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Stability and structure of mono- and dinuclear Cu(II), Ni(II) and Zn(II) complexes of pyrazole and triazole bridged bis-macrocycles †

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The two ligands $\mathbf{L^1}$ and $\mathbf{L^2}$, consisting of two 1,4,7-triazacyclononane rings bridged by a pyrazole or a triazole group, form with Cu^{2+}, Ni^{2+} and Zn^{2+} a series of mononuclear $[MLH_n]^{(n+2)+}$ ($n = -3, -2, -1, 0, 1, 2$) and dinuclear species $[M_2LH_m]^{(m+4)+}$ ($m = 0, -1, -2, -3$), the stabilities of which have been determined by potentiometric titrations. The triazole bridged ligand $\mathbf{L^1}$ forms complexes which are more stable than those of the pyrazole bridged system $\mathbf{L^2}$. It also shows a higher tendency to form dinuclear species compared to $\mathbf{L^2}$. In addition two dinuclear species $[Cu_2(\mathbf{L^2}H_{-1})(\mu\text{-}Ph_2PO_2)](ClO_4)_2\cdot MeCN$ and $[Cu_4(\mathbf{L^2}H_{-1})_2(\mu_4\text{-}PO_4)](ClO_4)_3\cdot MeCN\cdot H_2O$ have been isolated as solids and their X-ray structures have been determined. In the first complex we find a dinuclear Cu^{2+} species which is bridged by the pyrazolide group as well as by the exogenous diphenyl phosphinate. In the second case a μ_4-phosphate ion bridges two dinuclear units, resulting in a tetranuclear species.

Introduction

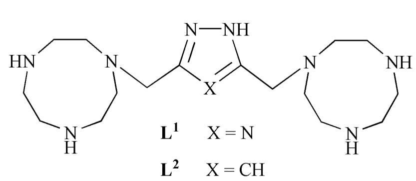
Imidazole, pyrazole and triazole are heterocyclic bases which are able to coordinate either one or as bridging ligands two metal ions. Especially interesting are their dinuclear complexes since with them one can study interactions between the two metal centres kept at a fixed distance by the bridging unit.[1]

An example for such a dinuclear species is found in the enzyme superoxide dismutase[2] in which an imidazole of a histidine side chain bridges the Cu^{2+} and Zn^{2+} ions present in the active site. In addition there are many examples of low molecular weight complexes in which these heterocyclic bases form homo- and heterodinuclear species. Thus imidazole containing ligands have been used to prepare dinuclear Cu^{2+},[3] Ni^{2+},[4] and Zn^{2+} [5] complexes as well as a series of model compounds which mimic superoxide dismutase.[6] Similary pyrazole based ligands can give dinuclear Cu^{2+},[7] Ni^{2+},[8] and Zn^{2+} [9] complexes some of which have been proposed as models for tyrosinase and laccase[10] or for urease.[11]

The situation for 1,2,4-triazole is somewhat different since this ligand can form dinuclear species using either N^1 and N^2,[12] the two nitrogen adjacent to each other, or N^1 and N^4 the two distal nitrogens, in the so called "long bridging mode".[13] In some instances triazole can even use all of its three nitrogens to bridge three metal ions as observed in a Zn^{2+} complex.[14]

For 1,2,4-triazole derivatives dinuclear complexes with Cu^{2+} and Ni^{2+},[15] in which the endogenous triazole bridges in the N^1,N^2 mode, and dinuclear complexes with Os^{2+} and Ru^{2+},[16] with triazole in the N^1,N^4 bridging mode, are known.

Having previously studied the coordination ability of the pyrazole bridged ligand $\mathbf{L^2}$ in solution[17,18] and in the solid state towards Cu^{2+},[17–19] we have now extended our investigations to Ni^{2+} and Zn^{2+}. In addition we have prepared the new ligand $\mathbf{L^1}$ with a triazole bridging unit to compare with $\mathbf{L^2}$.



L¹ X = N
L² X = CH

Experimental

Syntheses

All starting materials were purchased either from Fluka, Aldrich or Merck. Ligand $\mathbf{L^2}$ and 1,4,7-triazatricyclo[5.2.1.0^{4,10}]-decane **4** were synthesized according to reported methods.[19,20] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC250 instrument at room temperature and the chemical shifts are referred to the residual solvent signal. IR spectra were recorded on a Perkin-Elmer-1600 spectrophotometer (KBr pellets). Mass spectra were recorded on a Finnigan MAT Electrospray-Mass spectrometer; microanalyses were performed by the Microlaboratory of the Institute of Organic Chemistry of the University of Basel.

4-Amino-3,5-bis(hydroxymethyl)-1,2,4-triazole (1). Glycolic acid (38 g, 0.5 mol) and hydrazine monohydrate were heated for 6 h at 100 °C. Then the excess of hydrazine and the reaction water were evaporated in such a way that the temperature increased within 3 h from 112 to 165 °C. The reaction mixture was then kept for 3 h at 165–168 °C. After cooling to r.t., the solid crude product was recrystallized from water, washed with EtOH and dried under high vacuum: 49 g (68%). Mp. 207–208 °C (208 °C[21]). MS (FAB): 144 [M$^+$], 126 [M − H$_2$O]$^+$, 110 [M − H$_2$O − NH$_2$]$^+$. ^{1}H NMR (DMSO-d$_6$): δ 4.55 (d, 4H, 2 CH_2OH, $^3J_{HH} = 6.03$ Hz), 5.39 (t, 2H, 2 CH_2OH, $^3J_{HH} = 6.03$ Hz) and 5.81 (s, 2H, NNH$_2$).

3,5-Bis(hydroxymethyl)-1*H*-1,2,4-triazole hydrochloride (2). Compound **1** (12 g, 0.083 mol) was dissolved in 18% HCl (30 ml). After stirring the solution for 15 min, the HCl was evaporated. The residue was then dissolved in water (50 ml) and an aqueous solution of NaNO$_2$ (6.9 g, 0.1 mol, 25 ml), was added dropwise. After stirring the solution at r.t. the water was evaporated and the white solid was extracted with butanol (4 × 100 ml) at 100 °C and filtered hot. After evaporating the butanol, the white crude product was crystallized from MeCN: 7.9 g (74%). Mp. 138–140 °C (139–140 °C[22]). MS (FAB): 129 [M]$^+$, 128 [M − H]$^+$, 118 [M − H − H$_2$O]$^+$. ^{1}H NMR (DMSO-d$_6$): δ 2.09 (s, 2H, 2 CH_2OH) and 4.47 (s, 4H, 2 CH_2OH).

3,5-Bis(chloromethyl)-1*H*-1,2,4-triazole hydrochloride (3). Compound **2** (6.00 g, 46.5 mmol) and thionyl chloride (50 ml) were refluxed for 1 h. After evaporating the thionyl chloride, the

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† Electronic supplementary information (ESI) available: titration curves and species distribution curves. See http://www.rsc.org/suppdata/dt/b2/b212113a/

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residue was dissolved in EtOH (50 ml). Under ice cooling HCl gas was bubbled through the solution for 30 min. After adding Et_2O and bubbling HCl gas for another 20 min, the mixture was filtered and the obtained white solid was dried under high vacuum. **CAUTION:** The dichloride is strongly skin irritant: 7.10 g (75%). Mp. 108 °C. MS (FAB): 165 $[M - H]^+$, 130 $[M - Cl]^+$. ^1H NMR (DMSO-d_6): δ 4.78 (s, 4H, 2 CH_2Cl).

1,1′-[1*H*-1,2,4-Triazole-3,5-diyl)bis(methylene)]bis(1-azonia-4,7-diazatricyclo[5.2.1^{4,10}]decane) dichloride (5). A suspension of **4** (1.15 g, 5.70 mmol) in MeCN (30 ml) was heated with a solution of Et_3N (5.5 ml, 1 M) in MeCN and then filtered. This mixture was added over 15 min under N_2 at r.t. to **3** (1.59 g, 11.40 mmol), dissolved in absolute MeCN (30 ml), and stirred for 2 h at 50–60 °C. After stirring overnight under N_2 at r.t., the solution was filtered, the precipitate washed with Et_2O (3×), and dried at r.t. under high vacuum: 2.25 g (88%). ^1H NMR (CD_3OD): δ 2.91–3.98 (m, 28H, 12 CH_2N (macrocycle), 2 $C\mathit{H}_2N$–triazole) and 6.12 (s, 1H, CH).

4,4′-[(1*H*-Triazole-3,5-diyl)bis(methylene)]bis[octahydro-1*H*-1,4,7-triazonine-1-carbaldehyde] (6). A solution of **5** (2.25 g, 5.06 mmol) in H_2O (40 ml) was refluxed for 20 h. Evaporation gave 2.43 g of **6** (100%). MS (FAB): 408 $[M + H]^+$. ^1H NMR (CD_3OD): δ 2.84–4.01 (m, 28H, 12 CH_2N (macrocycle), 2 $C\mathit{H}_2N$–triazole) and 8.02, 8.14 (2s, 2H, 2 CHO).

1,1′-[(1*H*-1,2,4-Triazole-3,5-diyl)bis(methylene)]bis[octahydro-1*H*-1,4,7-triazonine] heptahydrochloride (7). A solution of **6** (2.43 g, 5.06 mmol) in H_2O (20 ml) and 36% HCl (10 ml) was stirred for 2 h at 70–75 °C and 19 h at r.t. Evaporation gave 2.49 g (81%) hygroscopic crystals. ^1H NMR (D_2O): δ 3.08 (t, 8H, 4 $C\mathit{H}_2NCH_2$–triazole, $^3J_{HH}$ = 5.35 Hz), 3.39 (t, 8H, 4 $C\mathit{H}_2CH_2NCH_2$–triazole, $^3J_{HH}$ = 5.35 Hz), 3.73 (s, 8H, 4 CH_2N (macrocycle)), 4.10 (s, 4H, 2 $C\mathit{H}_2$–triazole).

1,1′-[(1*H*-1,2,4-Triazole-3,5-diyl)bis(methylene)]bis[octahydro-1*H*-1,4,7-triazonine] pentahydrobromide (L^1·5HBr). A solution of **7** (2.49 g, 4.10 mmol) was converted into the free base by ion exchange (DOWEX 2 × 8, loaded with OH^-). The eluted solution was concentrated to 25 ml, to which 47% HBr (20 ml) and charcoal (2 g) were added. The mixture was stirred for 48 h, filtered and evaporated. After crystallization from MeOH the pure pentahydrobromide salt was obtained: 1.29 g (66%). ^1H NMR (D_2O): δ 3.08 (t, 8H, 4 $C\mathit{H}_2NCH_2$–triazole, $^3J_{HH}$ = 5.35 Hz), 3.37 (t, 8H, 4 $C\mathit{H}_2CH_2NCH_2$–triazole, $^3J_{HH}$ = 5.35 Hz), 3.70 (s, 8H, 4 CH_2N (macrocycle)), 4.11 (s, 4H, 2 $C\mathit{H}_2$–triazole). ^{13}C NMR (D_2O): δ 42.9, 43.0, 48.4 (CH_2N (macrocycle)), 49.9 ($N\mathit{C}H_2$–triazole); 157.09 (triazole). Found: C, 24.21; H, 5.10; N, 15.51; O, 4.69. Calc. for $C_{17}H_{39}N_9Br_5$·H_2O (810.52): C, 24.10; H, 5.38; N, 15.81; O, 4.61%.

μ-Diphenylphosphinato{μ-{1,1′-[(1*H*-pyrazol-1-ido-3,5-diyl)-bis(methylene)]bis[1,4,7-triazacyclononane]}}dicopper(II) perchlorate (8). L^2·5HBr (150 mg, 0.185 mmol) was converted by ion exchange (DOWEX 2 × 8, loaded with OH^-) into the free base. To the free base, dissolved in EtOH (2 ml), $Cu(ClO_4)_2$·$6H_2O$ (137 mg, 0.370 mmol) and Ph_2PO_2H (29 mg, 0.185 mmol), dissolved in 2 ml water, were added. The pH was adjusted with NaOH to 5.5. On standing overnight at 4 °C, blue crystals of the complex formed. The crystals were recrystallized from MeCN–Et_2O and used for the X-ray diffraction study. MS (ES): 793 $[M - ClO_4^-]^+$, 348 $[M - 2ClO_4^-, - Ph_2PO_2]^+$.

$[(Cu_2LH_{-1})_2(\mu_4\text{-}PO_4)](ClO_4)_3$·MeCN·$H_2O$ (9). L^2·5HBr (150 mg, 0.185 mmol) was converted by ion exchange (DOWEX 2 × 8, loaded with OH^-) into the free base. To the free base, dissolved in EtOH (2 ml), $Cu(ClO_4)_2$·$6H_2O$ (137 mg, 0.370 mmol) and NaH_2PO_4·H_2O (26 mg, 0.185 mmol), dissolved in water (2 ml), were added. The pH was adjusted with NaOH to 5.5. On standing overnight at 4 °C, blue crystals of the complex formed. The crystals were recrystallized from MeCN–Et_2O and used for the X-ray diffraction study. MS (ES, MeOH–H_2O = 20 : 1): 573 $[Cu_4L_2 - 2ClO_4^-]^{2+}$, 473 $[Cu_4L_2 - Cu_2L - ClO_4^- - PO_4^{3-} - 2H^+]^+$, 349 $[Cu_4L_2 - 3ClO_4^-]^{3+}$. IR (KBr): 3343m, 2934m, 2865m, 1632w, 1455w, 1088vs.

μ-Halogenido{μ-{1,1′-[(1*H*-pyrazol-1-ido-3,5-diyl)bis(methylene)]bis[1,4,7-triazacyclononane]}}dicopper(II) perchlorate (8). L^1·5HBr (150 mg, 0.185 mmol) was converted by ion exchange (DOWEX 2 × 8, loaded with OH^-) into the free base. To the free base, dissolved in EtOH (2 ml), $Cu(ClO_4)_2$·$6H_2O$ (137 mg, 0.370 mmol) and NH_4Br (18 mg, 0.185 mmol) or NH_4Cl (10 mg, 0.185 mmol) or NaN_3 (12 mg, 0.185 mmol) dissolved in water (2 ml), were added. The pH was adjusted with NaOH to 5. On standing overnight at 4 °C, blue crystals (bromide, chloride) or dark green crystals (azide) of the complexes formed. The crystals were recrystallized from MeCN–Et_2O.

Chloride as bridging ligand: MS (ES, MeOH : H_2O = 20:1): 612 $[M - ClO_4^-]^+$, 575 $[M - ClO_4^- - Cl^- - H^+]^+$, 512 $[M - 2ClO_4^- - 2H^+]^+$; 475 $[M - 2ClO_4^- - Cl^- - 2H^+]^+$; 256$[M - 2ClO_4^-]^{2+}$. IR (KBr): 3331m, 2928m, 2876m, 1630w, 1459w, 1090vs. Found: C, 25.13; H, 4.93; N, 16.65. Calc. for $Cu_2C_{16}H_{32}N_9Cl_3O_8$·$H_2O$ (810.52): C, 25.39; H, 4.60; N, 16.53%.

Bromide as bridging ligand: MS (ES, MeOH : H_2O = 20 : 1): 656 $[M - ClO_4^-]^+$, 575 $[M - ClO_4^- - Br^- - H^+]^+$, 556 $[M - 2ClO_4^- - H^+]^+$; 475 $[M - 2ClO_4^- - Br^- - 2H^+]^+$. IR (KBr): 3326m, 2932m, 2876m, 1630w, 1459w, 1100vs. Found: C, 24.96; H, 4.35; N, 16.08. Calc. for $Cu_2C_{16}H_{32}N_9BrCl_2O_8$·$2.5H_2O$ (810.52): C, 24.82; H, 4.43; N, 16.28%.

Azide as bridging ligand: $Cu_2C_{16}H_{32}N_{12}Cl_2O_8$ (718.50): MS (ES, MeOH : H_2O = 20 : 1): 619 $[M - ClO_4^-]^+$, 576 $[M - ClO_4^- - N_3^- - H^+]^+$, 518 $[M - 2ClO_4^- - H^+]^+$; 475 $[M - 2ClO_4^- - N_3^- - 2H^+]^+$, 288 $[M - 2ClO_4^- - N_3^-]^{2+}$, 259 $[M - 2ClO_4^-]^{2+}$. IR (KBr): 3331m, 2924m, 2874m, 2046s, 1631w, 1459w, 1090vs.

Potentiometric titrations. pH titrations were run under N_2 at 25 ± 0.1 °C and I = 0.5 M (KNO_3) on the automatic titrator previously described,[23] consisting of a Metrohm 605 pH-meter, a Metrohm 665 burette, a thermostatted titration vessel and a 286-AT PC controlling the set up. Typical concentrations were: $[L] = 1.36 \times 10^{-3}$ M with $[M^{2+}] = 0$, 1.16×10^{-3} M, or 2.49×10^{-3} M. The equilibration of the $Ni^{2+}/\mathbf{L}^2$ titrations were slow, so the titrations could not be run automatically. In this case the potentiometric titrations were carried out by using the batch method. Calibration of the electrode and determination of a_H and pK_w was performed as described.[23] The evaluation of the protonation and stability constants was done with the program TITFIT,[24] in which the stability constants are defined by eqn. (1) where a_H is the proton activity.

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

Spectrophotometric titrations. Spectrophotometric titrations were run under N_2 at 25 ± 0.1 °C and I = 0.5 M (KNO_3), using 1 cm quartz cuvettes. To determine the stability constant of the ternary complex, 2 ml of a 1.25×10^{-3} M buffered solution (0.1 M 2,6-dimethylpyridine-3-sulfonic acid (LSS) as a non-coordinating buffer,[25] pH = 4.76), of the dinuclear Cu^{2+} complex was titrated with 0.5 M NaN_3, which was added in 2.5–10 μl aliquots up to 0.2 ml. Equilibration was fast, so that the waiting time between the additions was kept at 40 s. The calculations were done with SPECFIT,[26] assuming that under these conditions, only the 2 : 1 species $[Cu_2\mathbf{L}^1H_{-1}]^{3+}$ is present.

X-Ray diffraction analysis

The crystal data and parameters for the structure determination of the complexes **8** and **9** are given in Table 1. The crystal was

Table 1 Crystal data and parameters of data collection for **8** and **9**

Formula	$[Cu_2(\mathbf{L^2}H_{-1})(\mu\text{-}Ph_2PO_2)](ClO_4)_2\cdot MeCN$ (**8**)	$[Cu_4(\mathbf{L^2}H_{-1})_2(\mu_4\text{-}PO_4)](ClO_4)_3\cdot MeCN\cdot H_2O$ (**9**)
M	933.76	1405.58
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/pm	9.7727(5)	19.525(1)
b/pm	14.2779(5)	13.4970(3)
c/pm	14.5730(6)	21.1452(7)
α/°	97.943(3)	90
β/°	107.231(4)	97.582(4)
γ/°	98.560(3)	90
Z	2	4
V/pm^3	1884.4	5523.7
D_c/kg dm^3	1.645	1.690
T/K	173	193
Θ_{max}/°	30	32
Radiation	Mo-Kα ($\lambda = 0.71073$ Å)	Mo-Kα ($\lambda = 0.71073$ Å)
μ/cm^{-1}	1.381	1.775
F(000)	964	2896
No. of measured refl.	44970	23391
No. of indep. refl.	10606	14920
No. of refl. in refinement	7201	8143
No. of variables	513	827
Final R value	0.0418	0.0518
Final R_w value	0.0501	0.0476
R_{int}	0.06	0.05

Table 2 Protonation constants of $\mathbf{L^1}$ at 25 °C and $I = 0.5$ M (KNO_3)

Species	$\log\beta_{mlh}$	pK_H
$\mathbf{L^1}H_4^{4+}$	44.40(3)	5.90
$\mathbf{L^1}H_3^{3+}$	38.49(3)	6.77
$\mathbf{L^1}H_2^{2+}$	31.72(3)	9.27
$\mathbf{L^1}H^{+}$	22.44(2)	10.96
$\mathbf{L^1}$	11.48(2)	11.48

glued on a glass fibre and mounted on the diffractometer. Data were collected on a Bruker-Nonius KappaCCD area detector. The structures were solved by direct methods using the program SIR92.[27] Anisotropic refinement on all non-hydrogen atoms was carried out using the program CRYSTALS.[28] All hydrogen atoms are in calculated positions with the exception of those bound to nitrogen and oxygens atoms, which have been refined isotropically using appropriate restraints. Scattering factors were taken from the International Tables, Vol. IV, Table 2.2B.[29] The plots were created using ORTEP-3 for Windows.[30]

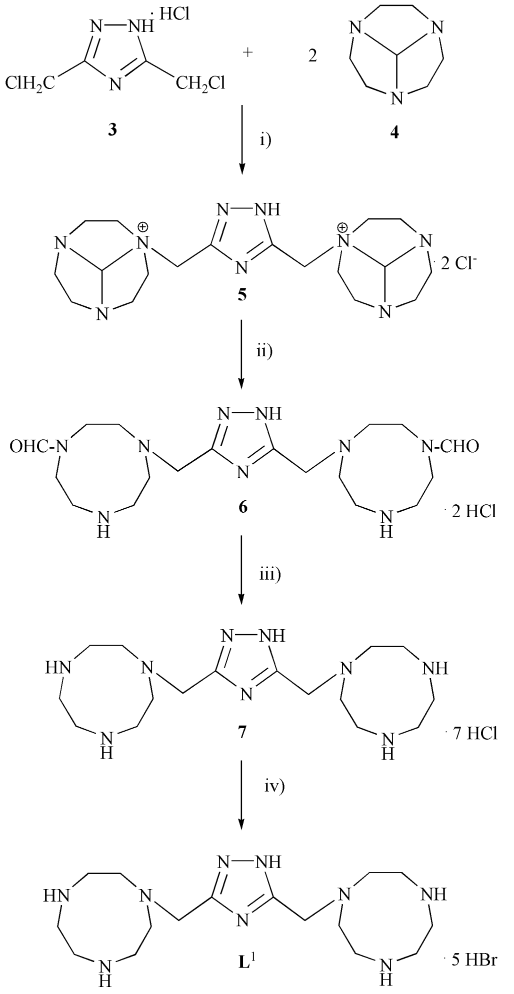
CCDC reference numbers 199305 and 199306.

See http://www.rsc.org/suppdata/dt/b2/b212113a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Symthesis

The synthesis of the bis-macrocyclic ligand $\mathbf{L^1}$ was carried out in analogy to that of ligand $\mathbf{L^2}$ by reaction of compound **4** with 3,5-bis(chloromethyl)-1*H*-1,2,4-triazole (**3**) as bifunctional alkylating agent (see Scheme 1), followed by the hydrolysis of the ortho amide in two steps.



Scheme 1 Reagents and conditions: (i) 1 equiv. Et_3N, MeCN, 80 °C, 2 h; (ii) H_2, 100 °C, 24 h; (iii) 36% HCl, 70 °C, 2 h; (iv) 47% HBr, charcoal, r.t., 24 h.

Potentiometric measurements

From potentiometric pH titrations of ligand $\mathbf{L^1}$ the pK_H values were determined (see Table 2). $\mathbf{L^1}$ can take up six protons but only four protonation steps can be determined. In addition $\mathbf{L^1}$ can be deprotonated at the triazole to give $\mathbf{L^1}H_{-1}^{-}$ Since the difference between the first and second protonation step ($\Delta\log K = 0.52$) as well as that between the fourth and fifth ($\Delta\log K = 0.87$) are close to the statistical values, and thus indicate that the proton additions are independent of each other, we propose that the sequence of protonations starting from $\mathbf{L^1}H_{-1}^{-}$ is such that each side of the molecule accepts one proton to give the symmetrical species $\mathbf{L^1}H^{+}$, followed by the protonation of the triazolide anion to give $\mathbf{L^1}H_2^{2+}$ and finally followed by the fourth and fifth protons which again are taken up by each side of the molecule to give $\mathbf{L^1}H_4^{4+}$. Titrations of the ligands (L = $\mathbf{L^1}$ or $\mathbf{L^2}$) in the presence of 0.85 or 1.85 equiv. of

Table 3 Complex stability of $\mathbf{L}^1$ and $\mathbf{L}^2$ at 25 °C and $I = 0.5$ M (KNO_3)

	$Cu^{2+}/\mathbf{L}^2$ (ref. 17)		$Ni^{2+}/\mathbf{L}^2$		$Zn^{2+}/\mathbf{L}^2$		$Cu^{2+}/\mathbf{L}^1$	$Zn^{2+}/\mathbf{L}^1$	
Species	$\log\beta_{mlh}$	pK_H	$\log\beta_{mlh}$	pK_H	$\log\beta_{mlh}$	pK_H	pK_H	$\log\beta_{mlh}$	pK_H
$[MLH_2]^{4+}$	35.64	5.90	33.3(1)	5.6	29.74(1)	6.02	4.72(1)	39.04(1)	5.68
$[MLH]^{3+}$	29.54	7.08	27.8(2)	7.6	23.72(2)	8.45	6.54(3)	33.36(1)	7.27
$[ML]^{2+}$	22.463	10.70	20.1(3)	9.8	15.27(3)	10.98	10.08(5)	26.09(1)	10.40
$[MLH_{-1}]^+$	11.763		10.3(3)	11.1	4.28(3)			15.69(2)	
$[MLH_{-2}]$			−0.8(3)						
$[M_2L]^{4+}$	32.90	3.69	29.5(1)	7.6	22.53(1)	7.27	2.11(1)	32.86(1)	4.16
$[M_2LH_{-1}]^{3+}$	29.21	6.55	21.9(2)	9.5	15.26(1)	8.29	7.78(2)	28.70(1)	8.97
$[M_2LH_{-2}]^{2+}$	22.66		12.4(2)		6.98(1)		12.17(4)	19.73(1)	10.88
$[M_2LH_{-3}]^+$								8.85(3)	

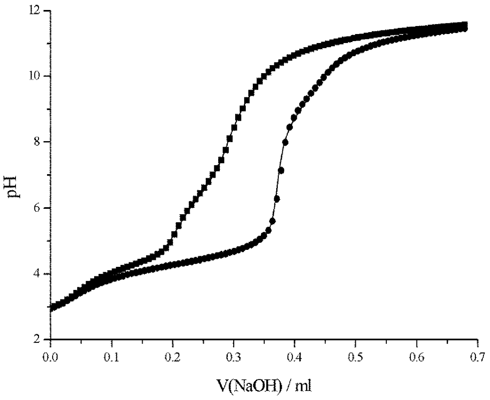


Fig. 1 Titration curves of $\mathbf{L}^1$ in the presence of 0.85 (■) and 1.85 (●) equivalents of Zn^{2+}, – fitting with the model given in Table 3.

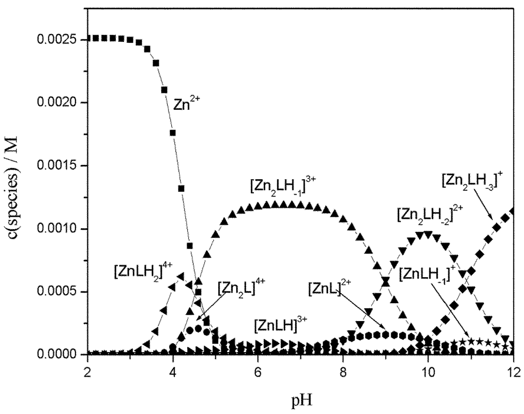


Fig. 3 Species distribution of the complexes of $\mathbf{L}^1$ with 1.85 equivalents of Zn^{2+}.

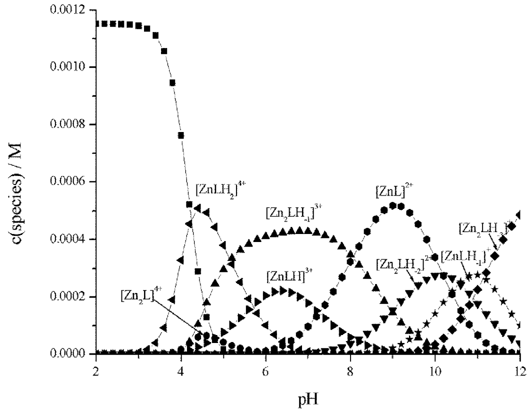


Fig. 2 Species distribution of the complexes of $\mathbf{L}^1$ with 0.85 equivalents of Zn^{2+}.

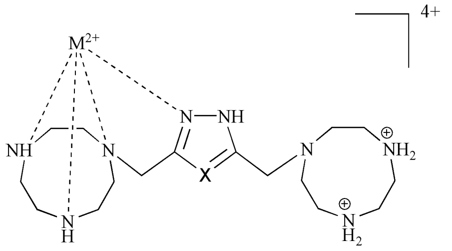


Fig. 4 Schematic structure for the mononuclear species $[MLH_2]^{4+}$. Solvent molecules have been omitted for clarity.

the respective metal ion (M = Cu^{2+}, Ni^{2+} or Zn^{2+}) were analyzed in batch calculations in which both titration curves are fitted at the same time with one model. The results of the fitting for Zn^{2+} are shown in Fig. 1. This allows the calculation of the stability constants and the pK_H-values of the mononuclear species ($[MLH_2]^{4+}$, $[MLH]^{3+}$, $[ML]^{2+}$, $[MLH_{-1}]^+$ and $[MLH_{-2}]$) as well as of the dinuclear complexes ($[M_2L]^{4+}$, $[M_2LH_{-1}]^{3+}$, $[M_2LH_{-2}]^{2+}$ and $[M_2LH_{-3}]^+$. The results are collected in Table 3 and the species distribution diagrams for Zn^{2+} and $\mathbf{L}^1$ are shown in Figs. 2 and 3.

Since in the case of Cu^{2+} and $\mathbf{L}^1$ the species $[Cu\mathbf{L}^1H_2]^{4+}$ is so stable, that it is already present at the beginning of the titration, no absolute stability constants could be determined.

In the mononuclear species (see Fig. 4), the metal ion probably coordinates to only one of the two macrocycles and possibly also to the heterocyclic base. The other triazacyclononane ring which is not involved in coordination can, therefore easily be protonated, which explains the appearance of species such as $[CuLH_2]^{4+}$.

The following protonated species result either from the deprotonation of the triazole or of the pyrazole group or of the protonated uncoordinated 1,4,7-triazacyclononane or of a water coordinated to the metal centre. It is difficult to assess the exact sequence of deprotonations starting from $[MLH_2]^{4+}$, specifically, at which pH the deprotonation of the heterocyclic moiety takes place in the mononuclear complexes. Analogous to the system $Cu^{2+}/\mathbf{L}^2$,[17] we assume that the deprotonation of $[MLH]^{3+}$ to $[ML]^{2+}$ corresponds to the formation of the pyrazolide anion respectively to the formation of the triazolide anion. The last deprotonation step to give $[MLH_{-1}]^+$ must therefore, be the neutralization of the last ammonium proton. In the case of Ni^{2+} and $\mathbf{L}^2$, however, the deprotonation of $[Ni\mathbf{L}^2]^{2+}$ to form $[Ni\mathbf{L}^2H_{-1}]^+$ corresponds to the formation of the pyrazolide anion, because the pK_H must be higher than the pK_H-value of $[Ni_2\mathbf{L}^2]^{4+}$ which represents the deprotonation of the pyrazole in the dinuclear complexes (see below). The formation of species $[Ni\mathbf{L}^2H_{-2}]$ can also be observed and corresponds to the coordination of a OH^- to the Ni^{2+}.

In the dinuclear species (see Fig. 5) each metal ion coordinates to one of the the two macrocycles and both metal ions interact with the pyrazole or triazole moiety. In analogy to the known $Cu^{2+}/\mathbf{L}^2$ system we assume that the deprotonation of $[M_2\mathbf{L}^1]^{4+}$ to give $[M_2\mathbf{L}^1H_{-1}]^{3+}$ corresponds to the deprotonation

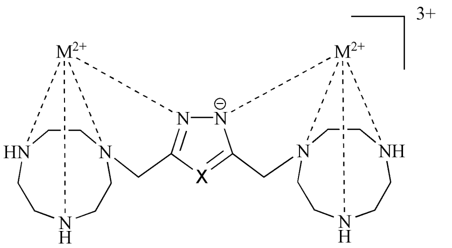


Fig. 5 Schematic structure for the dinuclear species $[M_2LH_{-1}]^{3+}$. Solvent molecules have been omitted.

of the triazole or pyrazole. The species $[M_2\mathbf{L}^1H_{-2}]^{2+}$ can be explained by the coordination of a hydroxide to one metal ion or as a bridging group between two ions. In the case of the system $Zn^{2+}/\mathbf{L}^1$ also the species $[M_2\mathbf{L}^1H_{-3}]^{2+}$ is found. This involves the coordination of a second hydroxyde.The stability of the individual mononuclear $[M\mathbf{L}^1H_n]^{(n\ +\ 2)+}$ and dinuclear species $[M_2\mathbf{L}^1H_m]^{(m\ +\ 4)+}$ decreases in the order $Cu^{2+} > Ni^{2+} > Zn^{2+}$ which corresponds with the Irving–Williams series.[31] The tendency to form dinuclear species also decreases in the same order. The triazole systems form more stable complexes than the pyrazole systems and have also a higher tendency to give dinuclear species.

Structures

The X-ray structure of the cation of the dinuclear complex **8** is shown in Fig. 6. In this structure, each Cu^{2+} is pentacoordinated with a somewhat distorted square pyramidal coordination geometry. In the equatorial plane there are two N-atoms stemming from the 1,4,7-triazacyclononane moiety, one from the pyrazolide and one O-atom of the diphenyl phosphinate. The equatorial Cu–N bond lengths are normal (1.94–2.06 Å) (see Table 4). In the axial position of the square pyramid, we find an additional N-atom from the 1,4,7-triazacyclononane unit, with a Cu–N bond distinctly longer (2.22 Å) than the equatorial ones. The two Cu^{2+}, the pyrazolide N-atoms, the P-atom and the two oxygen atoms of the exogenous bridging ligand form a nearly planar arrangement. The geometry and the bond lengths around the P-atom are similar to those of the free diphenyl phosphinate. The $Cu^{2+} \cdots Cu^{2+}$ distance is 4.21 Å. A search in the CSD database (September 2002) revealed that crystal structures of dinuclear complexes with different transition metals already exist in which two metal centres are μ-bridged by diphenyl phosphinate[32,33] but that our complex **8** is the first known dinuclear complex in which two Cu^{2+} centres are bridged in a μ-mode by diphenyl phosphinate.

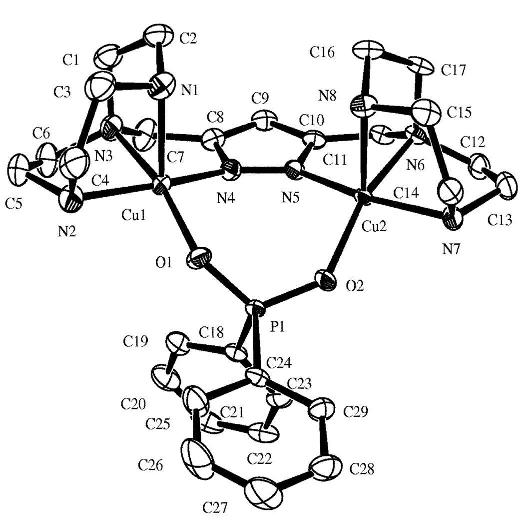


Fig. 6 Crystal structure of $[Cu_2(\mathbf{L}^2H_{-1})(\mu\text{-}Ph_2PO_2)](ClO_4)_2\cdot MeCN$ (**8**). The counter-ions and MeCN have been omitted for clarity.

Table 4 Selected atom distances (Å) and bond angles (°) for $[Cu_2(\mathbf{L}^2H_{-1})(\mu\text{-}Ph_2PO_2)](ClO_4)_2\cdot MeCN$ (**8**)

Cu(1)–N(1)	2.224(3)	Cu(2)–N(8)	2.221(2)
Cu(1)–N(2)	2.014(3)	Cu(2)–N(7)	2.01(2)
Cu(1)–N(3)	2.070(3)	Cu(2)–N(6)	2.059(2)
Cu(1)–N(4)	1.953(2)	Cu(2)–N(5)	1.949(2)
Cu(1)–O(1)	1.942(2)	Cu(2)–O(2)	1.935(19)
P(1)–O(1)	1.510(2)	P(1)–O(2)	1.510(2)
Cu(1) ··· Cu(2)	4.210		
N(1)–Cu(1)–N(2)	82.82(12)	N(7)–Cu(2)–N(8)	82.95(10)
N(1)–Cu(1)–N(3)	83.97(11)	N(6)–Cu(2)–N(8)	84.64(9)
N(1)–Cu(1)–N(4)	103.01(10)	N(5)–Cu(2)–O(2)	100.79(9)
N(1)–Cu(1)–O(1)	106.78(10)	N(8)–Cu(2)–O(2)	112.68(9)
N(2)–Cu(1)–N(3)	84.85(12)	N(6)–Cu(2)–N(7)	84.64(9)
N(2)–Cu(1)–N(4)	165.32(12)	N(6)–Cu(2)–O(2)	161.35(9)
N(2)–Cu(1)–O(1)	89.49(10)	N(7)–Cu(2)–O(2)	90.51(9)
N(3)–Cu(1)–N(4)	82.42(10)	N(5)–Cu(2)–N(6)	82.01(9)
N(3)–Cu(1)–O(1)	167.16(10)	N(5)–Cu(2)–N(7)	165.95(10)
N(4)–Cu(1)–O(1)	101.45(9)	N(5)–Cu(2)–N(8)	100.07(9)
O(2)–P(1)–O(1)	118.13(12)	O(2)–P(1)–C(18)	109.69(13)
O(1)–P(1)–C24	108.27(13)	O(1)–P(1)–C(18)	109.02(13)
C(24)–P(1)–C(18)	105.22(12)	O(2)–P(1)–C(24)	105.71(12)

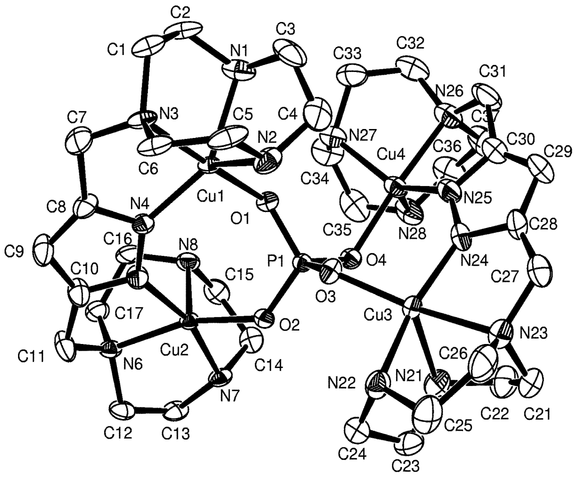


Fig. 7 Crystal sructure of $[Cu_4(\mathbf{L}^2H_{-1})_2(\mu_4\text{-}PO_4)](ClO_4)_3\cdot MeCN\cdot H_2O$ (**9**). The counter-ions and the solvent molecules have been omitted for clarity.

The cation complex **9** is shown in Fig. 7. The complex has a tetranuclear structure, with two dinuclear $[Cu_2\mathbf{L}^2H_{-1}]^{3+}$-units held together by a central tetradentate PO_4^{3-} group bridging all four coppers. The two dinuclear fragments are similar, but the two Cu^{2+} in the dinuclear moiety have somewhat different geometries: Cu(1) and Cu(4) exhibit a distorted trigonal bipyramidal coordination whereas Cu(2) and Cu(3) show a distorted square pyramidal geometry. In the equatorial plane of Cu(1) and Cu(4) there are two N-atoms stemming from the 1,4,7-triazacyclononane unit and one N-atom from the pyrazolide. In the axial positions of the trigonal bipyramid we find one O-atom of the phosphate ion and one N-atom from the 1,4,7-triazacyclononane unit. For Cu(2) and Cu(4) one of the N-atoms (N8 or N2) of the 1,4,7-triazacyclononane is in the apical position of the square pyramid giving a somewhat longer Cu–N bond. The bond lengths between the Cu^{2+} centres and the pyrazolidyl N-atoms are slightly shorter (*ca.* 0.1 Å) than normal Cu–N bond lengths, due to the influence of the negative charge and sp^2-hybridisation of the pyrazole moiety. The lengths of the four P–O-bonds, which are between 1.52 and 1.55 Å and the O–P–O angles, which are between 106.52 and 112.54° (see Table 5), indicate that the geometry around the phosphate can be considered as a slightly distorted tetrahedron. The $Cu^{2+} \cdots Cu^{2+}$ distance within a binuclear fragment is 4.03–4.10 Å.

Phosphate ions are well known to be able to bridge two metal centres,[34] and because of this such structures are of particular

Table 5 Selected atom distances (Å) and bond angles (°) for $[Cu_4(\mathbf{L}^2H_{-1})_2(\mu_4\text{-}PO_4)](ClO_4)_3\cdot MeCN\cdot H_2O$ (**9**)

Cu(1)–N(1)	2.111(4)	Cu(3)–N(21)	2.234(4)
Cu(1)–N(2)	2.149(4)	Cu(3)–N(22)	2.010(4)
Cu(1)–N(3)	2.072(4)	Cu(3)–N(23)	2.109(4)
Cu(1)–N(4)	1.936(3)	Cu(3)–N(24)	1.926(4)
Cu(1)–O(1)	1.913(3)	Cu(3)–O(3)	1.934(3)
Cu(2)–N(5)	1.955(4)	Cu(4)–N(25)	1.936(4)
Cu(2)–N(6)	2.092(3)	Cu(4)–N(26)	2.083(4)
Cu(2)–N(7)	2.023(4)	Cu(4)–N(27)	2.058(4)
Cu(2)–N(8)	2.196(4)	Cu(4)–N(28)	2.212(4)
Cu(2)–O(2)	1.923(3)	Cu(4)–O(4)	1.924(3)
P(1)–O(1)	1.537(3)	P(1)–O(2)	1.523(3)
P(1)–O(3)	1.532(3)	P(1)–O(4)	1.551(3)
Cu(1) ··· Cu(2)	4.03	Cu(3) ··· Cu(4)	4.10
N(1)–Cu(1)–N(2)	83.25(17)	N(5)–Cu(2)–N(6)	81.53(14)
N(1)–Cu(1)–N(3)	81.88(15)	N(5)–Cu(2)–N(7)	164.01(15)
N(1)–Cu(1)–N(4)	144.91(17)	N(5)–Cu(2)–N(8)	101.35(16)
N(1)–Cu(1)–O(1)	96.43(14)	N(5)–Cu(2)–O(2)	101.65(14)
N(2)–Cu(1)–N(3)	83.07(15)	N(6)–Cu(2)–N(7)	83.62(14)
N(2)–Cu(1)–N(4)	125.34(16)	N(6)–Cu(2)–N(8)	83.84(14)
N(2)–Cu(1)–O(1)	97.49(13)	N(6)–Cu(2)–O(2)	162.74(13)
N(3)–Cu(1)–N(4)	82.17(15)	N(7)–Cu(2)–N(8)	82.85(15)
N(3)–Cu(1)–O(1)	178.16(13)	N(7)–Cu(2)–O(2)	90.85(13)
N(4)–Cu(1)–O(1)	98.88(13)	N(8)–Cu(2)–O(2)	111.77(13)
N(21)–Cu(3)–N(22)	82.89(17)	N(25)–Cu(4)–N(26)	82.16(17)
N(21)–Cu(3)–N(23)	83.22(17)	N(25)–Cu(4)–N(27)	142.51(17)
N(21)–Cu(3)–N(24)	101.98(18)	N(25)–Cu(4)–N(28)	130.33(18)
N(21)–Cu(3)–O(3)	114.12(14)	N(25)–Cu(4)–O(4)	99.44(15)
N(22)–Cu(3)–N(23)	83.51(16)	N(26)–Cu(4)–N(27)	84.20(17)
N(22)–Cu(3)–N(24)	163.53(16)	N(26)–Cu(4)–N(28)	83.10(17)
N(22)–Cu(3)–O(3)	92.91(14)	N(26)–Cu(4)–O(4)	173.89(16)
N(23)–Cu(3)–N(24)	81.48(17)	N(27)–Cu(4)–N(28)	81.96(18)
N(23)–Cu(3)–O(3)	161.81(15)	N(27)–Cu(4)–O(4)	97.80(14)
N(24)–Cu(3)–O(3)	99.24(15)	N(28)–Cu(4)–O(4)	91.44(14)
O(1)–P(1)–O(2)	112.54(16)	O(1)–P(1)–O(3)	110.48(16)
O(1)–P(1)–O(4)	106.52(16)	O(2)–P(1)–O(3)	109.16(17)
O(2)–P(1)–O(4)	108.15(16)	O(3)–P(1)–O(4)	109.92(16)

interest for modelling the active site of alkaline phophatase. The μ_4-bridging mode of the phosphate ion has been found with phosphate groups embedded in polyoxometallates[35] and infinite layered sheets.[36] Besides these examples a μ_4-phosphate ion bridging four metal centres is known in a tetranuclear iron(III)[37] and in a tetranuclear copper(II) complex.[38]

Spectrophotometric measurements

As we can see from the X-ray structure (Fig. 6) the two Cu^{2+} ions can be bridged by exogenous bridging ligands. From earlier studies it is already known that azide can act as an exogenous bridging ligand.[17] The crystal structure of $[Cu_2\mathbf{L}^2H_{-1}(N_3)][(ClO_4)_2]$ showed that the azide anion binds to the two metal centers in an end-to-end bridging mode. Since the triazole ligand $\mathbf{L}^1$ and the pyrazole ligand $\mathbf{L}^2$ have similar chemical properties, we expected that also in the dinuclear complex $[Cu_2\mathbf{L}^1H_{-1}]^{3+}$ the azide anion is able to bridge the two Cu^{2+}-centres. Titrations of $[Cu_2\mathbf{L}^1H_{-1}]^{3+}$ with N_3^- (see Fig. 8) have clearly shown an interaction between the Cu^{2+} coordinated by the bis-macrocycle and the azide anion, since the the absorption maximum changes from 648.6 nm (ε = 194.1 M^{-1} cm^{-1}) over 625.8 nm (ε = 420.6 M^{-1} cm^{-1}) to 627.4 nm (ε = 502.6 M^{-1} cm^{-1}). Quantitative studies using the the program SPECFIT allow to fit the experimental data with eqns. (2) and (3)

$$[Cu_2\mathbf{L}^1H_{-1}]^{3+} + N_3^- \xrightleftharpoons{\beta_1} [Cu_2\mathbf{L}^1H_{-1}(N_3)]^{2+} \qquad (2)$$

$$[Cu_2\mathbf{L}^1H_{-1}]^{3+} + 2N_3^- \xrightleftharpoons{\beta_2} [Cu_2\mathbf{L}^1H_{-1}(N_3)_2]^{+} \qquad (3)$$

(see Fig. 9), where β_1 and β_2 are the stability constants of the azide complexes. First at low N_3^- concentrations the ternary complex $[Cu_2\mathbf{L}^1H_{-1}(N_3)]^{2+}$ is formed (see Fig. 10). In this species the two metal centers are probably end-to-end bridged by the azide anion. With increasing concentration of N_3^-, the species $[Cu_2\mathbf{L}^1H_{-1}(N_3)_2]^+$ becomes more important until at higher azide concentrations it becomes the dominating species. In $[Cu_2\mathbf{L}^1H_{-1}(N_3)_2]^+$ either each of the two Cu^{2+}-ions is coordinated by one azide ion or one azide is bridging the two metal ions and the other is bound "end-on" to one of the Cu^{2+}, as observed in an analogous Ni^{2+} complex with OCN^-.[39] In the case of the titration of $[Cu_2\mathbf{L}^2H_{-1}]^{3+}$ with increasing amounts of N_3^- only the ternary species $[Cu_2\mathbf{L}^2H_{-1}(N_3)]^{2+}$ is formed which is one logarithmic unit more stable than $[Cu_2\mathbf{L}^1H_{-1}(N_3)]^{2+}$.

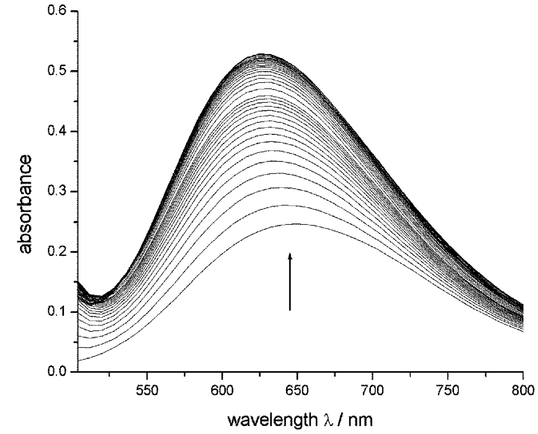


Fig. 8 Spectrophotometric titration of $[Cu_2\mathbf{L}^1H_{-1}]^{3+}$ (1.25×10^{-3} M) with increasing amounts of N_3^- at pH = 4.76.

In summary we can state that the results obtained in solution by potentiometric and spectrophotometric measurements as well as the X-ray structures solved for two ternary complexes show the interesting properties of this type of ligands containing a pyrazole or a triazole bridging unit between two 1,4,7-triazacyclononane rings.

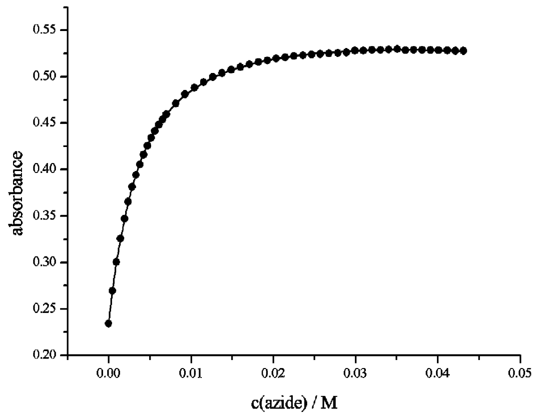


Fig. 9 Fitting of the experimental data at 624 nm with eqns. (2) and (3).

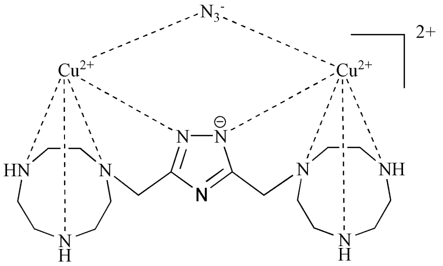


Fig. 10 Proposed structure for the dinuclear species $[Cu_2L^1H_{-1}(N_3)]^{2+}$.

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