55. Metal Complexes with Macrocyclic Ligands

Part XXXIX[1])

Mono- and Binuclear Copper(II) Complexes of a Bridging Bis[1,4,7-triazacyclononane]

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The new bis-macrocycle 1,1′-[(1*H*-pyrazol-3,5-diyl)bis(methylene)]bis[1,4,7-triazacyclononane] (**1**) was synthesized and its complexation with Cu^{2+} studied. Potentiometric and spectrophotometric titrations indicate that, in addition to the mononuclear species $[Cu(LH_2)]^{4+}$, $[Cu(LH)]^{3+}$, $[CuL]^{2+}$, and $[Cu(LH_{-1})]^{+}$, binuclear complexes such as $[Cu_2L]^{4+}$, $[Cu_2(LH_{-1})]^{3+}$, and $[Cu_2(LH_{-2})]^{2+}$ are also formed in solution. The stability constants and spectral properties of these are reported. The binuclear species $[Cu_2(LH_{-1})]^{3+}$ specifically reacts with an azide ion to give a ternary complex $[Cu_2(LH_{-1})(N_3)]^{2+}$, the stability and structure of which were determined spectrophotometrically and by X-ray diffraction, respectively. The two Cu^{2+} ions are in a square-pyramidal coordination geometry. The axial ligand is one of the N-atoms of the 1,4,7-triazacyclononane ring, whereas at the base of the square pyramid, one finds the other two N-atoms of the macrocycle, one N-atom of the pyrazolide and one of the azide, both of which are bridging the two metal centres. In $[Cu_2(LH_{-1})(N_3)]^{2+}$, a strong antiferromagnetic coupling is present, thus resulting in a species with a low magnetic moment of 1.36 B.M. at room temperature.

Introduction. – Binuclear metal complexes are interesting from several points of view. The coordination chemistry of binuclear Cu^{2+} species was extensively investigated in view of its relevance for Cu^{2+} in biological systems [2]. In particular, a large number of magnetic exchange studies in such Cu^{2+} complexes were performed and correlated to structural features [3].

In the field of macrocycles, several approaches to this problem were chosen [4]. Ligands having two macrocyclic units connected by a chain of different length generally form complexes in which the two metal ions are not bridged and, therefore, show only weak interactions through space [5]. Macrocycles with a large cavity, which allows to fit two metal ions, can also be used to hold the metal centres at a fixed distance [6]. In these systems, there is often an additional internal or external bridging group which completes the structures of the binuclear species. These systems have the advantage of being relatively rigid and thus give structurally well defined moieties.

Wieghardt et al. [7] studied numerous examples in which two metal ions complexed by the 1,4,7-triazacyclononane unit ($[9]aneN_3$) are bridged through OH^- and/or acetate groups. We have now synthesized a new ligand, **1** (see *Scheme*) which combines the facial complexation properties of $[9]aneN_3$, but at the same time contains a pyrazole moiety as an endogenous bridging unit. This group is well known to be a useful bridging ligand between two metal centres once it is deprotonated [8].

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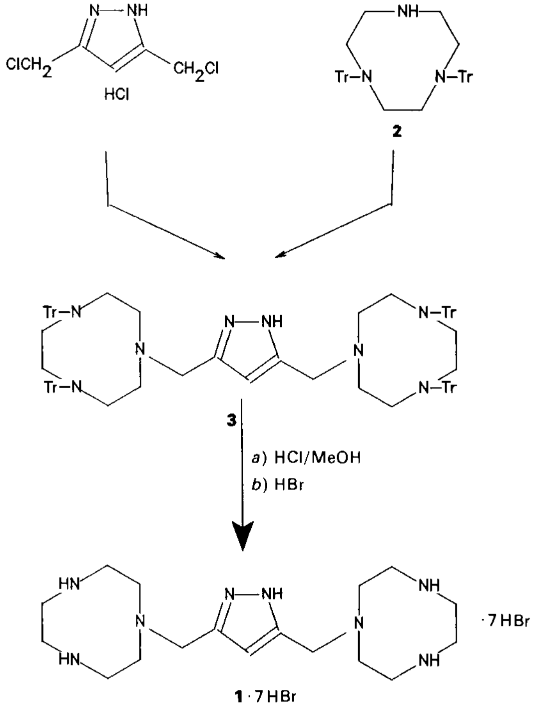
Scheme



Tr = triphenylmethyl

Experimental. – *1,4-Bis(triphenylmethyl)-1,4,7-triazacyclononane* (**2**). A soln. of 1,4,7-triazacyclononane trihydrochloride (14.32 g, 60 mmol) and NaOH (8 g, 200 mmol) in H_2O (130 ml) was evaporated and the residue taken up with $CHCl_3$ (800 ml). The org. phase was dried (Na_2SO_4) and filtered. To the filtrate, a soln. of triphenylmethyl chloride (33.1 g, 108 mmol) in $CHCl_3$ (50 ml) was added dropwise within 8 h. After an additional h, the solvent was distilled off. The crude product was dissolved in $CHCl_3$ (150 ml) and divided in two fractions. Each fraction was flash chromatographed (8 × 30 cm, silica gel 230–400 mesh (*Merck*), AcOEt): *1,4,7-tris(triphenylmethyl)-1,4,7-triazacyclononane* (R_f 0.8) as by-product and **2** (R_f 0.06; 11.4 g, 30.9%; containing *ca.* 5% of AcOEt). **2**: ^{1}H-NMR ($CDCl_3$): 2.70 (br. *s*, 8 H, CH_2NTr); 3.74 (br. *s*, 4 H, CH_2N); 7.00–7.33 (*m*, 18 arom. H); 7.48 (*d*, 12 arom. H). ^{13}C-NMR ($CDCl_3$): 45.3 (CH_2N); 53.89, 54.19 (CH_2NTr); 80.42 (Ph_3C); 126.09, 127.45, 127.57, 129.73 (arom. C).

*1,1'-[(1*H*-Pyrazole-3,5-diyl)bis(methylene)]bis[4,7-bis(triphenylmethyl)-1,4,7-triazacyclononane]* (**3**). Compound **2** (11.37 g, 18.5 mmol) and $(i\text{-}Pr)_2EtN$ (5.17 g, 40 mmol) were dissolved in THF (550 ml). Separately, 3,5-bis(chloromethyl)pyrazole monohydrochloride [9] (1.77 g, 8.8 mmol) in THF (50 ml) was neutralized by slow addition of 1.6M BuLi in hexane (5.5 ml, 8.8 mmol) under N_2. This soln. was added dropwise to the soln. containing **2** and left for 16 h at r.t. Then the mixture was extracted with half-sat. K_2CO_3 soln. (50 ml), the org. phase dried (Na_2SO_4) and evaporated, and the residue taken up with $CHCl_3$ (50 ml) and flash chromatographed (silica gel 230–400 mesh (*Merck*), AcOEt/$CHCl_3$ 1:5). The product fractions, after evaporation, were dried at 0.02 Torr: 8.71 g (75%) of **3**, still containing 6% of AcOEt. R_f (AcOEt/$CHCl_3$ 1:5) 0.06. ^{1}H-NMR ($CDCl_3$): 2.72 (br. *s*, 16 H, CH_2NTr); 3.20 (br. *s*, 8 H, CH_2NCH_2-pyrazole); 3.65 (*s*, 4 H, CH_2-pyrazole); 7.00–7.35 (*m*, 36 arom. H); 7.51 (*d*, 24 arom. H). ^{13}C-NMR ($CDCl_3$): 52.37, 53.28, 54.09 (CH_2N); 80.26 (Ph_3C); 103.29 (CH(pyrazole)); 125.91, 127.32, 129.79 (arom. C); 143.92 (C(pyrazole)).

*1,1'-[(1*H*-Pyrazole-3,5-diyl)bis(methylene)]bis[1,4,7-triazacyclononane]* (**1**). Compound **3** (8.71 g, 6.6 mmol) in MeOH (500 ml) and 37% HCl soln. (50 ml) was kept for 5 h at r.t. Then the solvent was evaporated, the residue taken up with H_2O (100 ml) and $CHCl_3$ (100 ml), and the aq. phase extracted twice with $CHCl_3$ (50 ml) and then treated with charcoal. After evaporation of the H_2O the crude product was purified by anion exchange (*Dowex 2, Fluka*) yielding the free base. The residue was dissolved in 47% HBr soln. (100 ml) and H_2O (80 ml), the soln. treated again with charcoal and evaporated and the residue dried: 4.0 g (66.1%) of **1** · 7 HBr. ^{1}H-NMR (D_2O): 3.03 (*t*, 8 H, CH_2NCH_2-pyrazole); 3.33 (*t*, 8 H, CH_2N); 3.68 (*s*, 8 H, CH_2N); 3.98 (*s*, 4 H, CH_2-pyrazole); 6.49 (*s*, 1 H, CH(pyrazole)). ^{13}C-NMR (D_2O): 44.79, 46.31, 50.06 (CH_2N); 52.07 (NCH_2-pyrazole); 109.29, 147.01 (pyrazole). Anal. calc. for $C_{17}H_{41}Br_7N_8 \cdot 5.67\ H_2O$ (1019.04): C 20.04, H 5.18, N 11.00, Br 54.89, H_2O 10.72; found: C 19.88, H 4.98, N 11.24, Br 56.06, H_2O 10.02.

μ-Azido{μ-{1,1′-[(1H-pyrazol-1-ido-3,5-diyl)bis(methylene)]bis[1,4,7-triazacyclononane]}}dicopper(II) Diperchlorate ($[Cu_2(LH_{-1})(N_3)](ClO_4)_2$). Ligand **1** (0.0675 mmol), $Cu(ClO_4)_2 \cdot 6\ H_2O$ (0.141 mmol), and NaN_3 (0.07 mmol) in 15 ml H_2O/EtOH (1:1) were mixed. On standing overnight, crystals of the complex formed. Anal. calc. for $C_{17}H_{33}Cl_2Cu_2N_{11}O_8 \cdot 0.5\ H_2O \cdot 0.5\ CH_3CH_2OH$ (749.557): C 28.84, H 4.98, Cl 9.46, Cu 16.96, N 20.56, O 19.21; found: C 28.88, H 4.92, Cl 9.64, Cu 16.60, N 20.12, O 19.64.

μ-Azido{μ-{1,1′-[(1H-pyrazol-1-ido-3,5-diyl)bis(methylene)]bis[1,4,7-triazacyclononane]}}dicopper(II) Bis-(hexafluorophosphate) ($[Cu_2(LH_{-1})(N_3)](PF_6)_2$; **4**). From a soln. (*ca.* 20 ml) containing $CuCl_2$ (24.7 mg, 0.142 mmol), **1** (0.067 mmol; obtained from **1** · 7HBr (68.8 mg) by anion exchange with *Dowex 2*), NaN_3 (4.8 mg, 0.07 mmol), $(NH_4)PF_6$ (34.8 mg, 0.21 mmol), and NaOH (3.6 mg, 0.09 mmol), green needles formed within 3 days. These were used for the X-ray diffraction study.

X-Ray Diffraction Measurements. The crystal data and parameters of the data collection for complex **4** are given in *Table 1*. Unit-cell parameters were determined by accurate centring of 24 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. The structures were solved by *Patterson* techniques using the program SHELXS-86 [10]. Absorption correction was calculated using DIFABS [11]. Anisotropic least-squares refinements were carried out on all non-H-atoms, using the program CRYSTALS [12]. H-Atoms are in calculated positions with C–H distances of 1.0 Å and fixed isotropic thermal parameters. Scattering factors are taken from the 'International Tables for Crystallography' [13]. Fractional coordinates are deposited at the *Cambridge Crystallographic Data Centre.*

Table 1. *Crystal Data and Parameters of Data Collection for* **4**

Formula	$(C_{17}H_{33}N_8Cu_2)(N_3)(PF_6)_2(H_2O)$	Temperature	room temp.
Mol. wt.	826.55	Θ_{max}	28
Crystal system	monoclinic	Radiation	MoK_α (λ = 0.71069 pm)
Space group	$P2_1/N$	Scan type	$\omega/2\Theta$
a [pm]	837.7 (9)	Refl.	$+/-h,+k,+l$
b [pm]	2523.8 (5)	μ [cm^{-1}]	16.581
c [pm]	1399.4 (5)	F(000)	1672
α [deg]	90	No. of indep. refl.	7106
β [deg]	91.97 (5)	No. of refl. in ref.	3806
γ [deg]	90	No. of variables	406
Z	4	Final R value	0.0393
Volume [pm^3]	$2957.01 \cdot 10^6$	Final R_w value	0.0427
Density [kg/dm^3]	1.857		

Potentiometric Titrations. Automatic titrator, as described previously [14], at 25 ± 0.1° and I = 0.5M (KNO_3). Typical concentrations: $C_L = 1.4 \cdot 10^{-3}$ M with $C_{Cu} = 0$, or $1.2 \cdot 10^{-3}$, or $2.4 \cdot 10^{-3}$ M. The equilibration of the Cu^{2+}/ligand titrations was relatively slow, so the waiting time between the 0.4M NaOH additions was kept at 480 s and the pH tolerance at 0.001 pH units. Calibration of the electrode and determination of α_H and pK_w was performed as described [14]. The evaluation of the protonation and stability constants was done with the program TITFIT [15], in which the stability constants are defined by *Eqn. 1* where a_H is the proton activity.

$$\beta_{mlh} = \frac{[M_m L_l H_h]}{[M]^m [L]^l a_H^h} \qquad (1)$$

Spectrophotometric Titrations. Automatic setup as described in [16], using 1-cm quartz cuvettes and working at 25 ± 0.1° and I = 0.5M (KNO_3). Typical concentrations: $C_L = 5 \cdot 10^{-3}$ M, $C_{Cu} = 4.5 \cdot 10^{-3}$ or $9 \cdot 10^{-3}$ M, titrant

0.4M NaOH. To determine the stability constant of the ternary complex $[Cu_2(LH_{-1})(N_3)]^{2+}$, 2 ml of a 10^{-3} M buffered soln. (0.1M 2,4,6-collidine pH 5.3–7.5, or 0.1M borax pH 9.14) of the binuclear Cu^{2+} complex was titrated with 0.05–0.5M NaN_3, which was added in 10-μl aliquots up to 0.25 ml. Equilibration was fast, so that the waiting time between the additions was kept at 60 s. The calculations were done with SPECFIT [17], assuming that under these conditions, only the 2:1 species are present.

Magnetic Measurements. The temperature dependence of the molar magnetic susceptibility of $[Cu_2(LH_{-1})(N_3)](PF_6)_2$ was measured between 1.7 and 400 K at 5000 G in a *Suprasil* quartz tube with a *SQUID* magnetometer *MPMS 5S* (*Quantum Design*, San Diego). Diamagnetic corrections were done using the values tabulated in [18]. In addition, the magnetic moment was also determined in aq. soln. by the method of *Evans* [19]. A $1.06 \cdot 10^{-5}$ M soln. of $[Cu_2(LH_{-1})(N_3)](ClO_4)_2$ in 2% *t*-BuOH/H_2O gave a shift $\Delta\nu = 5.16$ Hz of the NMR signal, resulting in a magnetic moment of 1.36 B.M.

Results and Discussion. – *Synthesis.* The synthesis of the new ligand **1** was straightforward (see *Scheme*). On one side we used the doubly *N*-protected 1,4,7-triazacyclononane derivative **2** with one N-atom still accessible for alkylation, and on the other side 3,5-bis(chloromethyl)-1*H*-pyrazole as bifunctional alkylating agent. The trityl (triphenylmethyl; Tr) group was, in our hands, the best protecting group since the disubstituted product could easily be isolated from the reaction mixture by flash chromatography, and the trityl group could be cleaved off under mild conditions at the end of the synthesis. The alkylation yielded compound **3**, the final product **1** being obtained by deprotection with diluted acid.

Structure. The ligand **1** binds two Cu^{2+} ions, and the complex can be crystallized, when N_3^- is added as an additional bridging group. The X-ray diffraction of this binuclear species shows two pentacoordinated Cu^{2+} ions with a somewhat distorted square pyramidal coordination geometry (*Fig. 1*). In the equatorial plane there are two N-atoms stemming from the 1,4,7-triazacyclononane moiety, one from the pyrazolide and one from the N_3^-, the latter two both bridging the two metal centres. The equatorial Cu–N bond lengths (*Table 2*) are normal (1.93–2.07 Å). In the axial position of the square pyramid, we find an additional N-atom from the 1,4,7-triazacyclonanone unit, with a Cu–N bond (2.16–2.18 Å) distinctly longer than the equatorial ones. The two Cu^{2+} ions, the pyrazolide N-atoms, and the azide ion form a nearly planar arrangement. The Cu^{2+}–Cu^{2+} distance is 4.15 Å.

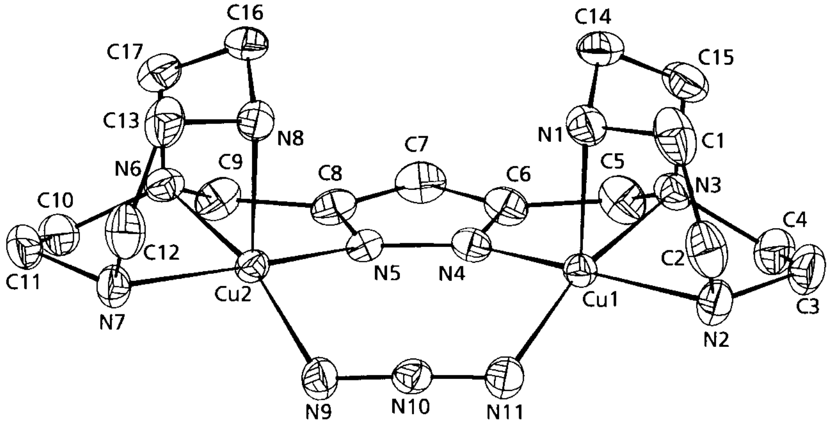


Fig. 1. *ORTEP Plot of* **4**

Table 2. *Selected Bond Lengths* [Å] *and Angles* [deg] *in the Structure of* **4**

Cu(1)–N(1)	2.180 (4)	Cu(2)–N(8)	2.164 (4)
Cu(1)–N(2)	1.990 (4)	Cu(2)–N(7)	1.994 (4)
Cu(1)–N(3)	2.070 (3)	Cu(2)–N(6)	2.061 (3)
Cu(1)–N(4)	1.934 (3)	Cu(2)–N(5)	1.938 (3)
Cu(1)–N(11)	1.987 (4)	Cu(2)–N(9)	2.000 (4)
N(1)–Cu(1)–N(2)	84.0 (2)	N(8)–Cu(2)–N(7)	84.1 (2)
N(1)–Cu(1)–N(3)	84.4 (1)	N(8)–Cu(2)–N(6)	85.2 (1)
N(1)–Cu(1)–N(4)	104.0 (2)	N(8)–Cu(2)–N(5)	101.5 (1)
N(1)–Cu(1)–N(11)	109.0 (2)	N(8)–Cu(2)–N(9)	109.5 (2)
N(2)–Cu(1)–N(3)	85.2 (2)	N(7)–Cu(2)–N(6)	85.2 (1)
N(2)–Cu(1)–N(4)	164.9 (2)	N(7)–Cu(2)–N(5)	166.1 (1)
N(2)–Cu(1)–N(11)	91.1 (2)	N(7)–Cu(2)–N(9)	91.2 (1)
N(3)–Cu(1)–N(4)	83.0 (2)	N(6)–Cu(2)–N(5)	82.6 (1)
N(3)–Cu(1)–N(11)	165.6 (2)	N(6)–Cu(2)–N(9)	164.4 (2)
N(4)–Cu(1)–N(11)	98.2 (2)	N(5)–Cu(2)–N(9)	98.8 (1)

The temperature dependence of the magnetic susceptibility measured from 1.7 to 400 K shows that, beside a small paramagnetic impurity, the binuclear complex exhibits a strong antiferromagnetic coupling (*Fig. 2*). The magnetic moment calculated at room temperature (298 K) is 1.30 B.M. for the two Cu^{2+}, instead of about 3.4 B.M., and is comparable to the value 1.36 B.M. obtained in H_2O solution, indicating that the structure found in the solid remains intact in solution.

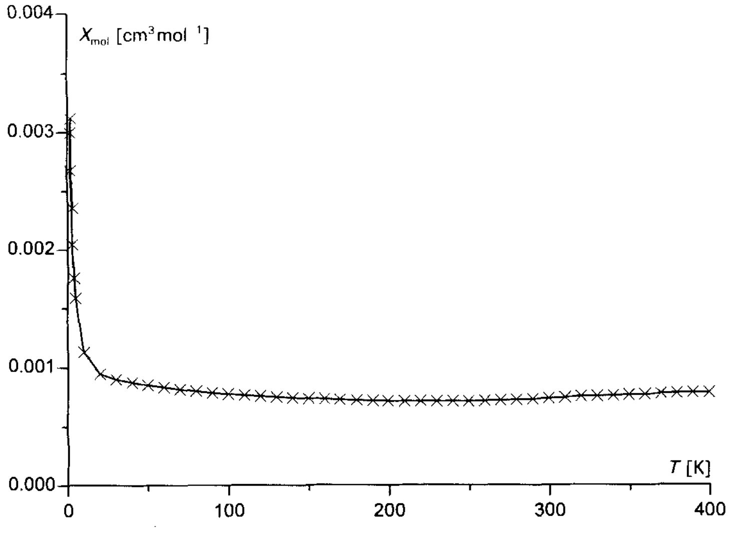


Fig. 2. *Temperature dependence of the corrected molar magnetic susceptibility of* **4**

Potentiometric and Spectrophotometric Titrations. The pH titration of the ligand gives four pK_H values, which correspond to the double protonation of the two 1,4,7-triazacyclononane units (*Table 3*). The differences $\Delta pK_{1,2}$ and $\Delta pK_{3,4}$ are close to the statistical values and indicate that the two protonation sites are relatively independent of each

Table 3. *Protonation and* Cu^{2+} *Complex Stability Constants of* **1** (= L) *at 25° and* I = *0.5* M (KNO_3)

	β_{mlh}[a])	pK_H Values	λ_{max} (ε)[b])
LH_4^{4+}	34.67 (3)	6.08	–
LH_3^{3+}	28.59 (3)	6.80	–
LH_2^{2+}	21.79 (2)	10.54	–
LH^+	11.25 (2)	11.25	–
$[Cu(LH_2)]^{4+}$	35.64 (2)[c])	5.90	650 (115)
$[Cu(LH)]^{3+}$	29.54 (2)	7.08	644 (120)
$[CuL]^{2+}$	22.46 (1)	10.70	624 (110)
$[Cu(LH_{-1})]^+$	11.76 (1)		623 (121)
$[Cu_2L]^{4+}$	32.90 (3)	3.69	649 (179)
$[Cu_2(LH_{-1})]^{3+}$	29.21 (3)	6.55	647 (238)
$[Cu_2(LH_{-2})]^{2+}$	22.66 (1)		626 (233)

[a]) Mean value and standard deviation between two batches.

[b]) λ_{max} in nm and ε in M^{-1} cm^{-1}.

[c]) Determined spectrophotometrically, all other values obtained potentiometrically.

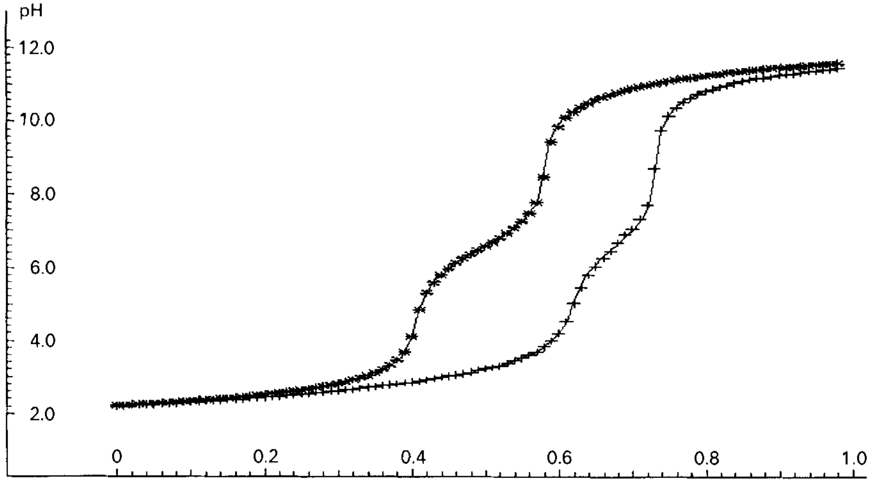


Fig. 3. *Titration of* **1** *in the presence of* Cu^{2+}. [L] = $1.42 \cdot 10^{-3}$ M, [Cu^{2+}] = $1.23 \cdot 10^{-3}$ M (*), and [Cu^{2+}] = $2.45 \cdot 10^{-3}$ M (+). Curves are calculated with the constants of *Table 3* to give $\sigma_{ml} = 1.0 \cdot 10^{-3}$.

other. The third protonation of the triaza ring, as well as the protonation of the pyrazole could not be determined and must be below 2.5.

Titrations of **1** in the presence of 1 or 2 equiv. of Cu^{2+} (*Fig. 3*) allow to detect a series of mononuclear ($[Cu(LH_2)]^{4+}$, $[Cu(LH)]^{3+}$, $[CuL]^{2+}$, and $[Cu(LH_{-1})]^+$) and binuclear ($[Cu_2L]^{4+}$, $[Cu_2(LH_{-1})]^{3+}$, and $[Cu_2(LH_2)]^{2+}$) complexes. The stability constants of these species can be determined potentiometrically, except that of $[Cu(LH_2)]^{4+}$, which is so stable, that it is already present at the beginning of the titration. We thus had to determine the stability constant of $[Cu(LH_2)]^{4+}$ by spectrophotometric titrations at low pH values. The fitting of the experimental data gives log β_{112} = 35.64 (*Fig. 4*). This value was trans-

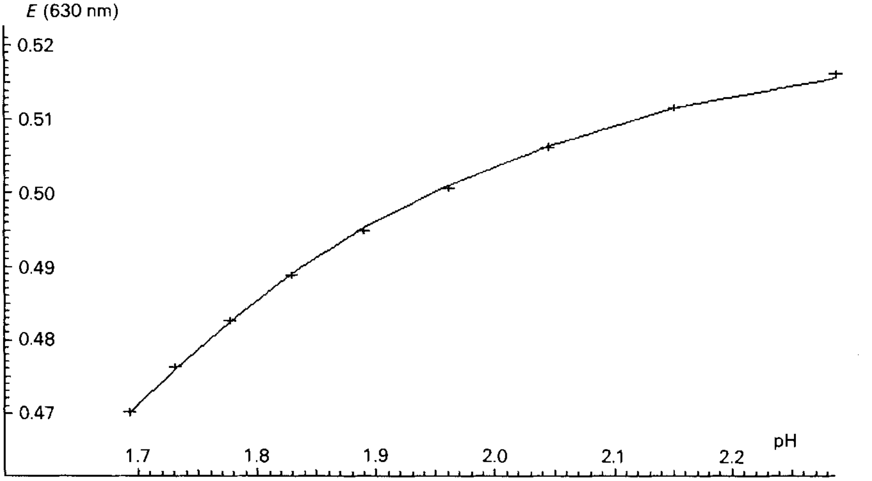


Fig. 4. *Spectrophotometric titration of* $[L] = 5 \cdot 10^{-3}$ M *and* $[Cu^{2+}] = 4.9 \cdot 10^{-3}$ M. The curve is calculated with $\log \beta_{112} = 35.64$.

ferred to the pH titrations and kept fixed, whereas the other log β values were varied as parameters to obtain the best fit of the two titration curves. The results are collected in *Table 3* and the species distribution is shown in *Figs. 5* and *6*.

In the mononuclear species, the metal ion probably coordinates to only one of the two macrocycles and possibly also to the pyrazole moiety. The other triazacyclononane ring not involved in coordination can, therefore, easily be protonated, which explains the appearance of species such as $[Cu(LH_2)]^{4+}$ and $[Cu(LH)]^{3+}$. Since it is well known that pyrazole can be deprotonated, when it binds to a metal ion, the question arises at what stage this happens. The absorption spectra of the species are here of help: $[Cu(LH_2)]^{4+}$ and $[Cu(LH)]^{3+}$ have absorption maxima at 650 and 644 nm, respectively, whereas $[CuL]^{2+}$ and $[Cu(LH_{-1})]^{+}$ absorb at 624 and 623 nm, respectively. Thus, we assume that the deprotonation of $[Cu(LH)]^{3+}$ to $[CuL]^{2+}$ corresponds to the formation of the pyrazolide anion which is accompanied by an increase of the ligand field and by the shift in the absorption maximum. The last deprotonation step to give $[Cu(LH_{-1})]^{+}$ must, therefore, be the neutralization of the last proton, attached to the uncoordinated triazacyclononane unit.

Ligand **1** was specifically designed to give binuclear species and indeed, we find $[Cu_2L]^{4+}$, $[Cu_2(LH_{-1})]^{3+}$, and $[Cu_2(LH_{-2})]^{2+}$ in solution (*Fig. 6*). In $[Cu_2L]^{4+}$, the two Cu-atoms interact with the two triazacyclononane units and possibly also with the pyrazole moiety. The absorption spectrum with λ 649 nm closely resembles that of $[Cu(LH_2)]^{4+}$ and $[Cu(LH)]^{3+}$, thus indicating a similar set of donor atoms. The structure of the species $[Cu_2(LH_{-2})]^{2+}$ is not problematic, since one can expect that the pyrazole moiety becomes deprotonated, which allows it to bridge the two metal centres, as shown in the crystal structure, and that an OH^- can be taken up additionally. More difficult is the discussion of the structure of $[Cu_2(LH_{-1})]^{3+}$, since the stoichiometry can be explained as well by the deprotonation of the pyrazole moiety as by the addition of one OH^-. The spectral change from $[Cu_2L]^{4+}$ to $[Cu_2(LH_{-1})]^{3+}$ is only minor from 649 to 647 nm, but we have to

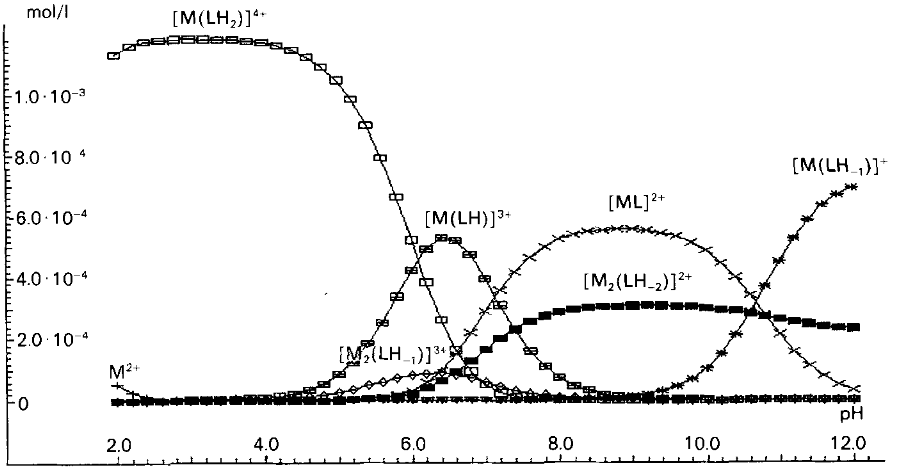


Fig. 5. *Calculated species distribution with the constants of* Table 3 *for* $[L] = 1.42 \cdot 10^{-3}$ M *and* $[Cu^{2+}] = 1.23 \cdot 10^{-3}$ M

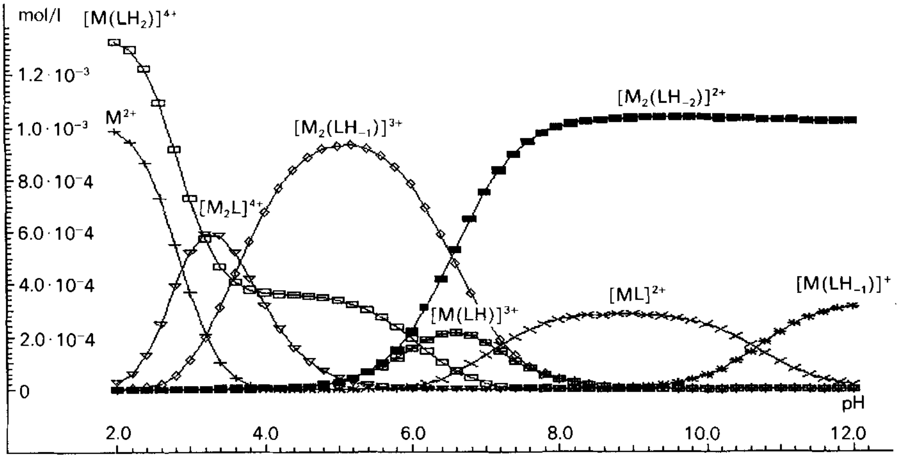


Fig. 6. *Calculated species distribution with the constants of* Table 3 *for* $[L] = 1.42 \cdot 10^{-3}$ M *and* $[Cu^{2+}] = 2.45 \cdot 10^{-3}$ M

remember that the ligand-field strength of the pyrazolide is now split between two metal ions and, therefore, cannot be so large as in the mononuclear species.

The best proof for the structure of $[Cu_2(LH_{-1})]^{3+}$ comes from the study of its reactivity with N_3^-, with which a ternary complex is formed. Titrations of $[Cu_2(LH_{-1})]^{3+}$ with N_3^- clearly shown an interaction between the Cu^{2+} coordinated by the bis-macrocycle and the azide anion, since the absorption spectrum strongly changes from 626 nm ($\varepsilon = 233$ M^{-1} cm^{-1}) to 601 nm ($\varepsilon = 606$ M^{-1} cm^{-1}) (*Fig. 7*). Quantitative studies using the program SPECFIT allow to fit the experimental data with *Eqn. 2*, where K_{ter} is the stability constant for the ternary complex.

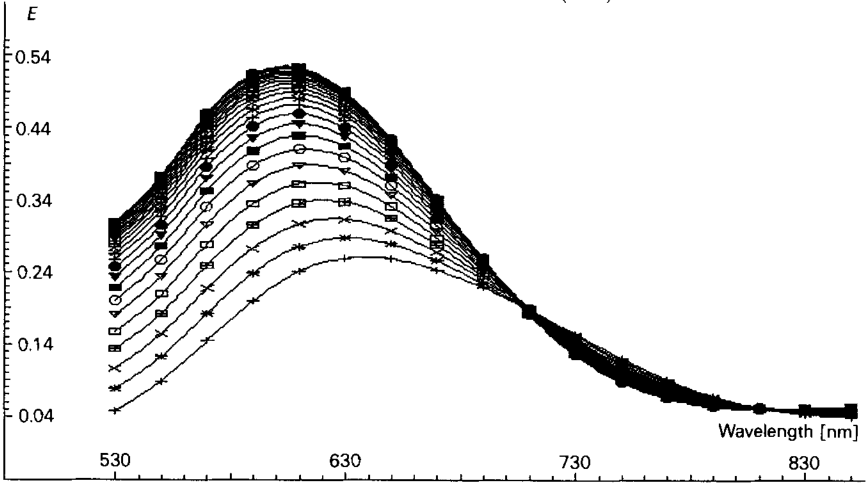


Fig. 7. *Spectrophotometric titration of* $[Cu_2L]^{4+}$ ($1 \cdot 10^{-3}$ M) *with increasing amounts of* N_3^- *at pH 5.35*

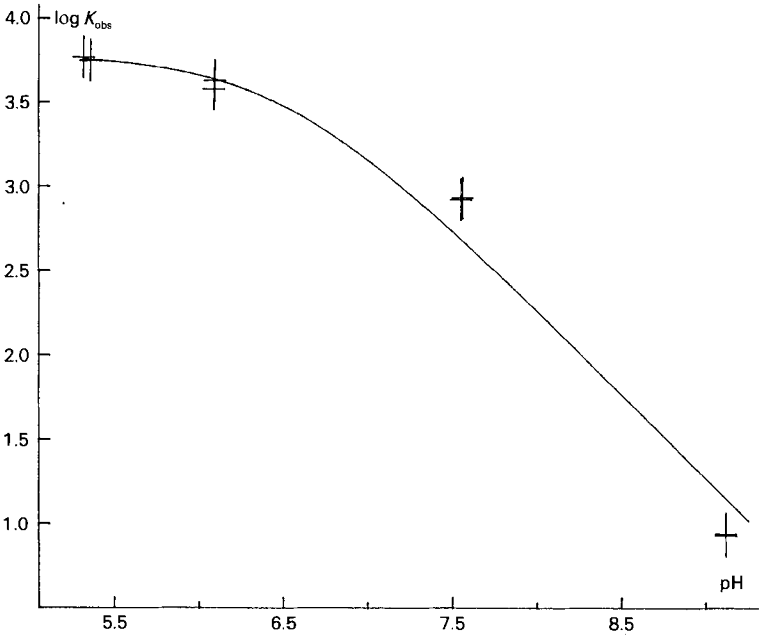


Fig. 8. *pH Dependence of log* K_{obs} *for the reaction of* Eqn. 3. The curve is calculated with log K_{ter} = 3.8 ± 0.1 and log K_H = 6.5 ± 0.2.

$$[Cu_2(LH_{-1})]^{3+} + N_3^- \rightleftharpoons [Cu_2(LH_{-1})(N_3)]^{2+};\ K_{ter} = [[Cu_2(LH_{-1})(N_3^-)]^{2+}]/[[Cu_2(LH_{-1})]^{3+}][N_3^-] \quad (2)$$

Experiments at different pH values reveal that the observed constant K_{obs} is pH dependent, so that *Eqn. 3* must also be taken into account. Combining *Eqns. 2* and *3*, one obtains *Eqn. 4*, which describes the pH dependence of the observed stability constant K_{obs}.

$$[Cu_2(LH_{-1})]^{3+} \rightleftharpoons [Cu_2(LH_{-2})]^{2+} + H^+; \; K_H \tag{3}$$

$$K_{obs} = K_{ter} \cdot \frac{K_H + [H^+]}{[H^+]} \tag{4}$$

As shown in *Fig. 8* the fitting of the values K_{obs} with *Eqn. 4* allows to determine log $K_{ter} = 3.8 \pm 0.1$ and log $K_H = 6.5 \pm 0.2$, which compares well with the potentiometric data (6.55). We, therefore, suggest that most probably OH^- and N_3^- are competing for the same coordination sites, the OH^- inhibiting the addition of N_3^-, whereas a similar competition with the pyrazolide ion seems less probable. Thus, we conclude that $[Cu_2(LH_{-1})]^{3+}$ is the species with the deprotonated pyrazole moiety bridging the two Cu^{2+} ions and that N_3^- is the second bridging group, as shown in the solid state by X-ray diffraction.

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