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Two pyrazolato-bridged, linear trinuclear Cu(II) complexes. Crystal structures and magnetic properties

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In honor of Professor Pierre Braunstein.

Abstract

The single-crystal X-ray structures of two new linear trinuclear copper(II) complexes of 3,5-pyrazoledicarboxylic acid (H_3L) are reported, viz. $[Cu_3(L)_2(Me_2en)_2(H_2O)_2]\cdot(H_2O)_8$ (**1**) and $[Cu_3(L)_2(MeOH)_6(H_2O)_4]$ (**2**), with Me_2en is N,N-dimethylethylenediamine. Both complexes are trinuclear and have been obtained from a precursor ligand, through copper-induced amide hydrolysis. In **1**, the central copper ion is in a distorted square-planar environment and the two outer copper ions are in a distorted square-pyramidal environment. All three copper ions in **2** are six-coordinated in an elongated octahedral environment. A weak, broad EPR signal centered around $g = 3.5$, indicative for an $S = 3/2$ state, is observed and confirms both complexes to be trinuclear. Magnetic susceptibility measurements of **1** and **2** from 4 to 300 K indicate a weak anti-ferromagnetic exchange coupling, with J values of -15 and -19 cm^{-1}, respectively.
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1. Introduction

A variety of metal ions, for example Cu(II) [1–5], Co(III) [6], Zn(II) [7], Ni(II) [7], Pd(II) [8] and Ce(IV) [9], are known to be able to hydrolyse amide bonds. The complexes of such metal ions are of interest as models for metallopeptidases, like carboxypeptidase A [10]. The present paper reports the preparation and characterization of two trinuclear copper(II) complexes indirectly obtained by the hydrolysis of diamide ligands. These linear trinuclear copper(II) complexes are of interest as models for the active sites of multicopper proteins, like ascorbate oxidase [11], ceruplasmin [12] and laccase [13], but are also of interest for a better understanding of the magnetic properties of multicopper compounds.

Trinuclear compounds can be classified in linear and non-linear compounds. Relatively few trinuclear copper compounds have been studied by EPR [14–18] or magnetic susceptibility [14,15,18,19]. Most of the known linear trinuclear copper complexes have two, three or four bridges between each copper ion, one or two of them consisting often of simple anions, like chloride [20–22], azide [15,19], hydroxide [23–25] or methoxide [26,27], while only some of them have just a single ligand bridge between each copper ion [28,29].

Deprotonated pyrazole ligands are known to act as bridging anionic ligands. A cyclic tetranuclear [30], a polymeric [31], and several dinuclear [32–37] copper complexes have been reported, with one of the latter containing two 3,5-dicarboxylato-pyrazolato ligands [37].

The present paper deals with the single-crystal X-ray structures and the magnetic properties of two new trinulear copper compounds.

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2. Results and discussion

2.1. General

In the course of our investigations towards possible models for type-3 copper sites the ligands 3,5-bis(*N*-((*N'*,*N'*-dimethyl)ethanediamine)carbamoyl)pyrazole (en_2pz) and 3,5-bis(*N*-(2-pyridylethyl)carbamoyl)pyrazole (py_2pz) have been synthesized (see Scheme 1), being amide derivatives of 3,5-pyrazoledicarboxylic acid (H_3L). Several attempts to prepare dinuclear copper(II) compounds of these mono-deprotonated ligands resulted in the hydrolysis of the ligands. However, two new and very interesting trinuclear copper(II) compounds could be isolated from the reaction mixtures, viz. $[Cu_3(L)_2(Me_2en)_2(H_2O)_2]\cdot(H_2O)_8$ (**1**) and $[Cu_3(L)_2(MeOH)_6(H_2O)_4]$ (**2**). Attempts to synthesize these compounds from their components always resulted in the formation of the dinuclear compound $Na_2[Cu_2L_2(H_2O)_2]$ [37].

2.2. Structure of $[Cu_3(L)_2(Me_2en)_2(H_2O)_2]\cdot(H_2O)_8$ (**1**)

The most characteristic feature of **1** is the linear arrangement of three Cu(II) ions, which are bridged by two threefold deprotonated 3,5-dicarboxylato-pyrazolato ligands. A PLUTON [38] projection of the molecular structure is given in Fig. 1. Relevant bond lengths and angles are given in Table 1. The central copper ion Cu1 is located on a crystallographic twofold axis. It is coordinated by one nitrogen and one oxygen atom of each bridging pyrazolato group with (normal) Cu–O and Cu–N distances of 1.948(5) and 1.965(5) Å, respectively. The geometry around Cu1 is somewhat distorted from square-planar, with coordination angles of 82.7(2) and 97.5(2)°. The shortest Cu1–OH$_2$ distance of 4.24 Å indicates that no water molecules are
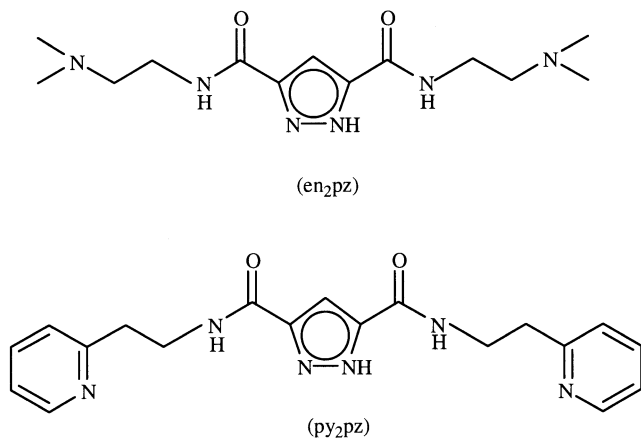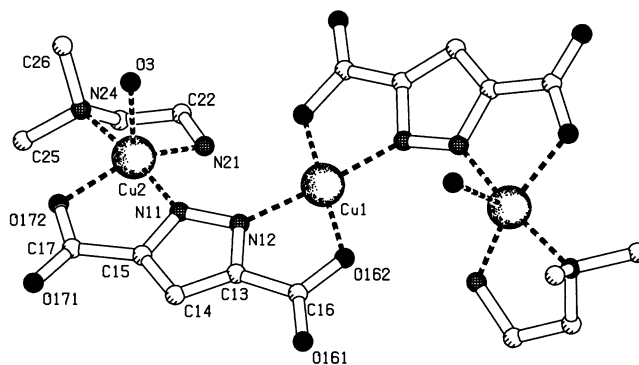
Fig. 1. PLUTON [38] representation of $[Cu_3(L)_2(Me_2en)_2(H_2O)_2]\cdot$ $(H_2O)_8$ (**1**). H-atoms and non-coordinating water molecules are omitted for clarity.

coordinated to Cu1. The Cu1 to Cu2 distance is 4.3992(12) Å. The outer copper ions Cu2 are in a distorted square-pyramidal environment of two nitrogen atoms of the amine ligand and an oxygen atom and a nitrogen atom of one pyrazolato group. The coordination distances in the basal plane are quite normal (see Table 1). The basal plane angles, which are together almost equal to 360° (i.e. 357.3°), deviate appreciable from 90° (see Table 1) as a consequence of the three bond ligand bites of both the amine ligand and the carboxylato–pyrazolato ligand, which restrict their coordination angles to 85.1(3) and 81.5(2)°, respectively. An oxygen atom of a water molecule is coordinated at the apex of the pyramid at a typical distance of 2.236(6) Å. The distortion towards a trigonal bipyramid is limited with an Addison τ value [39] of 0.34. Four non-coordinating water molecules are present in the asymmetric unit, which are involved in extensive hydrogen-bonding interactions with the coordinated carboxylate groups and the coordinated water molecule (see Table 1). The crystal packing shows the presence of stacked pyrazolato groups, with shortest ring–ring distances of 3.55 Å.

2.3. Structure of $[Cu_3(L)_2(MeOH)_6(H_2O)_4]$ (**2**)

The structure of **2** also shows a linear arrangement of three Cu(II) ions bridged by two triple anionic 3,5-dicarboxylato–pyrazolato ligands, but in this case the outer copper ions are coordinated by solvent molecules and all three copper ions are hexa-coordinated. A PLUTON [38] projection of the molecular structure is given in Fig. 2. Relevant bond lengths and angles are given in Table 2. The central copper ion Cu1 is located on a crystallographic inversion center. The Cu1 to Cu2 distance of 4.4518(11) Å is somewhat longer than in **1**. Both complexes belong to a small group of linear trinuclear complexes with Cu–Cu distances longer than 4 Å [40–42] as established by a search in the Cambridge Structural Database [43].

Scheme 1. The ligands 3,5-bis(*N*-((*N'*,*N'*-dimethyl)ethanediamine)carbamoyl)pyrazole (en_2pz) and 3,5-bis(*N*-(2-pyridylethyl)carbamoyl)pyrazole (py_2pz).

Table 1
Selected bond lengths (Å), bond angles (°) and H-bond distances (Å) for $[Cu_3(L)_2(Me_2en)_2(H_2O)_2]\cdot(H_2O)_8$ (**1**)

Bond lengths

Cu1–O162	1.948(5)
Cu1–N12	1.965(6)
Cu2–O3	2.236(6)
Cu2–O172	2.012(5)
Cu2–N11	1.989(7)
Cu2–N21	1.968(8)
Cu2–N24	2.057(7)
Cu1–Cu2	4.3992(12)
O3–O161 [b]	2.842(8)
O3–O171 [c]	2.756(8)
N21–O162 [a]	2.843(9)
N21–O161 [d]	3.136(9)
N21–O171 [e]	3.236(10)
O90–172 [c]	2.788(8)
O90–O161 [a]	2.754(8)
O91–O90	2.737(8)
O91–O92	2.760(9)
O92–O93 [f]	2.769(9)
O92–O91 [g]	2.783(9)
O93–O92 [h]	2.814(9)
O93–O91	2.813(9)

Bond angles

O162–Cu1–N12	82.7(2)
O162–Cu1–O162 [a]	175.7(3)
O162–Cu1–N12 [a]	97.5(2)
N12–Cu1–N12 [a]	173.9(3)
O3–Cu2–O172	93.8(2)
O3–Cu2–N11	88.6(2)
O3–Cu2–N21	112.9(3)
O3–Cu2–N24	96.6(3)
O172–Cu2–N11	81.5(2)
O172–Cu2–N21	153.1(3)
O172–Cu2–N24	94.0(3)
N11–Cu2–N21	96.7(3)
N11–Cu2–N24	173.4(3)
N21–Cu2–N24	85.1(3)

[a] $-x, y, 1/2-z$.
[b] $-x, 1-y, -z$.
[c] $x, 1-y, 1/2+z$.
[d] $-x, -y, -z$.
[e] $x, -y, 1/2+z$.
[f] $x, -1+y, z$.
[g] $1/2-x, 1/2-y, 1-z$.
[h] $1/2-x, 1/2+y, 1/2-z$.

All three copper ions are six-coordinated in an elongated octahedral fashion. The center Cu ion is coordinated equatorially by a nitrogen atom and an oxygen atom of each carboxylato–pyrazolato group and axially by the oxygen atoms of two methanol molecules. The outer Cu ions are equatorially coordinated by the oxygen and the nitrogen atom of a pyrazolato group and the oxygen atoms of two water molecules with the axial positions occupied by the oxygens of two MeOH molecules. The Cu–O (MeOH) distances are typical for axial ligands, i.e. 2.461(6) Å for the center Cu ion, and 2.341(6) and 2.599(5) Å for the outer Cu ions. The other Cu–O distances and the Cu–N distances (see Table 2)
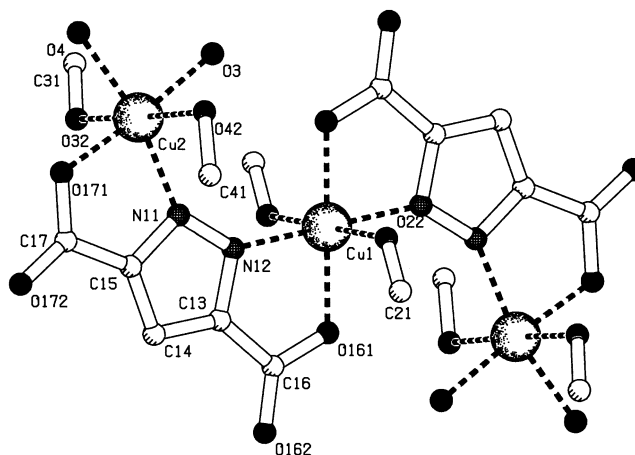

Fig. 2. PLUTON [38] representation of $[Cu_3(L)_2(MeOH)_6(H_2O)_4]$ (**2**). H-atoms are omitted for clarity.

are normal coordinating distances for tetragonal copper compounds [44]. In this compound also extensive hydrogen-bonding interactions are present (see Table 2). The crystal packing shows stacking of the pyrazolato groups along the *x*-axis with shortest ring–ring distances of 3.958 Å and a zigzag arrangement of the hydrogen bonded molecules along the *y*-axis.

2.4. EPR spectra

Polycrystalline powder EPR spectra of **1** and **2** were recorded at X-band frequency. The EPR spectrum of **1** at ambient temperature shows a very broad signal centered around $g = 2.12$ and a very weak and broad signal at about $g = 3.5$, which appears to be typical for trinuclear copper complexes [14,45]. In liquid nitrogen and in liquid helium the signal at $g = 2.12$ sharpens and the signal at $g = 3.5$ disappears. This change in EPR spectrum when lowering the temperature is not uncommon for linear trinuclear copper complexes [14], and must be related to the depopulation of the $S = 3/2$ level.

The EPR spectrum of **1** in frozen MeOH solution at 77 K shows a signal at $g = 2.09$ and a weak signal at about $g = 3.3$. The EPR spectra of **1** as frozen DMSO solutions at liquid nitrogen and at liquid helium temperatures show a signal at $g = 2.09$ and a weak signal at about $g = 3.5$. The observation of the $g = 3.3$ and 3.5 signals indicate that the trinuclear character of compound **1** remains intact in solution. Repetition of the latter measurement after 1 month with the same solution showed no change, which further confirms that the compound is stable in solution.

In contrast to **1**, the polycrystalline powder spectrum of **2** is EPR silent at ambient temperature, which is probably caused by a fast relaxation [46]. EPR silent trinuclear linear Cu(II) complexes are not uncommon [15,47]. At liquid nitrogen temperature, a signal at $g = 2.16$ appears. In frozen DMSO solution at liquid

Table 2
Selected bond lengths (Å), bond angles (°) and H-bond distances (Å) for [Cu$_3$(L)$_2$(MeOH)$_6$(H$_2$O)$_4$] (**2**)

Bond lengths	
Cu1–O22	2.461(6)
Cu1–O161	1.986(4)
Cu1–N12	1.984(5)
Cu2–O3	1.945(4)
Cu2–O4	1.995(4)
Cu2–O32	2.341(6)
Cu2–O42	2.599(5)
Cu2–O171	1.967(4)
Cu2–N11	1.996(5)
Cu1–Cu2	4.4518(11)
O3–O161 [a]	2.620(6)
O22–O172 [b]	2.759(7)
O4–O3 [c]	3.247(6)
O4–O171 [d]	3.255(6)
O4–O172 [d]	2.701(6)
O42–O4 [d]	2.852(6)
Bond angles	
O22–Cu1–O161	91.44(19)
O22–Cu1–N12	89.98(19)
O22–Cu1–O22 [a]	180.00
O22–Cu1–O161 [a]	88.56(19)
O22–Cu1–N12 [a]	90.02(19)
O161–Cu1–N12	81.87(17)
O161–Cu1–O161 [a]	180.00
O161–Cu1–N12 [a]	98.13(17)
O22–Cu1–N12 [a]	90.02(19)
N12–Cu1–N12 [a]	180.00
O3–Cu2–O4	89.72(18)
O3–Cu2–O32	92.39(18)
O3–Cu2–O42	87.28(16)
O3–Cu2–O171	172.22(17)
O3–Cu2–N11	103.6(2)
O4–Cu2–O32	88.0(2)
O4–Cu2–O42	90.16(18)
O4–Cu2–O171	84.42(18)
O4–Cu2–N11	166.7(2)
O32–Cu2–O42	178.10(19)
O32–Cu2–O171	92.51(18)
O32–Cu2–N11	91.0(2)
O42–Cu2–O171	87.63(16)
O42–Cu2–N11	90.92(19)
O171–Cu2–N11	82.40(19)

[a] $1-x, 1-y, 1-z$.
[b] $x, -1+y, z$.
[c] $3/2-x, 1/2+y, 3/2-z$.
[d] $3/2-x, -1/2+y, 3/2-z$.

nitrogen temperature the signal shifts to $g = 2.10$ and sharpens. Also two weak and broad signals at about $g = 3.3$ and 4.0 appear, suggesting trinuclear species to be present in frozen solution.

2.5. Magnetic susceptibility measurements

The magnetic susceptibility of powdered **1** and **2** was measured over the temperature range 4–300 K. In the inverse susceptibility versus temperature curve (Fig. 3 shows the curve for **1**) of both complexes, a change in slope occurs, which is characteristic for linear trinuclear compounds having an anti-ferromagnetic exchange between nearest neighbors [48–50]. This change occurs at about 15 K for **1** and at about 20 K for **2**, implying a relatively small anti-ferromagnetic coupling constant J. Also, the magnetic moment of both complexes of approximately 1.80 B.M. per copper ion at 276 K, which is close to the spin-only value of 1.73, indicates a relatively small magnetic interaction between the copper ions. The pyrazolato bridges apparently do not lead to a significant exchange despite the proper orbital orientation, a phenomenon observed before [50] with this type of bridging 1,2-heteroaromatics. The magnetic interaction might solely be due to a direct Cu–Cu interaction, being small because of the relatively large distance of about 4.4 Å between the central copper(II) and the outer copper(II) ions.

The molar susceptibility χ_m was fitted to the theoretical equation (1) [48]:

$$\chi_m = \{(N\beta^2 g^2)/(4kT)\}$$
$$\times \{[1 + \exp(-2J/kT) + 10 \exp(J/kT)]/[3$$
$$+ 3 \exp(-2J/kT) + 6 \exp(J/kT)]\} \qquad (1)$$

were J is the exchange integral between the central and outer copper ion. The exchange integral between the two outer copper ions was neglected, because of their large separation of about 8.9 Å. The magnetic parameters of complex **1** and **2** can be estimated, as $g = 2.11$, $J = -15$ cm^{-1} and $g = 2.17$, $J = -19$ cm^{-1}, respectively, in agreement with the assumption of a small coupling constant. The fitted g values of 2.11 (**1**) and 2.17 (**2**) are in good agreement with the measured g values of the EPR measurements at low temperatures (vide infra).

3. Concluding remarks

Two rather uncommon, but very interesting linear trinuclear copper(II) compounds have been fortuitously isolated and characterized. The three copper ions are magnetically only weakly coupled. The trinuclear molecules are associated by hydrogen bond interactions and stacking of the pyrazole rings.

4. Experimental

4.1. Reagents

The starting materials: 3,5-pyrazoledicarboxylic acid monohydrate, *N*,*N*-dimethylethylenediamine and 2,2-aminoethylpyridine were obtained from Acros Organics. Metal salts and solvents were commercially available of sufficient purity and used as such.
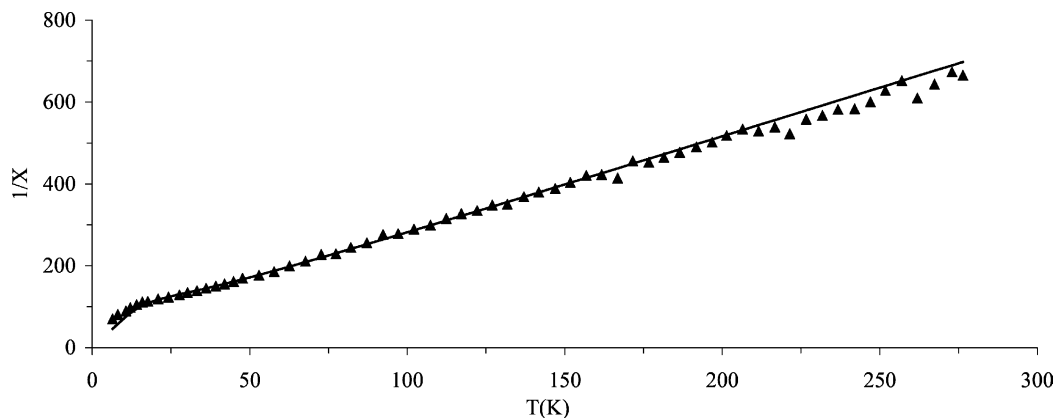
Fig. 3. Temperature dependence of the inverse magnetic susceptibility of $[Cu_3(L)_2(Me_2en)_2(H_2O)_2]\cdot(H_2O)_8$ (**1**). The black squares indicate the observed susceptibility. The solid line shows the theoretical susceptibility calculated by equation (1).

4.2. Equipment

Vis–NIR spectra (400–2000 nm) were obtained on a Perkin–Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference.

X-band powder EPR spectra were obtained on a JEOL RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a calibration standard.

Magnetic susceptibilities were measured in the temperature range between 4 and 300 K with a fully automated Manics DSM-8 susceptometer with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at approximately 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants [51].

4.3. Synthesis of 3,5-bis{N-[(N′,N′-dimethyl)ethanediamine]carbamoyl}pyrazole (py₂pz)

To a suspension of 20.14 g (115.7 mmol) 3,5-pyrazoledicarboxylic acid monohydrate in 300 ml dichloromethane, 44 ml $SOCl_2$ was added. After 6 h of reflux the solvent was evaporated and 10.09 g (52.8 mmol) of the resulting 3,5-bis(chloroformyl)pyrazole was suspended in 400 ml THF and 9.46 g (107.3 mmol) N,N-dimethylethylenediamine and 6.34 g (107.5 mmol) triethylamine was added under stirring. After 5 h of reflux the white product was filtered off and crystallized from MeOH.

NMR (^{1}H/MeOD/δ): 6.98 (1H, s, pz), 3.04 (4H, t, CH_2), 2.60 (4H, t, CH_2), 2.29 (12, s, CH_3).

Mass: $[M+H]^+ = 297$. Elemental analysis for $C_{13}H_{24}N_6O_2$ %wt. Found (Calc.): C, 52.47 (52.68); H, 8.09 (8.16); N, 28.50 (28.36)%. IR (KBr): $\nu_{(C=O)} = 1633$ cm^{-1}.

4.4. Synthesis of 3,5-bis{N-[2-pyridylethyl]carbamoyl}pyrazole (py₂pz)

This compound was synthesized in the same way as (en₂pz), using 14.43 g (74.8 mmol) 3,5-bis(chloroformyl)pyrazole in 100 ml THF, 18.27 g (149.8 mmol) 2,2-aminoethylpyridine and 15.13 g (149.8 mmol) triethylamine in 50 ml THF.

NMR (^{1}H/MeOD/δ): 8.44 (2H, m, py), 7.72 (2H, m, py), 7.30 (4H, m, py), 7.08 (1H, s, pz), 3.70 (4H, t, CH_2), 3.06 (4H, t, CH_2). Mass: $[M+H]^+ = 365$. Elemental analysis for $C_{19}H_{20}N_6O_2$ %wt Found (Calc.): C, 62.4 (62.6); H, 5.62 (5.50); N, 23.05 (23.1)%. IR (KBr): $\nu_{(C=O)} = 1643$ cm^{-1}.

4.5. $[Cu_3(L)_2(Me_2en)_2(H_2O)_2]\cdot(H_2O)_8$ (**1**)

The reaction of 0.590 g (2 mmol) en₂pz in 50 ml warm MeOH with 0.973 g (4 mmol) $Cu(NO_3)_2\cdot3H_2O$ in 50 ml MeOH and addition of 0.128 g (3 mmol) LiOH and 0.434 g (10 mmol) LiCl in 30 ml H_2O, resulted in small blue crystals.

LF (solid state, λ (nm)): 280, 660. IR (KBr, ν (cm^{-1})): 3422, 3264, 3116, 1651, 1599, 1508, 1387, 1336, 1314, 1289, 1063, 1012, 792.

4.6. $[Cu_3(L)_2(MeOH)_6(H_2O)_4]$ (**2**)

To 20 ml of a warm MeOH solution of 0.360 g (1 mmol) py₂pz, a solution of 0.339 g (2 mmol) $CuCl_2\cdot2H_2O$ in 20 ml MeOH was added. After several weeks light blue and dark blue crystals appeared. The dark blue crystals analyzed as dichloro[2-(2-aminoethyl)pyridine]copper(II) [52]. The light blue crystals appeared to be compound **2**.

LF (solid state, λ (nm)): 312, 738. IR (KBr, ν (cm^{-1})): 3360, 1636, 1517, 1388, 1338, 1284, 1062, 1014, 849, 789.

4.7. Attempts for the synthesis from the components of the final compounds

Attempts were made to synthesize **1** and **2** not by ligand degradation, but by using their components as starting material, all resulted in the dinuclear compound $Na_2[Cu_2L_2(H_2O)_2]$. For instance, to reproduce **1** a solution of 0.34 g (1.92 mmol) 3,5-pyrazoledicarboxylic acid monohydrate in 10 ml MeOH was mixed with a solution of 0.17 g (1.97 mmol) N,N-dimethylethylene-diamine in 5 ml MeOH. Subsequently a solution of 0.41 g (7.59 mmol) NaOMe in 15 ml MeOH and a solution of 0.51 g (3.79 mmol) $CuCl_2 \cdot 2H_2O$ in 10 ml MeOH were added. After several weeks a purple solid separated from the dark blue solution.

Elemental Analysis for $C_{10}H_6Cu_2N_4Na_2O_{10}$ %wt Found (Calc.): C, 23.18(23.32); H, 0.91(1.17); N, 10.63(10.87)%.

4.8. X-ray data collection and structure determination of $[Cu_3(L)_2(Me_2en)_2(H_2O)_2] \cdot (H_2O)_8$ (1)

A blue needle with dimensions $0.33 \times 0.08 \times 0.03$ mm was selected for X-ray measurements. The diffraction data were collected on a Nonius Kappa CCD diffract-ometer at 150 K with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), $\theta_{min./max.} = 2.2/24.0°$. A total of 12 636 reflections was collected, of which 2555 unique. An absorption correction based on multiple measurements was applied (0.38–0.55 transmission). The structure was solved with Patterson methods (DIRDIF-97 [53]) and refined with SHELXL-97 [54] against F^2 of all reflections. The structure refined to $R_1 = 0.0724$ for 1839 reflections with $I > 2\sigma(I)$. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 50.2047P]$ where $P = (F_o^2 + 2F_c^2)/3$ was adopted. Crystallographic calculations and checking for higher symmetry were performed with the PLATON [38] package. Crystallographic data are listed in Table 3.

4.9. X-ray data collection and structure determination of $[Cu_3(L)_2(MeOH)_6(H_2O)_4]$ (2)

A blue, hexagonal plate with dimensions $0.5 \times 0.4 \times 0.2$ mm was selected for the X-ray measurements and mounted on an Enraf–Nonius CAD-4. Data were collected using graphite-monochromed Mo Kα radiation ($\lambda = 0.71073$ Å) at ambient temperature. $\theta_{min./max.} = 2.1/29.9$. Data reduction was performed using the XTAL package [55]. The intensity data were corrected for Lorentz and polarization effects. The hydrogen atoms which could not be located in the difference Fourier maps, were placed on calculated positions. The structure has been refined on F to $R_1 = 0.053$ for 2049 reflections with $I > 2\sigma(I)$. Crystallo-graphic data are given in Table 3. Geometric calcula-tions and molecular graphics were performed with the PLATON program [38].

Table 3
Crystallographic data for $[Cu_3(L)_2(Me_2en)_2(H_2O)_2] \cdot (H_2O)_8$ (**1**) and $[Cu_3(L)_2(MeOH)_6(H_2O)_4]$ (**2**)

	1	**2**
Empirical formula	$C_{18}H_{46}Cu_3N_8O_{18}$	$C_{16}H_{34}Cu_3N_4O_{18}$
Formula weight	853.24	761.12
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
a (Å)	37.497(4)	8.8337(13)
b (Å)	6.8999(9)	8.7338(16)
c (Å)	12.7120(14)	19.574(3)
β (°)	96.916(6)	100.555(12)
V (Å^3)	3265.0(7)	1484.6(4)
Z	4	2
$F(000)$	1764	778
D_{calc} (g cm^{-3})	1.74	1.70
μ (Mo Kα) (mm^{-1})	2.02	2.21
R, $wR(2)$, S	0.0724, 0.1769, 1.06	0.053, 0.062, 2.59
$\Delta\rho$ min., max. (e Å^{-3})	−0.561, 0.840	−1.43, 1.16

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 146154 (**1**) and 144826 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.a-c.uk or www: http://www.ccdc.cam.ac.uk).

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