137. Metal Complexes with Macrocyclic Ligands

Part XXX[1])

Synthesis and Structure of Halocuprates of Tetraprotonated 1,4,8,11-Tetraazacyclotetradecane and its Cu^{2+} Complex

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By mixing acidic solutions of 1,4,8,11-tetraazacyclotetradecane (Cy) with CuX_2 ($X = Cl^-$, Br^-), either the hexahalocuprates of the tetraprotonated form of the macrocycle ($[CyH_4]$ $[CuX_6]$) or the tetrahalocuprates of its Cu^{2+} complex ([CuCy] $[CuX_4]$) are obtained. The structures of the chloro derivatives are established by X-ray diffraction analysis. In $[CyH_4]$ $[CuCl_6]$, the Cu^{2+} is in a tetragonally distorted octahedral geometry with four short and two long Cu–Cl bonds. The tetraprotonated macrocycle is centrosymmetric, and its conformation is exodentate, so that the four ammonium groups are as far as possible from each other to minimize the electrostatic repulsion. In [CuCy] $[CuCl_4]$, the Cu^{2+} ion complexed by the macrocycle is surrounded by four N-atoms in a square-planar arrangement. In addition, the axial positions are occupied by two Cl^- ions of two $CuCl_4^{2-}$ units, which act as bridges. The macrocycle is in the *trans-III*-configuration. The other Cu^{2+} ion is coordinated by four Cl^- ions in a distorted tetrahedral geometry. IR and VIS spectra of the chloro and bromo derivatives are used to discuss the structure of the bromo species.

Introduction. – Chloro- and bromocuprates(II) have been studied in detail, because *1*) chlorocuprates, being able to assume different geometries depending upon the nature of the cation, are ideal to test theoretical models [2–4]; *2*) they often exhibit thermochromic properties [2] [3], and *3*) they show temperature- and pressure-dependent phase-transfer changes [5–7].

They have often been synthesized, as in our case, accidentally, when copper halides and amine hydrochlorides were mixed in acidic solutions [8]. Regarding the structural aspects, the chloro compounds are especially interesting, since they form square planar as well as tetrahedral $CuCl_4^{2-}$, trigonal bipyramidal $CuCl_5^{3-}$, tetragonally distorted octahedral $CuCl_6^{4-}$ and dimeric species $Cu_2Cl_6^{2-}$ [2]. The square-planar geometry is generally observed with small cations or with cations which can form H-bonds to the Cl^- ions. In contrast, tetrahedral species are found with larger cations, which do not form H-bonds. Sometimes, as for $[Ph-CH_2-CH_2-NH_2-CH_3]_2$ $[CuCl_4]$, both geometries are found [6]: the square-planar geometry with two additional long bonds is observed in the low-temperature modification, whereas the tetrahedral geometry is observed in the high-temperature modification. The bromocuprates also exhibit several coordination geometries [9]. However, since Br^- is larger than Cl^- ion, it prefers a tetrahedral arrangement.

In the course of our studies on Cu^{2+} complexes with macrocycles, we often observed the formation of greenish yellow species in acidic solutions containing a large Cl^- excess. To investigate these species, we have prepared, in the case of 1,4,8,11-tetraazacyclotetradecane (Cy), several compounds of this type, which are either halocuprates of the

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tetraprotonated macrocycle (CyH_4^{4+}) or of its Cu^{2+} complex [$CuCy^{2+}$]. These compounds are ideal to study the properties and structures of halocuprates with relatively large cations, one of which can easily form H-bonds (CyH_4^{4+}), whereas H-bond formation is excluded for the other one [$CuCy^{2+}$], as well as structural aspects of the macrocyclic chemistry.

Experimental. – 1,4,8,11-Tetraazacyclotetradecance (Cy) was prepared as described in [10]. VIS spectra were recorded on a *Cary 118C* using the nujol technique [11]. IR spectra were measured on a *Perkin Elmer 157G* or a *Pye Unicam SP 3-100* spectrometer in KBr pills.

1,4,8,11-Tetraazoniacyclotetradecane Hexachlorocuprate(II). A mixture of 1 g (5 mmol) Cy, 2.14 g (12.5 mmol) $CuCl_2 \cdot 2\,H_2O$ in 5 ml of 36% HCl and 10 ml of H_2O was heated to 100°, and so much H_2O was added that a clear soln. was obtained. Slow cooling to r.t. afforded 1.5 g (3.1 mmol, 62%) of the product as yellow-green crystals. Anal. calc. for $C_{10}H_{28}Cl_6CuN_4$ (480.62): C 24.99, H 5.87, Cl 44.26, Cu 13.22, N 11.65; found: C 25.09, H 5.97, Cl 44.02, Cu 13.30, N 11.76.

1,4,8,11-Tetraazoniacyclotetradecane Tetrabromocuprate(II) Dibromide. To 1 g (5 mmol) of Cy in 10 ml of 47% HBr, so much H_2O was added that the hydrobromide dissolved. The soln. was heated to 100°, and 5 g (22.4 mmol) of $CuBr_2$ in 25 ml of 47% HBr were added. Slow cooling to r.t. gave 2 g (2.7 mmol, 54%) of the product as dark crystals. Anal. calc. for $C_{10}H_{28}Br_6CuN_4$ (747.31): C 16.07, H 3.78, Br 64.15, Cu 8.50, N 7.50; found: C 16.02, H 3.91, Br 64.14, Cu 8.59, N 7.57.

(1,4,8,11-Tetraazacyclotetradecane)copper(II) Tetrachlorocuprate(II). A soln. of 1 g (5 mmol) of Cy and 4.3 g (25 mmol) of $CuCl_2 \cdot 2\,H_2O$ in 20 ml of H_2O was heated to 60° for 1 h and then slowly cooled to r.t., whereby, 0.8 g (1.7 mmol, 34%) of the product were obtained as dark-brown crystals. Anal. calc. for $C_{10}H_{24}Cl_4Cu_2N_4$ (469.23): C 25.59, H 5.15, Cl 30.21, Cu 27.08, N 11.93; found: C 25.25, H 5.15, Cl 30.08, Cu 26.7, N 11.94.

(1,4,8,11-Tetraazacyclotetradecane)copper(II) Tetrabromocuprate(II). A soln. of 1 g (5 mmol) of Cy and 2.8 g (12.5 mmol) of $CuBr_2$ in 20 ml of H_2O was kept for 1 h at 100°. After addition of 2 ml of 47% HBr, the soln. was cooled to r.t., whereby 2.3 g (3.6 mmol, 71%) of the product were obtained as dark crystals. Anal. calc. for $C_{10}H_{24}Br_4Cu_2N_4$ (647.04): C 18.56, H 3.74, Br 49.40, Cu 19.64, N 8.66; found: C 18.33, H 3.70, Br 49.04, Cu 19.9, N 8.67.

X-Ray Structure Analysis. The crystal data and parameters of the data collection are given in *Table 1.*

Table 1. *Crystal Data for [CyH_4][$CuCl_6$] and [CuCy][$CuCl_4$]*

Formula	$C_{10}H_{28}Cl_6CuN_4$	$C_{10}H_{24}Cl_4Cu_2N_4$
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$ (No. 2)	*Panm* (No. 62)
		non-standard setting
a [Å]	7.159(3)	8.370(2)
b [Å]	9.859(3)	12.804(2)
c [Å]	9.684(1)	16.791(2)
α [deg]	88.54(3)	90
β [deg]	108.62(3)	90
γ [deg]	131.74(4)	90
Z; V [Å^3]	1; 465.7	4; 1799.5
θ_{max}	27	27
Radiation	MoK_α	MoK_α
Scan type	$\omega/2\theta$	$\omega/2\theta$
Collected reflections	$\pm h,+k,+l$	$+h,+k,+l$
μ [cm^{-1}]	19.31	28.42
F(000)	251	951.9
No. of indep. refl.	2032	2264
No. of refl. in refinement	1716	1048
No. of variables	153	101
Observations/variables	11.2	10.4
Largest peak on final ΔF [e/Å^3]	0.70	0.93
Final R	0.033	0.060
Final R_w	0.038	0.058
Weighting scheme	$1/[\sigma^2 + 4.74 \cdot 10^{-3} F^2]$	$1/[\sigma^2 + 8.86 \cdot 10^{-4} F^2]$

Unit-cell parameters were determined by accurate centering of 25 independent strong reflections by the least-squares method. Four standard reflections, monitored every hour during data collection, showed no significant variation of the intensity. The raw data set was corrected for polarization effects, but no correction for absorbance was applied. The structures were solved by *Patterson* techniques using the program SHELXS-86 [12]. Anisotropic least-squares refinements were carried out for all non-H-atoms. While, in the case of [CyH_4] [$CuCl_6$], all H-atoms were localized on a difference *Fourier* map and refined isotropically, in the case of [CuCy] [$CuCl_4$] the H-atoms were in calculated positions with C–H distance of 1.08 Å and $U_{iso} = 0.065$. Scattering factors were from *Cromer et al.* [13] or given in the SHELX-76 program [12]. Fractional coordinates are deposited by the *Cambridge Crystallographic Data Centre*.

Results and Discussion. – The halocuprates were synthesized following the procedure of *Remy* and *Laves* [8], and they were characterized as solids by elemental analysis, IR and VIS spectroscopy and, in the case of the chloro derivatives, by X-ray diffraction analysis as well.

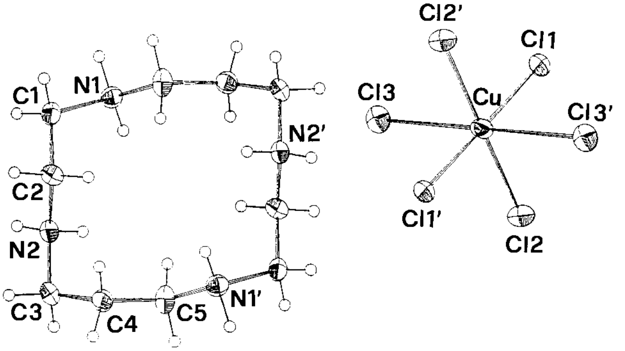

Fig. 1. *ORTEP plot of [CyH_4] [$CuCl_6$].* Both the Cu^{2+} and the centre of the macrocycle are situated on inversion centres of the unit cell.

The structure of [CyH_4] [$CuCl_6$] is interesting in two aspects *(Fig. 1)*. It represents the first example of an isolated hexachlorocuprate ion, whereas all of the known structures have infinite chains and give polymeric units [2]. On the other hand, it also gives insight into the conformation of a tetraprotonated tetraazamacrocycle. The $CuCl_6^{4-}$ unit has a tetragonally distorted octahedral geometry with four short Cu–Cl bonds (2.292–2.300 Å) and two long ones (3.173 Å). The Cl–Cu–Cl angles are close to 90° *(Table 2)*. There is no interaction between a $CuCl_6^{4-}$ unit and a second one, and only weak H-bonds with the ammonium groups of the macrocycle (N · · · Cl distances 3.14–3.32 Å) are expected. Since the macrocycle is tetraprotonated, all N- and C-atoms bear two H-atoms, and they are not easily dinstinguishable. To identify the atoms, we have calculated all the permutations, and the results presented here are those giving the lowest *R* value as well the most

Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *for [CyH_4][$CuCl_6$]*

Cu–Cl(1)	2.292(1)	N(2)–C(3)	1.518(3)
Cu–Cl(2)	2.300(1)	C(3)–C(4)	1.524(4)
Cu–Cl(3)	3.173(1)	C(4)–C(5)	1.520(3)
N(1)–C(1)	1.510(3)		
C(1)–C(2)	1.517(3)	Cl(1)–Cu–Cl(2)	89.9 (> 0.1)
C(2)–N(2)	1.495(3)	Cl(1)–Cu–Cl(3)	94.7 (> 0.1)
C(5)–N(1)	1.497(3)	Cl(2)–Cu–Cl(3)	91.0 (> 0.1)

regular thermal ellipsoids. The C—C and C—N bonds in CyH_4^{4+} are in the expected range of 1.517–1.524 Å and 1.495–1.510 Å, respectively.

CyH_4^{4+} has a crystallographically imposed inversion centre so that the four N-atoms are coplanar. The conformation of the macrocycle resembles a rectangle, at the corner of which four CH_2 groups are situated. This is in contrast to the recently published structure of $Cy \cdot 4HCl$, in which two NH_2 and two CH_2 groups are at the corners of the rectangle [14].

Whereas in its metal complexes ($[MCy]^{2+}$ [15]), its diprotonated (CyH_2^{2+} [16]), and non-protonated (Cy [14]) form, the conformation of the macrocycle is endodentate, that of CyH_4^{4+} is exodentate, so that the ammonium groups are as far as possible from each other, thus minimizing the electrostatic repulsion. The endodentate conformation of the species mentioned above is dictated by the fact that the free electron pairs of the amino groups either form coordinative bonds to the metal ion at the centre of the ring or are involved in H-bonds as in CyH_2^{2+} or Cy.

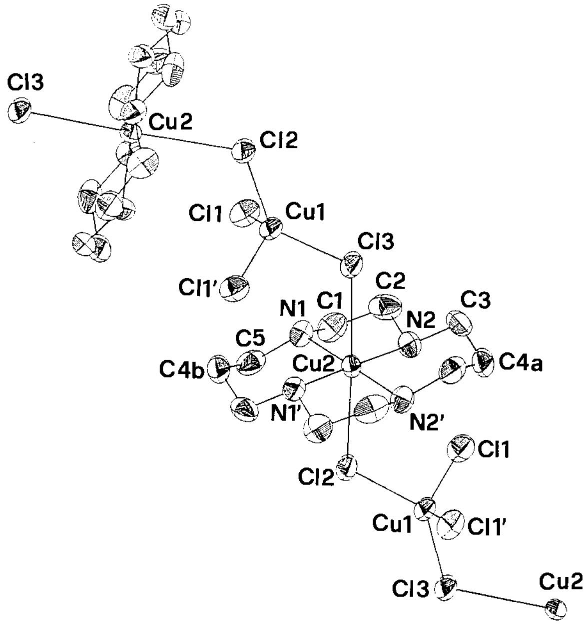

Fig. 2. *ORTEP plot of [CuCy] [CuCl$_4$]*. The atoms Cu(2), Cl(2), Cu(1), and Cl(3), forming the chain backbone, are situated in the mirror plane of the unit cell.

[CuCy] [$CuCl_4$] consists of Cu^{2+} macrocyclic units $[CuCy]^{2+}$, which are bridged by $CuCl_4^{2-}$ *(Fig. 2)*. The backbone of the chain, consisting of Cu(2), Cl(2), Cu(1), and Cl(3) as well as C(4a) and C(4b), are situated in the mirror plane of the unit cell. The $CuCl_4^{2-}$ group has a distorted tetrahedral geometry with Cu—Cl bonds ranging from 2.24 to 2.25 Å, the non-bridging Cl^- having longer Cu—Cl bonds than the bridging ones *(Table 3)*. The Cl–Cu–Cl angles are 132.3° for the bridging and 125.8° for the non-bridging Cl^-, giving a somewhat flattened tetrahedral geometry. The Cu—N bonds are all in the expected range of 2.006 to 2.018 Å. The coordination sphere of the Cu^{2+} is completed by two axially

Table 3. *Selected Bond Lengths* [Å] *and Angles* [°] *for* [$CuCy$][$CuCl_4$]

Cu(1)–Cl(1)	2.253(3)	Cu(2)–Cl(2)	2.856(4)
Cu(1)–Cl(2)	2.235(4)	Cu(2)–Cl(3)	2.853(4)
Cu(1)–Cl(3)	2.236(4)		
Cu(2)–N(1)	2.018(8)	Cu(2)–N(2)	2.006(7)
N(1)–C(1)	1.480(12)	C(1)–C(2)	1.474(14)
C(2)–N(2)	1.495(13)	N(2)–C(3)	1.503(12)
C(3)–C(4a)	1.500(13)	C(5)–C(4b)	1.520(13)
C(5)–N(1)	1.479(12)		
Cl(1)–Cu(1)–Cl(2)	99.9(1)	Cl(1)–Cu(1)–Cl(3)	101.4(1)
Cl(2)–Cu(1)–Cl(3)	132.3(1)	Cl(1)–Cu(1)–Cl(1′)	125.8(1)
Cl(2)–Cu(2)–Cl(3)	177.6(1)	Cl(2)–Cu(2)–N(1)	90.6(2)
Cl(2)–Cu(2)–N(2)	88.4(2)	Cl(3)–Cu(2)–N(1)	87.8(2)
Cl(3)–Cu(2)–N(2)	93.3(2)	N(1)–Cu(2)–N(1′)	94.7(3)
N(1)–Cu(2)–N(2)	85.7(3)	N(2)–Cu(2)–N(2′)	94.0(3)
N(1)–Cu(2)–N(2′)	178.9(3)		

bound Cl^- of two $CuCl_4^{2-}$ moieties. The axial Cu–Cl bonds are 2.85 Å long. The $[CuCy]^{2+}$ structure is very similar to that described for [CuCy] $(ClO_4)_2$ [17], except for the nature of the axial ligands. The macrocycle is in the thermodynamically stable *trans-III*-configuration.

The IR *(Fig.3)* and VIS spectra *(Table 4)* of the four compounds allow to draw some conclusions on the bromo derivatives, for which we have no crystal structures. The IR

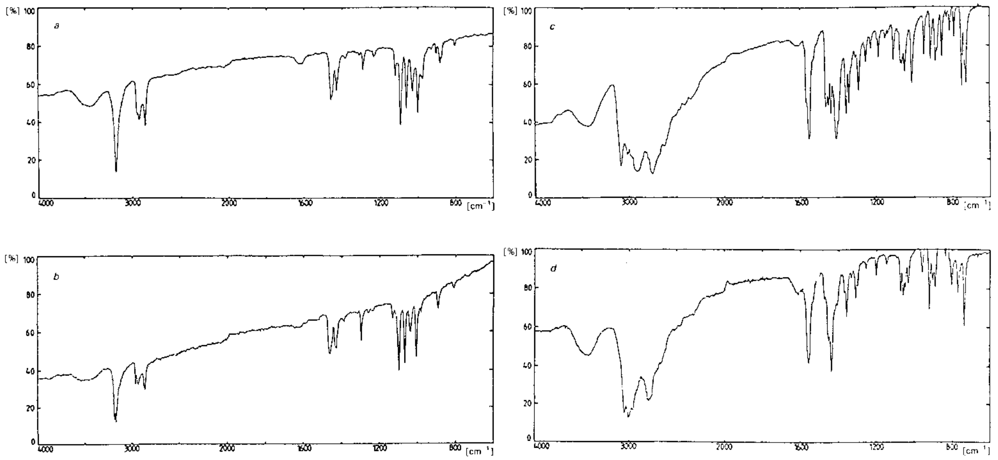

Fig. 3. *IR Spectra of* a) [$CuCy$] [$CuCl_4$], b) [$CuCy$] [$CuBr_4$], c) [CyH_4] [$CuCl_6$], *and* d) [CyH_4]]$CuBr_6$]

Table 4. *VIS Spectra of the Halocuprates in Nujol Mulls* [11]

Compound	λ_{max} [nm]
$[CyH_4][CuCl_6]$	370, 430 (sh)
$[CyH_4][CuBr_6]$	370 (sh), 440 (sh), 540, 600
$[CuCy][CuCl_4]$	420, 520 (sh)
$[CuCy][CuBr_4]$	370 (sh), 440 (sh), 540, 600

spectra of [CuCy] [CuX_4] in the range 4000–600 cm^{-1} are very similar to each other indicating that the two compounds with $X^- = Cl^-$ and Br^- probably have the same structure. In contrast, the IR spectra of [CyH_4] [CuX_6] are distinctly different. This can be rationalized, since, in the case of Cl^-, the CuX_6^{4-} unit is a distorted octahedron, whereas, for Br^-, one would expect a tetrahedral $CuBr_4^{2-}$ moiety and two additional Br^- ions.

The VIS spectra at room temperature are characterized by strong bands with not well-separated peaks. In [CuCy] [$CuCl_4$], one finds the typical absorption of the Cu^{2+} macrocyclic chromophore at 520 nm. The spectra of [CyH_4] [$CuBr_6$] and [CuCy] [$CuBr_4$] are similar to those observed for Cs_2CuBr_4 [9], which contains the tetrahedral $CuBr_4^{2-}$ ion [18], so that [CyH_4] [$CuBr_6$] should more correctly be described as a tetrabromocuprate with two additional Br^- ions, [CyH_4] [$CuBr_4$]Br_2. The compound [CyH_4] [$CuCl_6$] has been carefully studied at low temperatures using polarized light by *McDonald* and *Hitchman* [19].

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