37. Metal Complexes with Macrocyclic Ligands

Part XXVIII[1])

Structures and Stabilities of the Cu^{2+} Complexes with 1,4,7-Triazacyclononane-1-acetic Acid

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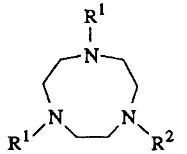
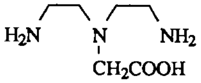
The potentiometric study of the complexation of 1,4,7-triazacyclononane-1-acetic acid (**1**) with Cu^{2+} ($I = 0.5$ (KNO_3), $T = 25°$) indicates the presence of the species [Cu(**1**)], [Cu(**1**)OH], [Cu(**1**)$_2$], and [(Cu(**1**))$_2$OH], the stability constants of which are determined. The two complexes [Cu(**1**)]ClO_4 and [(Cu(**1**)$_2$)OH]ClO_4 were also characterized by X-ray structure analysis. In both cases, the Cu^{2+} ion is in a distorted square-pyramidal arrangement, pentacoordinated by the three N-atoms of the macrocycle, an O-atom of the carboxylate, and an additional O-atom either from a second carboxylate or from an OH^-, acting as a bridge between two metal centres.

Introduction. – The introduction of functional groups in the side chain of macrocycles leads to interesting compounds with respect to their complexation properties [2]. Whereas many studies on tetrasubstituted tetraaza-macrocycles have appeared [3], much less is known on mono-*N*-functionalized derivatives. We have previously shown that it is relatively easy to prepare mono-*N*-functionalized polyaza-macrocycles with a carboxylate group in their side chain [4]. Compared to their parent compounds, these ligands have one additional donor group, and if this group has the appropriate geometry, it can participate in the complexation of the metal ion. It is, therefore, interesting to study the thermodynamic as well as the structural properties of these compounds.

As a first example, we have choosen the system 1,4,7-triazacyclononane-1-acetic acid (**1**) and Cu^{2+}, because of the abundant data on triazacyclononane derivatives [5] and the



1 $R^1 = H, R^2 = CH_2COOH$
2 $R^1 = R^2 = H$
3 $R^1 = R^2 = CH_3$



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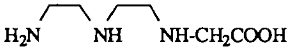

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possibility to compare it with the well-known parent macrocycle [9]aneN_3 (**2**) [6] and its trimethyl derivative (**3**) [7–9].

Experimental. – *Caution*: perchlorates can be explosive. The synthesis of 1,4,7-triazacyclononane-1-acetic acid (**1**) has been described in [4].

[1-(Carboxylatomethyl)-1,4,7-triazacyclononane]copper(II) Perchlorate. A soln. of 1.0 g (3.8 mmol) of **1** · 2HCl and 0.66 g (3.8 mmol) of $CuCl_2 \cdot 2H_2O$ in a few ml of H_2O was adjusted with 0.5M NaOH to pH 3. After 2 h, so much $NaClO_4$ was added that the complex soln. was saturated at 100°. Slow cooling to r.t. gave 0.81 g (61%) of the product in crystalline form. IR (KBr): 1600, 1550 (COO^-). Anal. calc. for $C_8H_{16}ClCuN_3O_6$ (349.22): C 27.51, H 4.58, Cl 10.15, Cu 18.19, N 12.02; found: C 27.55, H 4.51, Cl 10.11, Cu 18.00, N 12.02.

μ-Hydroxo-bis{[1-(carboxylatomethyl)-1,4,7-triazacyclononane]copper(II)} Dinatrium Triperchlorate Dihydrate. From the mother liquor of the previous preparation adjusted to pH 9, the complex crystallized. IR (KBr): 1600 (COO^-).

Characterisation by X-Ray Structure Analysis. The crystal data and parameters of the data collection are collected in *Table 1*. Unit cell parameters were determined by accurate centering of 25 independent strong reflections by the least-squares method. Four standard reflections monitored every h 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 SHELX-76 [10]. Anisotropic least-squares refinements were carried out on all non-H-atoms of the ligand, the Cu- and the Cl-atoms. The O-atoms of the ClO_4^- group were isotropically refined, and all H-atoms are in calculated positions. Scattering factors are from *Cromer et al.* [11] or given in the SHELX-76 program. Fractional coordinates are deposited in the *Cambridge Crystallographic Data Base*.

Table 1. *Crystal Data and Parameters of Data Collection for the two Cu^{2+} Complexes*

Formula	$C_8H_{16}ClCuN_3O_6$	$C_{16}H_{33}ClCu_2N_6O_9 \cdot 2NaClO_4 \cdot 2H_2O$
Mole mass [g]	349.22	896.88
Space group	orthorhombic $P2_12_12_1$	monoclinic $P2_1/c$
a [Å]	7.802(2)	8.423(7)
b[Å]	7.921(2)	22.737(3)
c[Å]	21.187(3)	17.926(3)
α[°]	90	90
β[°]	90	92.90(3)
γ[°]	90	90
V[Å^3]	1309.3	3429.1
Z	4	4
Θ_{max}	26	26
Radiation	MoK_α	MoK_α
Scan type	$\omega/2\theta$	$\omega/2\theta$
Collected refl.	$+h, +k, +l$	$\pm h, +k, +l$
μ [cm^{-1}]	18.13	15.01
F(000)	716	1840
No. of indep. refl.	1459	6850
No. of refl. in ref.	1226	3372
No. of variables	189	454
Observ./variables	6.5	7.4
Largest peak on ΔF	0.75	0.56
Final R	0.056	0.060

Potentiometric measurements were run at 25° and $I = 0.5$ (KNO_3) using the fully automatic pH-titration unit described in [12]. The pH electrode was calibrated with two buffer solns. of pH 4 and 7 (*Methrohm*) and checked daily. The titrations were obtained by titrating with 0.4M NaOH solns. containing $2 \cdot 10^{-3}$–$5 \cdot 10^{-3}$ M ligand and 0%, 50% or 90% $CuCl_2$ adjusted with KNO_3 so that $I = 0.5$M.

Results and Discussion. – The pH-titrations of the free ligand and of its Cu^{2+} complexes were calculated using the computer program *TITFIT* [13]. The choice of the model necessary to fit all experimental data (*Eqns. 1–7*, charges omitted) was dictated by the value of the standard deviation σ_{ml} and the F test.

$$\begin{array}{lclll}
L + H & \rightleftarrows & LH & K^{H}_{LH} & (1) \\
LH + H & \rightleftarrows & LH_2 & K^{H}_{LH_2} & (2) \\
LH_2 + H & \rightleftarrows & LH_3 & K^{H}_{LH_3} & (3) \\
Cu + L & \rightleftarrows & CuL & K_1 & (4) \\
CuLH_{-1} + H & \rightleftarrows & CuL & K_2 & (5) \\
CuL + L & \rightleftarrows & CuL_2 & K_3 & (6) \\
CuL + CuLH_{-1} & \rightleftarrows & Cu_2L_2H_{-1} & K_4 & (7)
\end{array}$$

Omission of either one of the species CuL, CuL_2, $CuLH_{-1}$, or $Cu_2L_2H_{-1}$ increased the value of σ_{ml}, whereas no further species could be found which would decrease σ_{ml} significantly. The final calculation with the stability constants in *Table 2* gave σ_{ml} $9.2 \cdot 10^{-4}$

Table 2. *Protonation and Stability Constants for* **1** *and the Related Ligands* **2**, **4**, *and* **5**

	1[a])	**2**[b])		**4**[c])	**5**[c])		**1**[a])	**2**[a])		**4**[c])	**5**[c])
$\log K^{H}_{LH}$	11.47(2)	10.94	11.03	10.81	9.92	$\log K_3$	5.79(1)	10.69	12.34		
$\log K^{H}_{LH_2}$	7.45(2)	7.24	7.73	9.59	8.70	$\log K_4$	2.42(2)				
$\log K^{H}_{LH_3}$	2.82(3)	< 2	< 2	3.24	4.32	$\log K_5$			20.41		
$\log K_1$	18.99(1)	15.84	15.78	18.07	17.29	$\log K_6$				10.16	11.82
$\log K_2$	9.39(1)			9.89	9.50	$\log K_7$		19.00	18.15		

[a]) This work. [b]) Data from [6a] [6b]. [c]) Data from [14].

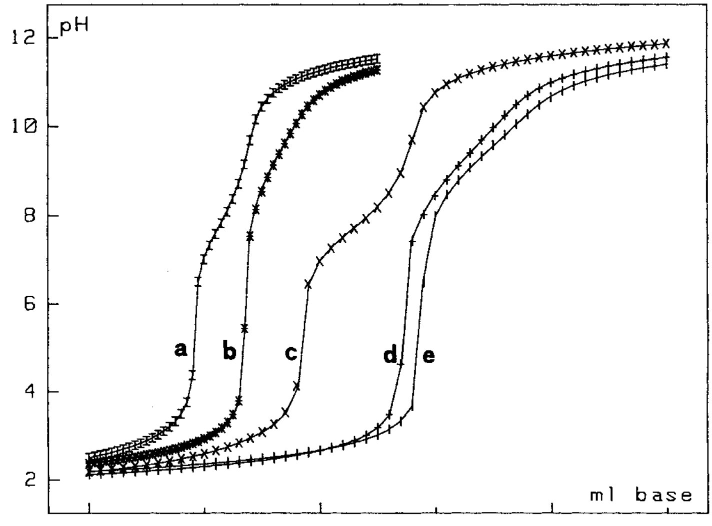

Fig. 1. *Titration curves of* **1** $\cdot$ *2 HCl in the presence of* Cu^{2+}. *a*) $c_L = 2.24$ mM and $c_M = 1.00$ mM, *b*) $c_L = 1.96$ mM and $c_M = 1.76$ mM, *c*) $c_L = 5.23$ mM and $c_M = 2.35$ mM, *d*) $c_L = 3.93$ mM and $c_M = 3.52$ mM, *e*) $c_L = 3.17$ mM and $c_M = 2.98$ mM. Curves determined from the constants listed in *Table 2*.

for 255 points from 5 curves with different metal/L ratios. The quality of the fit can be seen from *Fig. 1* and from the standard deviations of the constants.

The species and the stability constants obtained for **1** can be compared with those of **2** [6] and other triamino-monocarboxylates such as **4** and **5** [14]. For these ligands, however, additional equilibria *(Eqns. 8–10)* were postulated in order to explain the data *(Table 2)*.

$$\mathrm{Cu + L + LH \rightleftarrows CuL_2H} \qquad K_5 \qquad (8)$$

$$\mathrm{Cu + LH \rightleftarrows CuLH} \qquad K_6 \qquad (9)$$

$$\mathrm{2\,Cu + 2\,L \rightleftarrows Cu_2L_2H_{-2} + 2\,H} \qquad K_7 \qquad (10)$$

If we first compare ligand **1** with the parent compound **2**, we find an increased stability of the 1:1 and a decreased stability of the 1:2 complex. Both changes can be explained by the presence of the additional carboxylate group in **1**, which stabilizes a 1:1 complex, but prevents formation of the 1:2 species. Compared to the open-chain ligands **4** and **5**, which have the same number of donor atoms, **1** gives the most stable 1:1 complex, independently of the linear or tripodal arrangement of the donor groups of **4** and **5**, probably because of the very favorable facial coordination of the three N-atoms of **1**. The hydroxylated species also need some comments. The monomeric $\mathrm{CuLH_{-1}}$ is not observed for the parent compound, which, however, gives a very stable dimer $\mathrm{(CuLH_{-1})_2}$. This is a consequence of the different number of donor atoms of the two ligands and of the number of free coordination sites remaining available for $\mathrm{OH^-}$. Also unique is the mono-bridged species $\mathrm{Cu_2L_2H_{-1}}$ found for **1**, but not observed in other cases.

The X-ray diffraction study of two complexes allows discussion of the structural aspects in more detail *(Table 3)*. In [Cu(**1**)]ClO$_4$, the $\mathrm{Cu^{2+}}$ ion is penta-coordinated by the three N-atoms of the cyclic amine and two O-atoms of two carboxylates *(Fig. 2)*. The geometry is distorted square-pyramidal with two N-atoms (N(1) and N(2)) and two O-atoms (O(1) and O(2)) at the base and N(3) in the apical position with a somewhat longer Cu–N(3) bond. The carboxylate group connects, as a bridge, two Cu centres,

Table 3. *Selected Bond Lengths* [Å] *and Angles* [°] *for [Cu(***1***)]ClO$_4$ and [(Cu(***1***))$_2$OH]ClO$_4$*

	[Cu(**1**)]ClO$_4$	[(Cu(**1**))$_2$OH]ClO$_4$[a])	
		Molecule 1	Molecule 2
Cu–N(1)	2.063(8)	2.023(8)	2.015(8)
Cu–N(2)	2.027(10)	2.041(6)	2.046(9)
Cu–N(3)	2.195(7)	2.217(6)	2.200(9)
Cu–O(1)	1.952(7)	2.016(6)	1.965(6)
Cu–O(2)	1.982(7)		
Cu–OB		1.937(6)	1.931(6)
O(1)–Cu–N(2)	158.1(3)	167.4(3)	156.8(3)
O(2)–Cu–N(1)	169.9(3)		
OB–Cu–N(1)		165.6(3)	171.0(3)
N(3)–Cu–N(1)	83.3(4)	84.2(2)	82.7(3)
N(3)–Cu–N(2)	82.8(4)	82.0(3)	82.2(4)
N(3)–Cu–O(1)	113.6(4)	100.4(3)	116.2(3)
N(3)–Cu–O(2)	106.6(4)		
N(3)–Cu–OB		110.2(3)	105.8(3)

[a]) Atoms X in molecule 1 and 2 are labeled X_n and X_{n1}, respectively.

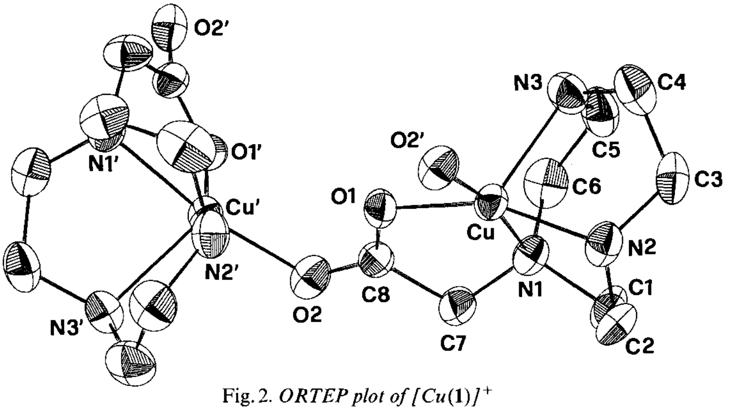

Fig. 2. *ORTEP plot of [Cu(**1**)]$^+$*

thus, forming chains. The bond lengths Cu—O(1) and Cu—O(2) are nearly equal (1.95 and 1.98 Å), and the geometry of the carboxylate unit allows a symmetrical arrangement.

$[(Cu(\mathbf{1}))_2OH]ClO_4 \cdot 2NaClO_4 \cdot 2H_2O$ consists of a dimeric cation $[(Cu(\mathbf{1}))_2OH]^+$ with two slightly different Cu^{2+} units, which are very similar to that of $[Cu(\mathbf{1})]ClO_4$. The Cu^{2+}, penta-coordinate in a distorted square-pyramidal arrangement, is surrounded by the three N-atoms of the macrocycle, one O-atom of the carboxylate group, and one hydroxo group, bridging the two CuL units *(Fig. 3)*. In the dimeric species, the Cu—Cu distance is 3.17 Å, and the dihedral angle between the two best planes N(1), N(2), O(1), O(2) and N(11), N(21), O(11), O(21) is 112.0°. In this compound, two molecules of $NaClO_4$ and of H_2O were also found. The Na^+ ions are surrounded by the O-atoms of the H_2O molecules, of ClO_4^-, and COO^- with bond lengths of 2.30 to 2.45 Å.

Our structures can be compared to those published by *Wieghardt et al.* for the μ-azido [7], the μ-hydroxo [8], and the μ-terephthalato [9] dimers containing 1,4,7-trimethyl-1,4,7-

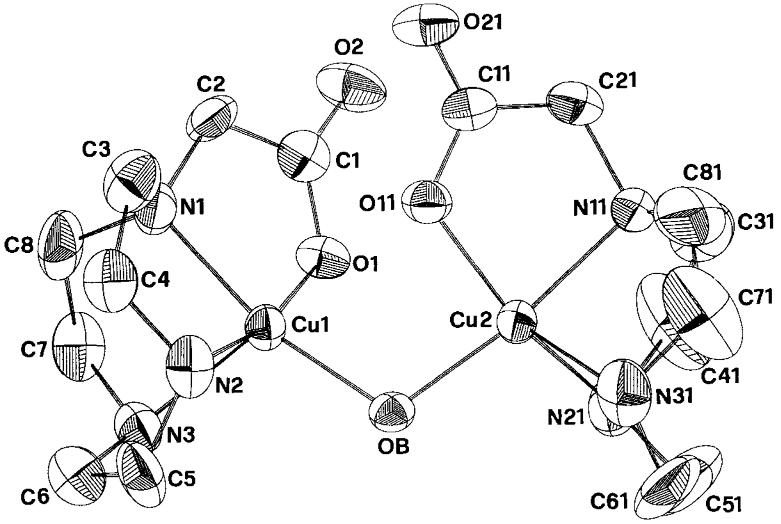

Fig. 3. *ORTEP plot of [(Cu(**1**))$_2$OH]$^+$*

triazacyclononane (**3**) as ligand. In all these examples, the Cu^{2+} ion is penta-coordinated with square-pyramidal geometry, and the Cu–N bonds are, as in our case, distinctly different: basal Cu–N bonds range between 2.03–2.08 Å, whereas axial Cu–N bonds are between 2.22–2.24 Å.

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