219. Metal Complexes of Macrocyclic Ligands

Part XXIV[1])

Binuclear Complexes with Tetraazamacrocycle-N,N',N'',N'''-tetraacetic Acids

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The three ligands H_4dota, H_4teta, and H_4heta give binuclear complexes with Cu^{2+} and Ni^{2+}, the spectral properties of which have been studied. The structures of Cu_2(dota)·$5H_2O$ and Cu_2(teta)·$6H_2O$ have been established by X-ray diffraction analysis.

Introduction. – Tetraazamacrocycle-N,N',N'',N'''-tetraacetic acids have been studied in many respects [2–4]. Since these ligands have up to eight potential donor groups to bind a metal ion, it is, in general, difficult to propose a structure for these complexes on the basis of spectroscopic data alone. To obtain structural insight in such species, it is, therefore, essential to run X-ray determinations, from which then, by analogy, other structures can be deduced.

In [1], we have discussed the mononuclear species formed by H_4dota and H_4teta, showing that, in the case of H_4dota, six donor groups, four amino-N-atoms and two carboxylates, are involved in the coordination of the metal ion. Beside mononuclear complexes, however, these ligands also form binuclear species M_2L, as was shown with a H_4teta analog [4], but no structures have been reported so far. Our interest in this paper is dedicated to two such structures and to the spectral properties of binuclear Cu^{2+} and Ni^{2+} complexes with the three ligands H_4dota, H_4teta, and H_4heta.

H_4dota H_4teta H_4heta
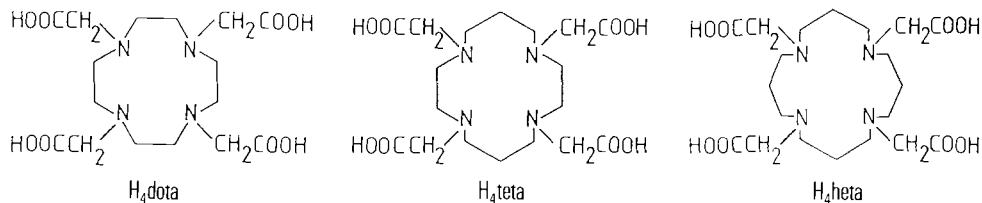
Experimental. – H_4dota [2][5] and H_4teta [2][6] were prepared according to the literature.

H_4heta·H_2O. To a mixture of 3.63 g (38.6 mmol) of $ClCH_2COOH$ in 10 ml of H_2O and 3.31 g (82.8 mmol) of NaOH in 40 ml of H_2O at 0°, 2.10 g (9.2 mmol) of 1,5,9,13-tetraazacyclotetradecane [7] in 10 ml of H_2O were added, and the soln. was left over night, then heated for 2 h at 60°. To crystallize the product, the soln. was acidified to pH

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2 with HCl, evaporated to about 30 ml, and kept in the cold. The product was purified by dissolving it in NaOH at pH 12 and precipitating it at pH 3. Yield: 3.55 g (83%). Dec. 246°. IR (KBr): 3500 (OH), 2450 (NH$^+$), 1620 (COO$^-$). ^{1}H-NMR (D$_2$O, NaOD): 1.6 (4 C–CH$_2$–C); 2.5 (8 C–CH$_2$–N); 3.1 (4 N–CH$_2$–COO$^-$); br. signals. Anal. calc. for C$_{20}$H$_{36}$N$_4$O$_8$·H$_2$O (478.54): C 50.20, H 8.00, N 11.71; found: C 50.19, H 7.81, N 11.74.

Cu$_2$(dota)·5H$_2$O. The pH of a soln. of 477 mg (1.0 mmol) of H$_4$dota·2 HCl and 500 mg (2.0 mmol) of CuSO$_4$·5H$_2$O in 100 ml of H$_2$O was adjusted to 4 with NaOH. After 2–3 days, dark-green crystals were formed, which were collected and air-dried. Yield: 370 mg (60%). Anal. calc. for C$_{16}$H$_{24}$Cu$_2$N$_4$O$_8$·5H$_2$O (617.56): C 31.12, H 5.51, Cu 20.58, N 9.07, H$_2$O 14.59; found: C 30.82, H 5.61, Cu 20.6, N 8.92, H$_2$O 14.46.

Cu$_2$(teta)·6H$_2$O. A soln. of 320 mg (0.74 mmol) of H$_4$teta and 253 mg (1.48 mmol) of CuCl$_2$·2H$_2$O in 50 ml of H$_2$O was refluxed at pH 5 for 1 h. Then, the pH was slowly increased to 7–8 by addition of NaOH, and the soln. was refluxed further for 1 h. After cooling, the soln. was centrifuged. The dark-blue soln. was concentrated and passed over a *Sephadex G-10* column. From the first fraction, 42 mg (9%) of dark-blue crystals were obtained. The second fraction probably contained the mononuclear Cu^{2+} complex. Anal. calc. for C$_{18}$H$_{28}$Cu$_2$N$_4$O$_8$·6H$_2$O (663.62): C 32.58, H 6.08, Cu 19.15, N 8.44, H$_2$O 16.29; found: C 32.50, H 5.45, Cu 19.1, N 8.34, H$_2$O 16.74.

Cu$_{2.5}$(heta)Cl·11H$_2$O. The pH of a soln. of 200 mg (0.42 mmol) of H$_4$heta·H$_2$O in a little 0.1 M NaOH was adjusted to 7. To this, a soln. of 143 mg (0.84 mmol) of CuCl$_2$·2H$_2$O was added. The volume was *ca.* 30 ml and the pH 7. The mixture was refluxed for 2 h, filtered, evaporated to 2 ml, and treated with EtOH to precipitate the product, which was recrystallized from H$_2$O/EtOH. Yield: 256 mg (72%). Anal. calc. for C$_{20}$H$_{32}$ClCu$_{2.5}$N$_4$O$_8$·11H$_2$O (848.98): C 28.30, H 6.41, Cu 18.7, N 6.60, H$_2$O 23.34; found: C 28.30, H 6.43, Cu 18.1, N 6.51, H$_2$O 23.49.

Ni$_3$(heta)Cl$_2$·7H$_2$O. A soln. of 200 mg (0.42 mol) of H$_4$heta·H$_2$O and 199 mg of NiCl$_2$·6H$_2$O in 30 ml of H$_2$O at pH 7 was refluxed for 7 days. The green soln. was evaporated to about 10 ml, filtered, and treated with EtOH, until a weak turbidity was obtained. After a few days, the green crystals were filtered. Yield: 30 mg (9%). Anal. calc. for C$_{20}$H$_{32}$Cl$_2$N$_4$Ni$_3$O$_8$·7H$_2$O (829.65): C 28.95, H 5.59, N 6.75, H$_2$O 15.20; found: C 29.21, H 5.92, N 6.74, H$_2$O 15.55.

Measurements. VIS spectra were measured on a *Cary 118C* using the nujol technique [8] or in aq. solns. in 1-cm cells. IR spectra were run on a *Perkin Elmer 157G* in KBr pellets.

Crystal Structures. The atomic parameters of the two structures are available from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1 EW. A list of the observed and calculated structure factors is available from the authors.

Cu$_2$(dota)·5H$_2$O: Monoclinic, space group $P2_1/c$, a = 11.607(5), b = 16.953(5), c = 12.986(2) Å, β = 110.83(3)°, V = 2388.5 Å^3, $D_{calc.}$ = 1.717, $D_{exp.}$ = 1.70 gcm^{-3}, Z = 4, F(000) = 1264, μ = 17.74 cm^{-1}.

Cu$_2$(teta)·6H$_2$O: Triclinic, space group $P\bar{1}$, a = 9.254(4), b = 10.220(3), c = 15.937(2) Å, α = 92.01(3), β = 100.01(2), γ = 113.71(2)°, V = 1349.7 Å^3, $D_{calc.}$ = 1.633, $D_{exp.}$ = 1.63 gcm^{-3}, Z = 2, F(000) = 684, μ = 15.77 cm^{-1}.

Intensities of 3928 and 3469 reflections with MoKα radiation were collected to θ = 27° in the θ–2θ scan mode on an *Enraf Nonius CAD4* diffractometer equipped with a graphite monochromator for Cu$_2$(dota) and Cu$_2$(teta), respectively. Unit cell parameters were obtained from accurate centering of 25 reflections. The structures were solved by *Patterson* and *Fourier* techniques. Cu$_2$(dota) yielded 2368 and Cu$_2$(teta) 2214 reflections with $F_0 > 2\sigma(F_0)$ which were used in the anisotropic refinement with a weighting scheme $\omega = 1/\sigma^2$ (F). The final R indices were 0.0573 and 0.0556 for Cu$_2$(dota) and Cu$_2$(teta), respectively. Programs used were written by *Germain et al.* [9], *Sheldrick* [10], and partly by ourselves.

Results and Discussions. – That tetraazamacrocycle-tetraacetic acids can give crystalline binuclear complexes was previously reported [4], although such species have never been found in solution during equilibrium studies. In the case of H$_4$dota and H$_4$teta, these complexes cannot be identified and their stability cannot be determined in solution, probably due their insolubility. In [1], we have studied the structures and spectral properties of a series of mononuclear complexes with H$_4$dota and H$_4$teta. It is now interesting to compare these structures with those of the binuclear complexes. Two complexes of H$_4$heta are also included here which have been indicated as binuclear ones, although the analysis clearly shows that they have more than two metal ions per ligand molecule. These solids have properties very different from those of the genuine binuclear complexes of H$_4$dota and H$_4$teta. It is, therefore, not clear what their structures are and

whether the excess of metal chloride gives a polymetric bridged structure, or the metal chloride co-precipitates under the experimental conditions.

Structure of Cu$_2$(dota). In the binuclear complex Cu$_2$(dota), the two copper ions have completely different coordination spheres (see *Fig. 1*). So, Cu(1) is bound by two carboxylates and four amino-N-atoms of the macrocycle, which is folded to give a *cis*-octahedral geometry, similar to that found in the mononuclear complex Cu(H$_2$dota) [1]. The coordination geometry of Cu(1) is distored, since the axial Cu(1)–N$_{axial}$ bonds (2.326 and 2.298 Å) are longer than the equatorial ones (2.119 and 2.116 Å), and the N(2)–Cu(1)–N(4) angle is 151.3°, so that the linearity expected for on octahedron is not attained. This might be a consequence of the size of the macrocycle, which does not allow
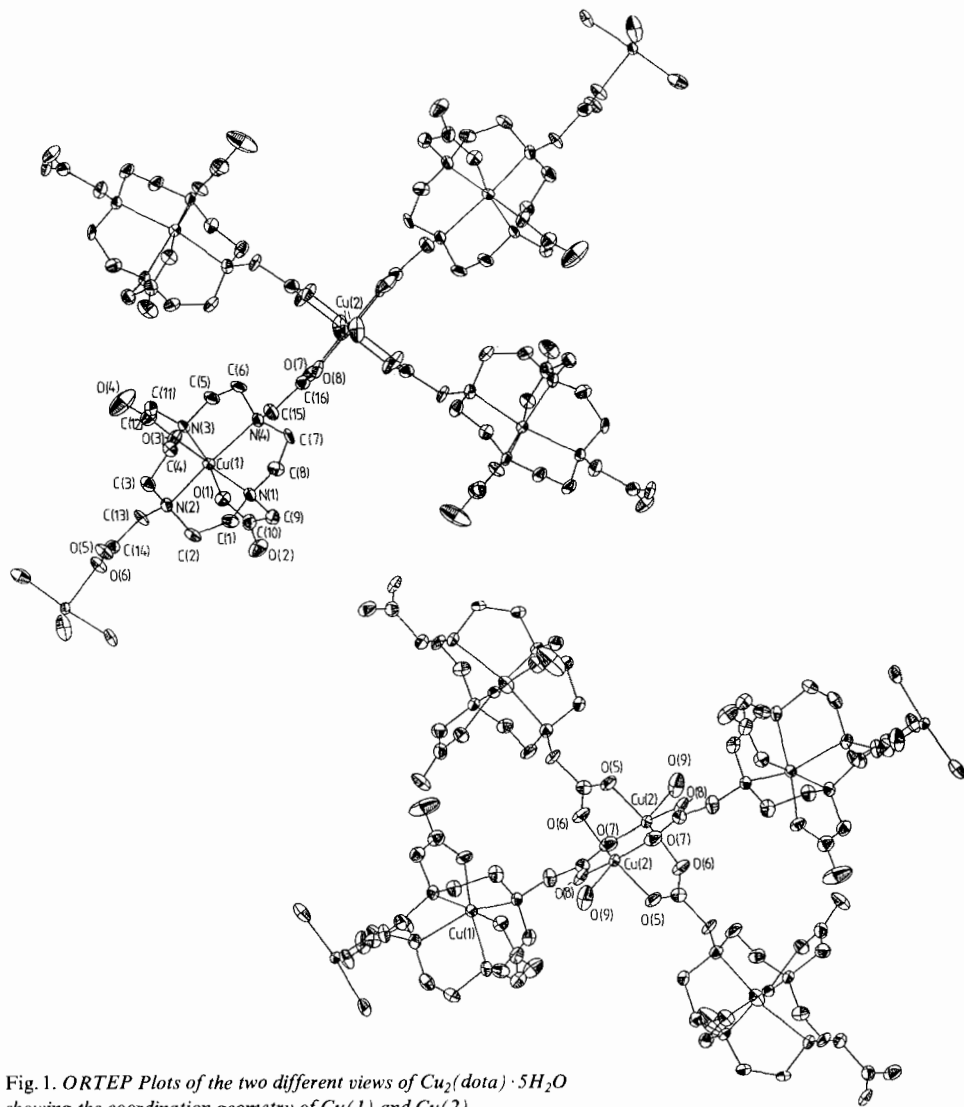

Fig. 1. *ORTEP Plots of the two different views of Cu$_2$(dota)·5H$_2$O showing the coordination geometry of Cu(1) and Cu(2)*

the N(2) and N(4) to come exactly into the axial positions. The two acetate residues, attached to N(2) and N(4) and not involved in coordinating Cu(1), are used to bind Cu(2). The structural unit which results is that found in many dicopper tetracarboxylate species. The two Cu(2) are bridged through four carboxylate groups each stemming from a different macrocycle, and additionally each Cu(2) binds a H$_2$O molecule. The Cu(2)−Cu(2') distance of 2.652 is practically the same as in Cu$_2$(acetate)$_4$(H$_2$O)$_2$ (2.65 Å) [11]. The two structural units containing Cu(1) and Cu(2) form a two dimensional net (see *Fig. 1*). The bond distances and angles are given in *Table 1*.

Table 1. *Bond Lengths and Angles of Cu$_2$(dota)·5H$_2$O*

Distances [Å]				Angles [°]	
Cu(1)−O(1)	1.957 (7)	Cu(2)−Cu(2')	2.652 (2)	N(1)−Cu(1)−N(2)	82.3 (2)
Cu(1)−O(3)	1.982 (5)	Cu(2)−O(5)	1.954 (8)	N(1)−Cu(1)−N(3)	105.5 (3)
Cu(1)−N(1)	2.119 (6)	Cu(2)−O(6)	1.959 (8)	N(1)−Cu(1)−N(4)	80.3 (2)
Cu(1)−N(2)	2.326 (7)	Cu(2)−O(7)	1.962 (6)	N(1)−Cu(1)−O(1)	82.9 (3)
Cu(1)−N(3)	2.116 (7)	Cu(2)−O(8)	1.969 (8)	N(1)−Cu(1)−O(3)	170.8 (3)
Cu(1)−N(4)	2.298 (6)	Cu(2)−O(9)	2.164 (8)	N(2)−Cu(1)−N(3)	80.7 (2)
O(1)−C(10)	1.252 (9)	O(5)−C(14)	1.250 (13)	N(2)−Cu(1)−N(4)	151.3 (3)
O(2)−C(10)	1.245 (12)	O(6)−C(14)	1.250 (12)	N(1)−Cu(1)−O(1)	94.4 (3)
O(3)−C(12)	1.276 (11)	O(7)−C(16)	1.261 (11)	N(2)−Cu(1)−O(3)	101.0 (2)
O(4)−C(12)	1.224 (11)	O(8)−C(16)	1.251 (12)	N(3)−Cu(1)−N(4)	82.1 (2)
N(1)−C(1)	1.514 (12)	N(3)−C(4)	1.496 (12)	N(3)−Cu(1)−O(1)	169.5 (2)
N(1)−C(8)	1.480 (10)	N(3)−C(5)	1.469 (9)	N(3)−Cu(1)−O(3)	83.5 (3)
N(1)−C(9)	1.508 (13)	N(3)−C(11)	1.491 (10)	N(4)−Cu(1)−O(1)	105.9 (3)
N(2)−C(2)	1.477 (10)	N(4)−C(6)	1.487 (11)	N(4)−Cu(1)−O(3)	99.7 (2)
N(2)−C(3)	1.480 (13)	N(4)−C(7)	1.501 (10)	O(1)−Cu(1)−O(3)	88.5 (3)
N(2)−C(13)	1.461 (10)	N(4)−C(15)	1.472 (13)	Cu(1)−N(1)−C(1)	110.0 (4)
C(1)−C(2)	1.517 (12)	C(9)−C(10)	1.539 (14)	Cu(1)−N(1)−C(8)	110.2 (4)
C(3)−C(4)	1.510 (11)	C(11)−C(12)	1.514 (15)	Cu(1)−N(1)−C(9)	106.0 (5)
C(5)−C(6)	1.526 (14)	C(13)−C(14)	1.512 (11)	C(1)−N(1)−C(8)	110.6 (7)
C(7)−C(8)	1.526 (12)	C(15)−C(16)	1.509 (12)	C(1)−N(1)−C(9)	109.9 (6)
				C(8)−N(1)−C(9)	110.2 (6)
				Cu(1)−N(2)−C(13)	105.0 (5)
				C(2)−N(2)−C(13)	111.9 (6)
				C(3)−N(2)−C(13)	114.5 (6)
				Cu(1)−O(1)−C(10)	118.8 (6)
				N(1)−C(1)−C(2)	110.8 (8)
				N(1)−C(9)−C(10)	110.7 (7)
				O(1)−C(10)−O(2)	125.9 (9)
				O(1)−C(10)−C(9)	116.7 (8)
				N(2)−C(13)−C(14)	116.7 (8)
				O(5)−C(14)−C(13)	118.8 (7)

Structure of Cu$_2$(teta). The binuclear Cu^{2+} complex with H$_4$teta has a structure which is completely different from that of Cu$_2$(dota) (*Fig. 2*) The two Cu^{2+} have a relative similar coordination sphere, being coordinated by two N-atoms, two carboxylate groups and an additional O donor. It results a square pyramidal geometry, in which Cu(1) and Cu(2) are displaced from the N$_2$O$_2$ plane by 0.17 and 0.22 Å, respectively. The difference between the two Cu^{2+} is found in the nature of the apical oxygen: for Cu(1) it is a H$_2$O molecule [O(9)], whereas for Cu(2) it is a carboxylate group which functions as a bridge. The two
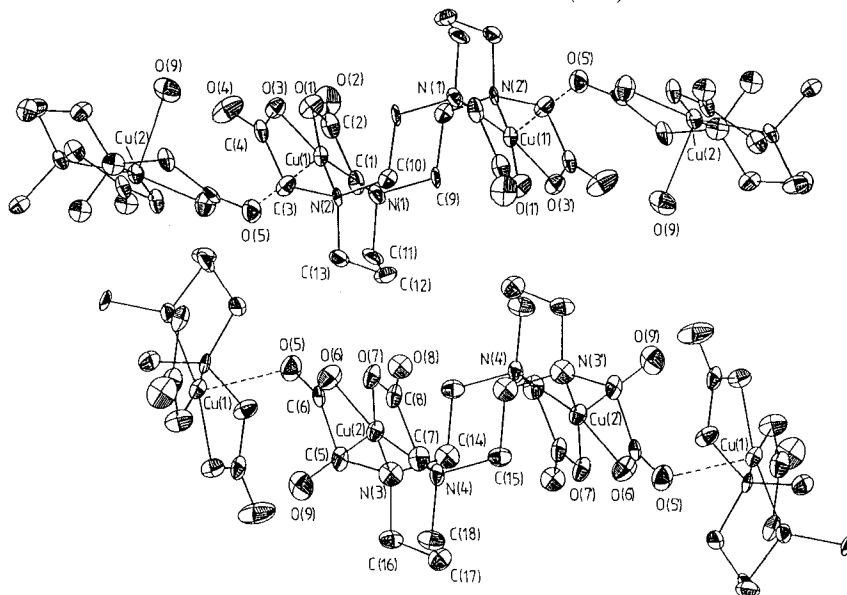
Fig. 2. *ORTEP Plots of the two different views of* $Cu_2(teta) \cdot 6H_2O$ *showing the coordination geometry of Cu(1) and* *Cu(2)*

different Cu^{2+} ions belong to two different macrocyclic entities which are linked by a bridging carboxylate group (*Fig. 3*).

The structure here found resembles in many aspects that observed for N,N',N'',N'''-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane, in which, however, there is no bridging between the different binuclear units [12].

The bond distances and angles, given in *Table 2*, are all normal. There are three different Cu^{2+}–Cu^{2+} distances: between Cu^{2+} ions in the same macrocyclic unit Cu(1)–Cu(1') 4.78 Å, and Cu(2)–Cu(2') 4.88 Å, and between Cu^{2+} ions belonging to two different macrocycles Cu(1)–Cu(2) 5.53 Å.

It is interesting to note, that the chelating unit is given by the aminoacetate groups, which have a C_3 chain between the two amino-N-atoms and not by those with an ethylene bridge. Therefore, each Cu^{2+} has a chelate ring sequence 5,6,5, which is known to be less strained than the 5,5,5 sequence, which would result the other way around. The six-membered chelate ring is in the chair conformation. In the crystal, there are five more H_2O molecules which have been localized, but they do not interact with the Cu^{2+} ions.
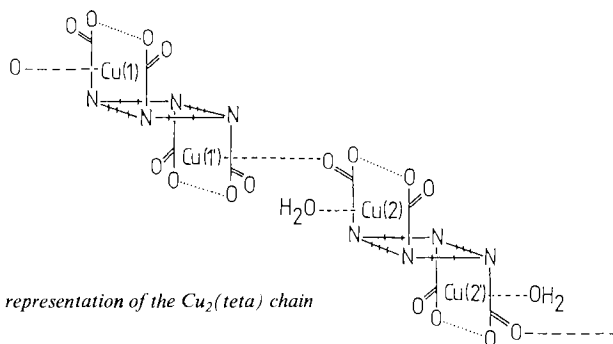

Fig. 3. *Schematic representation of the* $Cu_2(teta)$ *chain*

Table 2. *Bond Lengths and Angles of Cu₂(teta)·6H₂O*

Distances [Å]

Cu(1)–O(1)	1.942 (6)	N(2)–C(13)	1.526 (10)	O(8)–C(8)	1.254 (12)
Cu(1)–O(3)	1.937 (5)	C(1)–C(2)	1.512 (12)	N(3)–C(5)	1.463 (12)
Cu(1)–O(5)	2.243 (7)	C(3)–C(4)	1.518 (14)	N(3)–C(14)	1.508 (8)
Cu(1)–N(1)	2.023 (6)	C(9)–C(10)	1.577 (13)	N(3)–C(18)	1.495 (11)
Cu(1)–N(2)	2.021 (7)	C(11)–C(12)	1.519 (12)	N(4)–C(7)	1.508 (10)
O(1)–C(2)	1.276 (8)	C(12)–C(13)	1.519 (12)	N(4)–C(15)	1.487 (10)
O(2)–C(2)	1.233 (12)	Cu(2)–O(6)	1.948 (6)	N(4)–C(16)	1.499 (12)
O(3)–C(4)	1.317 (12)	Cu(2)–O(7)	1.927 (7)	C(5)–C(6)	1.538 (13)
O(4)–C(4)	1.214 (10)	Cu(2)–O(9)	2.236 (6)	C(7)–C(8)	1.525 (13)
N(1)–C(1)	1.509 (10)	Cu(2)–N(3)	2.027 (7)	C(14)–C(15)	1.546 (14)
N(1)–C(9)	1.447 (12)	Cu(2)–N(4)	2.038 (7)	C(16)–C(17)	1.536 (12)
N(1)–C(11)	1.528 (11)	O(5)–C(6)	1.208 (11)	C(17)–C(18)	1.518 (13)
N(2)–C(3)	1.505 (11)	O(6)–C(6)	1.278 (12)		
N(2)–C(10)	1.477 (10)	O(7)–C(8)	1.260 (11)		

Angles [°]

N(1)–Cu(1)–N(2)	97.8 (3)	N(3)–Cu(2)–N(4)	97.1 (3)
N(1)–Cu(1)–O(1)	84.9 (3)	N(3)–Cu(2)–O(6)	84.7 (3)
N(1)–Cu(1)–O(3)	170.2 (3)	N(3)–Cu(2)–O(7)	166.5 (2)
N(1)–Cu(1)–O(5)	95.5 (2)	N(3)–Cu(2)–O(9)	98.8 (3)
N(2)–Cu(1)–O(1)	170.4 (2)	N(4)–Cu(2)–O(6)	167.8 (3)
N(2)–Cu(1)–O(3)	84.9 (3)	N(4)–Cu(2)–O(7)	85.3 (3)
N(2)–Cu(1)–O(5)	92.3 (3)	N(4)–Cu(2)–O(9)	93.8 (3)
O(1)–Cu(1)–O(3)	91.0 (2)	O(6)–Cu(2)–O(7)	90.3 (3)
O(1)–Cu(1)–O(5)	96.6 (2)	O(6)–Cu(2)–O(9)	97.9 (3)
O(3)–Cu(1)–O(5)	93.9 (3)	O(7)–Cu(2)–O(9)	94.3 (2)
Cu(1)–N(1)–C(1)	103.4 (4)	N(1)–C(1)–C(2)	110.9 (5)
Cu(1)–N(1)–C(9)	114.6 (6)	O(1)–C(2)–O(2)	123.2 (8)
Cu(1)–N(1)–C(11)	110.2 (5)	O(1)–C(2)–C(1)	117.6 (8)
C(1)–N(1)–C(9)	111.0 (7)	O(2)–C(2)–C(1)	119.2 (6)
C(1)–N(1)–C(11)	107.5 (5)	N(1)–C(11)–C(12)	114.2 (5)
C(9)–N(1)–C(11)	109.8 (6)	C(11)–C(12)–C(13)	115.7 (8)
Cu(1)–O(1)–C(2)	113.3 (6)		

Spectral Properties. – The VIS spectra of the complexes were recorded in the solid state and when possible in solution (*Table 3*).

Cu₂(dota) has absorption properties very similar to those of the mononuclear Cu(H₂dota), which has the same structure as one of the subunits of the binuclear species with a $CuN_2O_2(N_2)_{ax}$ chromophore. The complexes Cu₂(teta) and Cu₂(heta) have similar

Table 3. *Absorption Spectra of the Binuclear Complexes with H₄dota, H₄teta, and H₄heta. For comparison, the spectra of the corresponding mononuclear complexes are also included.* λ_{max} [nm].

	Solid	Solution
Cu₂ (dota)	710	
Cu (H₂dota)	715	740 (pH 7)
Cu₂ (teta)	610	
Cu (H₂teta)	650	635 (pH 13)
Cu₂ (heta)[a]	595	595 (pH 2–13)
Ni₂ (heta)[a]	400, 660	390, 650, 710 (pH 6)

[a] The analysis indicates more than two metal ions per macrocycle.

Table 4. *IR Spectra* [cm^{-1}] *of the Binuclear* Cu^{2+} *and* Ni^{2+} *Complexes of* H_4*dota,* H_4*teta, and* H_4*heta*

Cu$_2$ (dota)	Cu$_2$ (teta)	Cu$_2$ (heta)^a)	Ni$_2$ (heta)^a)
1600	1610, 1640	1620	1620

^{a}) The analysis indicates more than two metal ions per macrocycle.

absorption maxima, although it is not clear whether Cu$_2$(heta) is a binuclear species at all. The absorption maximum for Cu$_2$(teta) at shorter wavelength than that of Cu$_2$DOTA is a consequence of the different chromophores: in Cu$_2$(dota), we have CuN$_2$O$_2$(N$_2$)$_{ax}$ in contrast to CuN$_2$O$_2$(O)$_{ax}$ for Cu$_2$(teta). All Ni^{2+} complexes have spectral properties typical for hexacoordinated high spin Ni^{2+}. The IR spectra (*Table 4*) show the typical COO$^-$···M^{2+} bands at 1600–1640 cm^{-1}, but no absorptions attributable to COOH groups (1720–1740 cm^{-1}) or protonated amines (intercombination bands 2500–2800 cm^{-1}) [13]. This means that these groups are not protonated and are all involved in coordinating the metal ions. Cu$_2$(teta) shows two peaks at 1610 and 1640 cm^{-1}, stemming from the non-equivalence of the four carboxylate groups.

Conclusions. – The previous [1] and present study on metal complexes with H$_4$dota, H$_4$teta, and H$_4$heta as well as the equilibrium measurements in solution show how many-sided the complexation properties of this type of ligands is. From the stoichiometric point of view, mononuclear complexes with different protonation degrees (MLH$_n^{(n-2)+}$) and binuclear species (M$_2$L) are found. Their structures, however, can be very different. It is clear that, with ligands having so many donor groups, the spectral properties of the complexes are not sufficient to propose a detailed structure. Only X-ray diffraction studies of the solids can in these cases give a final answer to the structural problem.

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