in terms of an acid-base equilibrium [eqn. (4)]



and the equilibrium [eqn. (3)] between the bromo and aqua complexes [$K_1(\text{Br}^-)$]. The inclusion of the latter equilibrium is only important when the solutions contain significant amounts of the bromo complex; in solutions with $[\text{Cu}^{\text{II}}] = 1.8 \times 10^{-3} \text{ M}$ the ratio $[\text{Cu(L)(H}_2\text{O)}^{2+}]/[\text{Cu(L)(Br)}^+]$ is about 70. Non-linear least-squares calculations were performed using the known value of $K_1(\text{Br}^-)$. The data did not suggest the presence of other species than those shown in eqns. (3) and (4), as seen by the fact that the same values for K_a were obtained for $[\text{Cu}^{\text{II}}] = 1.8 \times 10^{-3}$ and $5 \times 10^{-3} \text{ M}$. Likewise, the same result was obtained in the presence of a large amount of bromide ($[\text{Br}^-] = 0.1 \text{ M}$). The results are given in Tables 5 and 7. In Table 7 is also given the equilibrium constant for the reaction in eqn. (5)



calculated from $K(\text{OH}^-) = K_a/K_w$ using published data for K_w . (See Ref. 17 and references therein.)

The aqua ligand in the $\text{Cu(L)(H}_2\text{O)}^{2+}$ species is equatorial for both a TBP and SP configuration, and the value of $K(\text{OH}^-)$ is very large considering that coordination of hydroxide (axial) to the corresponding cyclam and tetramethylcyclam copper(II) complexes does not occur even in strong alkali solutions.³⁸⁻⁴⁰ Similarly, for the complex $\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})^+$, which is SP, the formation constant for binding of (axial) hydroxide has been reported to be $K(\text{OH}^-) = 9.3 \text{ M}^{-1}$.⁴¹ For the four isomers of the copper(II) complexes with the tetraamines tet a and tet b the values of $K(\text{OH}^-)$ are in the region $1-500 \text{ M}^{-1}$.^{36,37} The lowest value is found for the compound derived from the red tet a isomer, which has an almost planar arrangement⁴² of the four nitrogen atoms, and the fifth donor atom in an axial position, while the

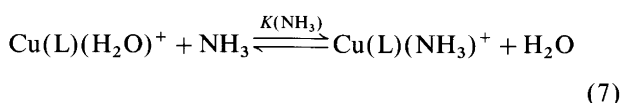
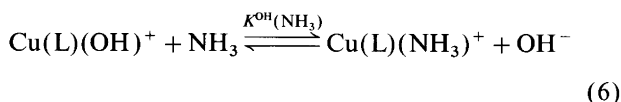
Table 5. Potentiometric determination of the acid dissociation constant K_a of $\text{Cu(L)(H}_2\text{O)}^{2+}$ at $I = 1.00 \text{ M}$.^a

$T/^\circ\text{C}$	$[\text{Cu(II)}]/\text{M}$	$[\text{NaBr}]/\text{M}$	$K_a^{\text{obs}}/\text{M}$	$K_a^{\text{average}}/\text{M}$
25.0	5.0×10^{-3}	0	8.00×10^{-10}	7.93×10^{-10}
—	1.8×10^{-3}	0	7.70×10^{-10}	—
—	6.6×10^{-3}	10^{-2}	8.10×10^{-10}	—
40.0	6.4×10^{-3}	0	1.573×10^{-9}	1.642×10^{-9}
—	6.4×10^{-3}	0.1	1.711×10^{-9}	—

^aIonic strength kept constant with NaClO_4 .

largest value is found for the complex derived from the blue tet b isomer, which has a TBP arrangement with the fifth donor atom in an equatorial position.^{43,44} The variation of the acid strength of these species seems to indicate that equatorial aqua ligands are much stronger acids than axial aqua ligands in pentacoordinated tetraamine copper(II) complexes.

Determination of the ammine formation constant $K_{\text{OH}}(\text{NH}_3)$. In the presence of aqueous ammonia the aqua and hydroxo complexes form an equilibrium with the ammine complex as shown in eqns. (6) and (7):



The ammine complex is formed quantitatively at low hydroxide concentration, as shown by spectroscopic measurements in the region 450–750 nm; the same spectra were obtained in ammonia/ammonium buffer solutions with $[\text{NH}_3] = 0.2$ and 0.5 M and for each solution $[\text{OH}^-] = 4.6 \times 10^{-5}$ or $9.2 \times 10^{-5} \text{ M}$. The spectrum of the ammine complex is shown in Fig. 6. Analyses of the spectra of solutions with $[\text{NH}_3] = 0.5-1.0 \text{ M}$ and $[\text{OH}^-] = 0.01-0.02 \text{ M}$ were consistent with the presence of significant amounts of Cu(L)(OH)^+ and $\text{Cu(L)(NH}_3)^+$, and no other species. From these spectra the equilibrium constant $K^{\text{OH}}(\text{NH}_3)$ was calculated using the known spectra of the hydroxo and ammine species, and the result is given in Table 6. The ΔH° and ΔS° values are given in Table 7. Parameters for the equilibrium in eqn. (7) have been calculated using the relation $K(\text{NH}_3) = K^{\text{OH}}(\text{NH}_3)K_a/K_w$ as shown in Table 6.

The equatorial ammine ligand in $\text{Cu(L)(NH}_3)^{2+}$ is bound strongly to copper(II). Similarly, the blue isomer of $\text{Cu}(\text{tet b})(\text{H}_2\text{O})^{2+}$, which has a TBP structure with H_2O in an equatorial position, reacts readily with ammonia, and the value $K(\text{NH}_3) = 84.1 \text{ M}^{-1}$ has been reported.⁴⁴ A much weaker binding is observed for the fifth ammine ligand in the (essentially) square pyramidal complex $\text{Cu}(\text{NH}_3)_5^{2+}$ for which $K_5 [K(\text{NH}_3)]$ has been determined to 0.418 M^{-1} .⁴¹ Likewise, for the planar

Table 6. Spectrophotometric determination of $K_{\text{OH}}(\text{NH}_3)$ at $I = 1.00 \text{ M}$.^a

$T/^\circ\text{C}$	$[\text{NH}_3]/\text{M}$	$[\text{NaOH}]/\text{M}$	$K^{\text{OH}}(\text{NH}_3)^{\text{obs}}$	$K^{\text{OH}}(\text{NH}_3)^{\text{average}}$
25.0	0.500	0.0100	0.0518	0.0496
—	0.500	0.0200	0.0525	—
—	0.500	0.100	0.0481	—
—	1.000	0.0200	0.0461	—
40.0	0.500	0.0100	0.0317	0.03165
—	1.000	0.0200	0.0316	—

^aIonic strength kept constant with NaClO_4 .

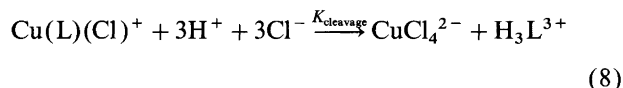
Table 7. Summary of thermodynamic data at $I=1.00$ M and 25°C .^a

Constant	K	$\Delta H^\circ/$ kJ mol^{-1}	$\Delta S^\circ/$ $\text{J mol}^{-1} \text{K}^{-1}$
$K(\text{Br}^-)/\text{M}^{-1,b}$	8.33(18)	-8.4(18)	-11(6)
$K(\text{I}^-)/\text{M}^{-1,b}$	12.35(55)	-13.2(33)	-23(11)
$K(\text{NH}_3)/\text{M}^{-1,c}$	$2.49(9) \times 10^3$	-42.9(46)	-79(16)
$K(\text{OH}^-)/\text{M}^{-1,d}$	$5.02(13) \times 10^4$	-19.6(33)	24(11)
$K^{\text{OH}}(\text{NH}_3)^e$	$4.96(13) \times 10^{-2}$	-23.3(33)	-103(11)
K_a/M^f	$7.93(21) \times 10^{-10}$	37.7(33)	-48(11)

^aIonic strength kept constant with NaClO_4 . ^bEqn. (3). ^cEqn. (7), $K(\text{NH}_3) = K^{\text{OH}}(\text{NH}_3)/K_a/K_w$. ^d $K(\text{OH}^-) = K_a/K_w$. ^eEqn. (6). ^fEqn. (4), $pK_a = 9.101(16)$.

$\text{Cu}(\text{cyclam})^{2+}$ ion $K(\text{NH}_3) = 0.02 \text{ M}^{-1}$ (16 M NH_3). The observation that equatorial ammonia is bound stronger than axial ammonia in pentaamine and pentaammine complexes follows the trend mentioned above for coordination of hydroxide.

Inertness of copper(II) nitrogen bonds. While the $\text{Cu}(\text{L})\text{X}^{2+}$ species are labile with respect to substitution reactions of the fifth ligator X, they are very inert with respect to the hydrolysis of the $[2^4.3^1]$ adamanzane ligand. Thus, in hydrochloric acid the complex is cleaved to form the tetrachlorocuprate(II) anion, but only very slowly. The reaction in 5 M HCl (25°C) was followed spectrophotometrically in the region $370\text{--}800 \text{ nm}$. The change of the absorbance with time followed the expression for a first-order reaction, and $k_{\text{cleavage}} = 1.48 \times 10^{-6} \text{ s}^{-1}$ was estimated for the overall reaction in eqn. (8):



The analogous cleavage of $\text{Cu}(\text{cyclen})^{2+}$ to copper(II) aqua ions has been studied.¹⁵ In this case also only one step was observed and the value $k_{\text{cleavage}} = 1.2 \times 10^{-3} \text{ s}^{-1}$ has been reported for 5 M HClO_4 (25°C). The kinetic data were explained in terms of a fast equilibrium between $\text{Cu}(\text{cyclen})^{2+}$ and $\text{Cu}(\text{cyclenH})(\text{H}_2\text{O})^{3+}$ followed by a rate-determining cleavage of the latter species (cyclenH = monoprotonated cyclen coordinated by the remaining three unprotonated amine groups). In the present study we found that the rate of hydrolysis of $\text{Cu}(\text{cyclen})^{2+}$ is increased considerably in the presence of chloride, $k_{\text{cleavage}} = 0.72 \text{ s}^{-1}$ in 5 M HCl (25°C). This enhancement in rate is qualitatively explained by the formation of the more reactive intermediate $\text{Cu}(\text{cyclenH})(\text{Cl})^{2+}$. The present copper(II) complex with $[2^4.3^1]$ adamanzane reacts with 5 M HCl 5×10^5 slower than the cyclen complex. This extreme difference in reactivity may be explained by the different geometry and flexibility of the two ligands: in the cyclen complex the copper(II) ion is coordinated 0.5 \AA above the plane formed by the four nitrogen atoms of cyclen, making the

cleavage of one of the Cu–N bonds as well as the subsequent formation of a Cu–Cl bond facile, since no substantial conformational change of the relatively flexible amine ligand is required.^{15,45} In contrast, Cu–N cleavage in CuL^{2+} requires a significant distortion of the very rigid $[2^4.3^1]$ adamanzane ligand, and furthermore coordination of water or chloride will be sterically hindered by the proximity of the uncoordinated (protonated) nitrogen donor atom.

Summary

The bowl amine $[2^4.3^1]$ adamanzane forms pentacoordinated copper(II) complexes as shown for the fifth ligator being bromide, iodide, hydroxide, water and ammonia. The crystal structures of the bromo and iodo complexes show that the rigid C_{2v} geometry of the macrobicyclic ligand is maintained in the copper(II) coordination compounds, and the coordination geometries are intermediates between TBP and SP. Extrusion of copper(II) from the bowl amine is 5×10^5 times slower than copper(II) extrusion from $\text{Cu}(\text{cyclen})^{2+}$ and is explained by the very different geometries and flexibilities of the coordinated amines. Preliminary redox studies show that $[2^4.3^1]$ adamanzane stabilizes Cu^{II} relative to Cu^{I} and that the process is quasi-reversible. The spectra of the compounds are shown in Figs. 5 and 6 for the wavelength region used in the thermodynamic and kinetic studies. The $(\epsilon, \lambda)_{\text{max}}$ values including the near-infrared region are given in Table 8.

Appendix

The name $[2^4.3^1]$ adamanzane is obtained by an extension of the simplified nomenclature¹⁴ used for the tricyclic tetraaza derivatives having one extra carbon chain connecting the two secondary nitrogen atoms. These tricyclic amines are called adamanzanes, and the number of carbon (and hetero) atoms in the six chains are given as a prefix in a square bracket with the additional rule that the carbon chains are listed in the order as shown in Fig. 7.

The tricyclic tetraamine 1,4,8,11-tetraazatricyclo-[6.6.2.2^{4,11}]octadecane reported recently⁴⁶ (Fig. 8) is thus named $[2.2.2.2.3.3]$ adamanzane = $[2^4.3^2]$ adamanzane

Table 8. Summary of spectral data for CuLX^{2+} species in aqueous solution at 25°C .

X^-	$(\epsilon/\text{M}^{-1} \text{cm}^{-1}, \lambda/\text{nm})_{\text{max}}$	$(\epsilon/\text{M}^{-1} \text{cm}^{-1}, \lambda/\text{nm})_{\text{max}}$
NH_3	(152, 595)	(92, 982)
H_2O	(107, 597) ^a	(77, 1073) ^a
Br^-	(382, 605)	(142, 1110)
I^-	(818, 612)	(187, 1122)
OH^-	(118, 633)	(45.5, 1030)

^aObtained from a $1.0 \times 10^{-3} \text{ M}$ solution of $[\text{Cu}(\text{L})\text{Br}]\text{ClO}_4$ in 1 M NaClO_4 and corrected for the small amount (1%) of the bromo complex.

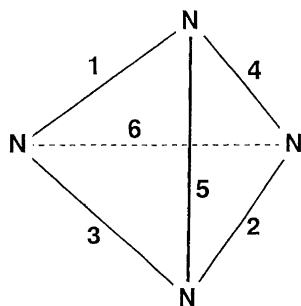


Fig. 7. Order of listing the five and six carbon chains, respectively, in bowl and cage adamanzanes.

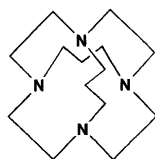


Fig. 8. The cage amine [2⁴.3²]adamanzane (1,4,8,11-tetraazatricyclo[6.6.2.2^{4,11}]octadecane) has been synthesized from the parent bowl, [2⁴.3¹]adamanzane.

(the latter short notation is used for cases with several carbon chains of equal length in sequence).

By an extension of this nomenclature the present bowl amine, L in Fig. 1, is given the name [2⁴.3¹]adamanzane. In chemical formulae adamanzane is abbreviated adz.

Acknowledgement. Financial support by the Danish Natural Research Council is gratefully acknowledged. We thank Bente Nielsen for technical assistance.

References

- Sargeson, A. M. *Pure Appl. Chem.* 56 (1984) 1603.
- Kimura, E. *Top. Curr. Chem.* 128 (1985) 113.
- Bianchi, A., Micheloni, M. and Paoletti, P. *Pure Appl. Chem.* 60 (1988) 525.
- Alder, R. W. *Chem. Rev.* 89 (1989) 1215.
- Hancock, R. D. and Martell, A. E. *Chem. Rev.* 89 (1989) 1875.
- Alders, R. W. *Tetrahedron* 46 (1990) 683.
- Dietrich, B., Viout, P. and Lehn, J.-M. *Macrocyclic Chemistry*, VCH, Weinheim, Germany 1993.
- Ciampolini, M., Nardi, N., Voltaconi, B. and Michloni, M. *Coord. Chem. Rev.* 120 (1992) 223.
- Weisman, G. R., Rogers, M. E., Wong, E. H. Jasinski, J. P. and Paight, E. S. *J. Am. Chem. Soc.* 112 (1990) 8604.
- Benchini, A., Bianchi, A., Bazzicalupi, C., Ciampolini, M., Dapporto, P., Fusi, V., Micheloni, M., Nardi, N., Paoli, P. and Valtancoli, B. *J. Chem. Soc., Perkin Trans. 2* (1993) 115.
- Benchini, A., Bianchi, A., Bazzicalupi, C., Ciampolini, M., Dapporto, P., Fusi, V., Micheloni, M., Nardi, N., Paoli, P. and Valtancoli, B. *J. Chem. Soc., Perkin Trans. 2* (1993) 715.
- Benchini, A., Bianchi, A., Borselli, A., Ciampolini, M., Micheloni, M., Paoli, P. and Valtancoli, B. *J. Chem. Soc., Perkin Trans. 2* (1990) 209.
- Springborg, J., Kofod, P., Olsen, C. E., Toftlund, H. and Søvtofte, I. *Acta Chem. Scand.* 49 (1995) 547.
- Springborg, J., Pretzmann, U. and Olsen, C. E. *Acta Chem. Scand.* 50 (1996) 294.
- Hay, R. W. and Pujari, M. P. *Inorg. Chim. Acta* 100 (1985) L1.
- Christensson, F. and Springborg, J. *Acta Chem Scand. Ser. A* 36 (1982) 21.
- Springborg, J. *Acta Chem. Scand.* 46 (1992) 1047.
- Cosier, J. and Glazer, A. M. *J. Appl. Crystallogr.* 19 (1986) 105.
- Lundgren, J.-O. *Crystallographic Computer Programs*. Report UUIC-B13-4-06D. University of Uppsala, Sweden 1985.
- Flack, H. D. and Schwarsenbach, D. *Acta Crystallogr., Sect. A44* (1988) 499.
- Flack, H. D. *Acta Crystallogr., Sect. A39* (1983) 876.
- Sheldrick, G. M., *Acta Crystallogr. Sect. A46* (1990) 467.
- Sheldrick, G. M., *SHELXL93. Program for Crystal Structure Refinement*. University of Göttingen, Germany 1993.
- International Tables for X-Ray Crystallography*. Kynoch Press, Birmingham 1974, Vol. IV. (Present distributor: Kluwer Academic Publishers, Dordrecht).
- Motherwell, W. D. S. and Clegg, W. *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, UK 1978.
- Spek, A. L. *Acta Crystallogr., Sect. A46* (1990) C-34.
- Holmes, R. R. *Progr. Inorg. Chem.* 32 (1984) 119.
- Kobayashi, K., Sakurai, T., Hasegawa, A., Tsuboyama, S. and Tsuboyama, K. *Acta Crystallogr., Sect. B38* (1984) 1154.
- Tsuboyama, S., Kobayashi, K., Sakurai, T. and Tsuboyama, K. *Acta Crystallogr., Sect. C40* (1984) 1178.
- Bencini, A., Bianchi, A., Borselli, A., Chimichi, S., Ciampolini, M., Dapporto, P., Micheloni, M., Nardi, N., Paoli, P. and Valtancoli, B. *Inorg. Chem.* 29 (1990) 3282.
- Pajunen, A. and Pajunen, S. *Acta Crystallogr., Sect. C42* (1986) 53.
- Alcock, N. W., Balakrishnan, K. P. and Moore, P. *J. Chem. Soc., Dalton Trans.* (1986) 1743.
- Noyle, P. and Hathaway, B. J. *Acta Crystallogr., Sect. C47* (1991) 1386.
- Chen, J.-W., Chang, C.-C. and Chung, C.-S. *Inorg. Chem.* 26 (1987) 335.
- Wu, S.-Y., Lee, C.-S. and Chung, C.-S. *Inorg. Chem.* 23 (1984) 2548.
- Liang, B.-F. and Chung, C.-S. *Inorg. Chem.* 19 (1980) 572.
- Liang, B.-F., Margerum, D. E. and Chung, C.-S. *Inorg. Chem.* 19 (1979) 2001.
- Micheloni, M., Paoletti, P., Burki, S. and Kaden, T. A. *Helv. Chim. Acta* 65 (1982) 587.
- Hancock, R., Darling, E. A., Hodgson, R. and Ganesh, K. *Inorg. Chim. Acta* 90 (1984) L83 41.
- Tasker, P. A. and Sklap, L. *J. Cryst. Mol. Struct.* 5 (1975) 329.
- Bjerrum, J. and Agarwala, B. V. *Acta Chem. Scand., Ser. A34* (1980) 475.
- Clay, R. M., Murray-Rust and J. Murray-Rust, P. *J. Chem. Soc., Dalton Trans.* (1979) 1135.
- Bauer, R. A., Robinson, W. R. and Margerum, D. W. *J. Chem. Soc., Chem. Commun.* (1973) 289.
- Chang, C.-C. and Chung, C.-S. *J. Chem. Soc., Dalton Trans.* (1991) 1685.
- Clay, R. M., Murray-Rust, P. and Murray-Rust, J. *Acta Crystallogr., Sect B35* (1979) 1894.43.
- Springborg, J., Olsen, C. E. and Søvtofte, I. *Acta Chem. Scand.* 49 (1995) 555.

Received June 4, 1996.