Copper complexes with a pyrazole derivative ligand. Crystal structure of tetrakis{[(3,5-bis(pyridin-2-yl)pyrazolate)-(aqua)copper(II)] nitrate monohydrate}

J. Pons*, X. López, J. Casabó
Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona (Spain)

F. Teixidor*, A. Caubet, J. Rius and C. Miravitlles
Institut de Ciència dels Materials (C.S.I.C.), 08193 Bellaterra, Barcelona (Spain)

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Abstract

Reaction of the pyrazole-derived ligand 3,5-bis(pyridin-2-yl)pyrazole (bpypz) with $Cu(NO_3)_2$, $CuCl_2$ and $CuBr_2$ yields polynuclear copper(II) compounds with remarkable structural and magnetic properties. The magnetic behaviour was studied by fitting the experimental data with a dimer and tetramer magnetic model. Strong antiferromagnetic exchange interactions were found in all cases. The molecular structure of the nitrate compound was solved by X-ray diffraction methods. The compound is tetranuclear, orthorhombic, space group *Fddd*, $a=18.572(4)$, $b=23.816(8)$, $c=27.337(9)$ Å, $V=12092$ Å^3, $Z=8$.

Introduction

Research on the coordination chemistry of pyrazole-derived ligands has progressed very rapidly in the last few years. One of the major research areas of interest is the metallocycles of the type $M(pz)_nM'$ where pz is the pyrazole or pyrazole-derived ligand [1]. Very recently, interest in these $M(pz)_nM'$ compounds has increased due to the possibility of synthesis of mixed, μ-OH, μ-pz bridged compounds of Rh(III), Ni(II), Pd(II) or Pt(II). These compounds are very interesting due to the considerable nucleophilicity of the OH group, evidenced by its high field proton nuclear magnetic resonance [2, 3].

Numerous double pz bridged, bimetallic complexes, $M(pz)_2M'$, are known, normally with monodentate or bidentate ligand groups completing the coordination of the metal ions. With few exceptions, the $(AA)M(pz)_2M'(AA)$ complexes display boat configurations, the $M(pz)_2M'$ core not being planar. Recently we have reported [4, 5] an interesting tetradentate, dinucleating pyrazole derived ligand: 3,5-bis(pyridin-2-yl)pyrazole (bpypz) (Fig. 1), affording strictly planar, dinuclear, di-μ-pz bridged complexes with first transition metal ions.

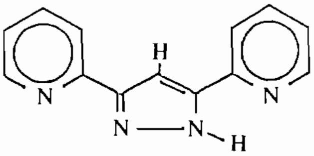

Fig. 1. Schematic molecular drawing of the 3,5-bis(pyridin-2-yl)pyrazole compound.

To the best of our knowledge there are no fully characterized examples of $\pi(\eta^5)$ metal–pyrazole ring bonding. However, intermolecular interactions have been described between pyrazole derived complexes, but the metal ion in one unit is interacting with pyrazole nitrogen atoms in the second unit, not with the whole pyrazole ring [6]. In this paper we report on three copper(II) complexes with the ligand bpypz. In the solid state, the nitrate complex appears to be structurally tetranuclear formed by two weakly associated dimeric units joined by π copper–pyrazole interactions. It represents a genuine example where such type of interactions take place. However, the magnetic exchange interactions analysis demonstrates that these interactions are very small, behaving from this point of view as isolated dimers.

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*Authors to whom correspondence should be addressed.

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Experimental

General

All reagents were commercial grade materials and were used without further purification. All solvents were previously deoxygenated in a vacuum line and all reactions were routinely carried out under nitrogen atmosphere. The compound 3,5-bis(pyridine-2-yl)-pyrazole (bpypz) was synthesized as previously reported [4, 5].

Analyses (C, N, H) were performed in our microanalytical laboratory on a Perkin-Elmer 240-B instrument. IR spectra were run on a Perkin-Elmer FT spectrophotometer as KBr pellets or Nujol films. Electronic spectra were run on a Kontron V-UV spectrophotometer in solid state (KBr pellets, reflectance diffuse) or methanolic solution. Magnetic measurements were carried out on a Faraday type magnetometer (Manics DMS8) in the 300–5.8 K temperature range. The balance was calibrated with standard Hg[Co(SCN)$_4$]. Diamagnetic corrections were calculated from Pascal tables direct measurements of the ligand's magnetic susceptibility.

Synthesis of tetrakis{[(3,5-bis(pyridine-2-yl)-pyrazolate)(aqua)copper(II)] nitrate monohydrate}

To a solution of 3,5-bis(pyridine-2-yl)pyrazole (0.1 g; 4.5×10^{-4} mol) in ethanol (20 ml), solid Cu(NO$_3$)$_2$·2H$_2$O (0.20 g; 9×10^{-4} mol) was added and the mixture was allowed to stand at room temperature for 1 h. A crystalline green–blue solid appeared which was filtered, washed with ethanol and ether and vacuum dried. Good crystals suitable for X-ray analyses were obtained by slow evaporation of a methanolic solution of the synthesized material. Yield 48%. *Anal.* Calc.: N, 19.20; C, 42.79; H, 3.02. Found: N, 19.1; C, 42.6; H, 3.0%. Slightly soluble in methanol.

Synthesis of {[(3,5-bis(pyridin-2-yl)pyrazolate)(aqua)-copper(II)] chloride}

To a solution of 3,5-bis(pyridine-2-yl)pyrazole (0.1 g; 4.5×10^{-4} mol) in ethanol (40 ml), CuCl$_2$·2H$_2$O (0.08 g; 4.5×10^{-4} mol) dissolved in methanol (20 ml) was added, and the mixture was allowed to stand at room temperature for 1 h. A crystalline green–blue solid appeared which was filtered, washed with ethanol and ether and vacuum dried. Yield 32%. *Anal.* Calc.: N, 16.56; C, 46.16; H, 3.28; Cl, 10.63. Found: N, 16.5; C, 46.1; H, 3.3; Cl, 10.5%. Slightly soluble in methanol and ethanol.

Synthesis of {[(3,5-bis(pyridine-2-yl)pyrazolate)(aqua)-copper(II)] bromide}

The synthesis was done as before starting from 3,5-bis(pyridin-2-yl)pyrazole (0.15 g; 6.75×10^{-4} mol), methanol (40 ml) and solid CuBr$_2$ (0.15 g; 6.75×10^{-4} mol). Yield 51%. *Anal.* Calc.: N, 14.64; C, 40.80; H, 2.90; Br, 20.88. Found: N, 14.6; C, 40.7; H, 2.8; Br, 20.8%. Slightly soluble in methanol and ethanol.

Crystal structure determination of $[Cu_4(bpypz)_4(H_2O)_4](NO_3)_4\cdot4H_2O$

Crystal data: orthorhombic, space group *Fddd*, $a=18.572(4)$, $b=23.816(8)$, $c=27.337(9)$ Å, $V=12092$ Å^3, λ(Mo Kα)$=0.71069$ Å, $\mu=14.8$ cm^{-1}, $D_c=1.68$ mg m^{-3}, $Z=8$, $F(000)=6240$. After multiple attempts, a small dark green crystal ($0.24\times0.19\times0.12$ mm) could be successfully isolated. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer using ω–2θ scan mode upto $2\theta=47°$ ($-20\leqslant h\leqslant20$, $-26\leqslant k\leqslant26$, $0\leqslant l\leqslant30$). 9134 measured reflections, 2243 unique reflections. Standard reflection decay during the data collection process was 1.67%.

The structure was solved by multisolution direct methods using the Ω-tangent formula (OMEGA88) [7]. The disordered nitrate group was found in the subsequent *F* syntheses. After several cycles of refinement using anisotropic, full-matrix least-squares methods (SHELX76) [8], the value of $R=0.046$ ($R_w=0.044$, $w=1/[\sigma^2(F)+0.00072F^2]$) was achieved over 1179 observed reflections ($F>5\sigma(F)$) (200 free parameters). The average bond distances of the bpypz ligand taken from ref. 4 were introduced as additional observations in the least-squares refinement. To reduce the number of free parameters, the thermal ellipsoids of the atoms of the ligand were allowed to rotate in the *xy* plane only, i.e. by making $U_{13}=U_{23}=0$. The H atoms of the ligand and of O18 were located in the *F* syntheses and refined with a global thermal coefficient. The maximum and minimum peaks in the final Fourier difference map are 0.30 and -0.27 e Å^3, respectively. See also 'Supplementary material'.

Results and discussion

General chemistry

The nitrate compound had been previously described as a dinuclear compound by some of us [4] because of the great difficulty in obtaining good single crystals suitable for X-ray diffraction analyses. Only after multiple failed attempts did we succeed in growing acceptable crystals for studying the molecular structure of this interesting compound, which revealed its structural 'tetrameric; arrangement. The chloride and bromide compound reported in this paper present the same problems concerning the growth of appropriate single crystals.

Molecular structure of *$[Cu_4(bpypz)_4(H_2O)_4](NO_3)_4 \cdot 4H_2O$*

Figure 2 shows the geometry of the homodinuclear Cu(II) cation complex $[Cu_2(bpypz)_2(H_2O)_2]^{2+}$ and the atom numbering scheme. The atomic coordinates and selected bond distances and angles of the compound are reported in Tables 1 and 2, respectively. The bpypz ligands in the Cu(II) complex are nearly planar (r.m.s. deviations from the mean plane = 0.03 Å). One important feature of this Cu(II) complex is the formation of a couple of dimers in the crystal structure. The crystallographic point group symmetry of the tetramer is 222. Figure 3 represents one such coupled dimer viewed normal to the twofold symmetry axis parallel to [001]. In this way, each copper atom is octahedrally coordinated by two pyridine and two pyrazole nitrogen atoms and, at the axial positions, by one water molecule (Cu–O28 = 2.22 Å) and one pyrazole ring at approximately 3.68 Å belonging to the other dimeric complex constituting the 'tetrameric' copper(II) compound.

The crystal structure contains two nitrate groups for each dimeric Cu(II) complex. One nitrate group, i.e. N20, 2× = O21, O22 (N20–O21 = 1.197(6) Å; N20–O22 = 1.195(8) Å) is located on the twofold symmetry axis parallel to [001] (Fig. 3), and the second one, i.e. N23, O24, O25, O26 (N23–O25 = 1.198(9) Å; N23–O26 = 1.190(9) Å) is placed at a general position with an occupation factor of 1/2. The position of this second nitrate group is also statistically occupied (occupation factor 0 1/2) by a water molecule with the positional parameters of the oxygen atoms very close to those of O24. Due to the difficulty of refining both atoms separately, a single oxygen atom with full occupation has been refined in an averaged position. This fact explains the too short refined distance N23–O24 = 0.95(1) Å. To distinguish between the oxygen atom in the nitrate group and in the water molecule, they are denoted by O24 and O24*, respectively.

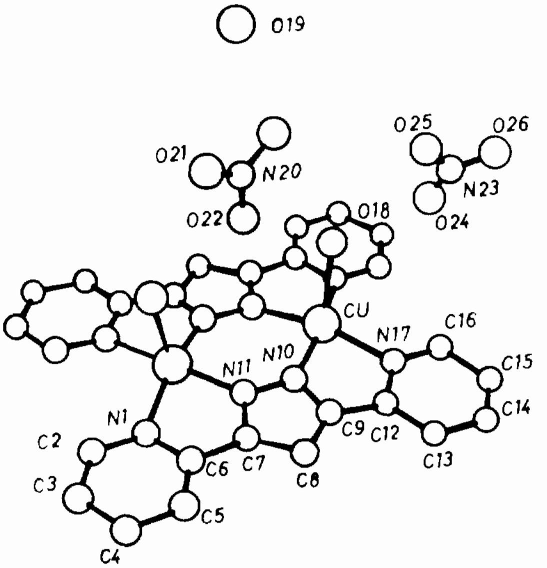

Fig. 2. Perspective view and atom numbering scheme of the dimeric units forming tetrakis{[(3,5-bis(pyridin-2-yl)-pyrazolate)(aqua)copper(II)] nitrate monohydrate}.

TABLE 1. Final positional parameters (×10⁴) for non-H atoms and equivalent temperature coefficients (Å²) with e.s.d.s in parentheses

Atom	Site	Occupancy	*x/a*	*y/b*	*z/c*	B_{eq}
Cu	32(h)	1	5516(.5)	623(.4)	1960(.4)	3.98
N1	32(h)	1	6753(3)	2731(2)	1875(2)	3.75
C2	32(h)	1	7213(4)	3166(3)	1866(3)	5.16
C3	32(h)	1	6975(5)	3722(3)	1864(3)	5.55
C4	32(h)	1	6244(5)	3831(3)	1878(3)	5.50
C5	32(h)	1	5763(4)	3378(3)	1884(3)	4.60
C6	32(h)	1	6038(3)	2843(3)	1877(3)	3.91
C7	32(h)	1	5582(3)	2345(2)	1878(3)	3.66
C8	32(h)	1	4840(3)	2251(3)	1864(3)	4.29
C9	32(h)	1	4794(3)	1669(3)	1877(3)	3.88
N10	32(h)	1	5453(3)	1440(2)	1911(2)	4.05
N11	32(h)	1	5942(3)	1856(2)	1907(2)	4.16
C12	32(h)	1	4204(3)	1264(3)	1876(3)	3.82
C13	32(h)	1	3485(4)	1424(4)	1860(3)	4.91
C14	32(h)	1	2955(4)	1013(4)	1861(3)	5.98
C15	32(h)	1	3158(5)	460(4)	1881(4)	6.49
C16	32(h)	1	3891(4)	329(3)	1910(4)	6.13
N17	32(h)	1	4410(3)	721(2)	1901(2)	4.28
O18	32(h)	1	7054(3)	2039(3)	2759(2)	6.67
O19	16(g)	1	5/8	1/8	4994(4)	10.27
N20	16(g)	1	5/8	1/8	3677(4)	5.88
O21	32(h)	1	6440(4)	1662(3)	3892(3)	11.04
O22	16(g)	1	5/8	1/8	3240(4)	12.80
N23	32(h)	1/2	8356(8)	2816(7)	3299(6)	4.48
O24	32(h)	1	8133(5)	2819(4)	2987(3)	10.62
O25	32(h)	1/2	8117(9)	2517(6)	3612(6)	10.23
O26	32(h)	1/2	8864(10)	3075(9)	3437(6)	15.32

To preserve the electroneutrality, the two-related O18 atoms of one Cu(II) complex must have as nearest atoms two nitrate groups and one O24*. The excess positive charge is thus compensated by hydrogen bonds involving O18. The most probable H-bond network is: O18–H...O22 = 2.74(1) Å (2×); O18–H...O24 = 2.80(2) Å (1×); O24*-H...O19′ = 2.84(2) Å (1×); O19′-H...O24″ = 2.84(2) Å (1×); O19′-H...O21′ = 3.19(2) Å (1×).

The copper atoms in the associated pair of dimer units can be described as forming an elongated tetrahedron. The Cu–Cu distance is 4.044 Å. The remaining edges of the tetrahedron are 4.744(1) (2×) and 4.898(1) (2×) Å.

Spectroscopic properties

The copper(II) nitrate compound exhibits one single band at 1764 cm⁻¹ in the IR spectra, assigned to the

TABLE 2. Selected bond lengths (Å) and bond angles (°) with e.s.d.s in parentheses

N10–Cu	1.954(5)
N17–Cu	2.074(5)
N1*–Cu	2.092(5)
N11*–Cu	1.942(5)
C2–N1	1.344(6)
C6–N1	1.356(5)
C3–C2	1.396(11)
C4–C3	1.383(11)
C5–C4	1.401(10)
C6–C5	1.372(9)
C7–C6	1.457(6)
C8–C7	1.396(6)
N11–C7	1.346(5)
C9–C8	1.389(6)
N10–C9	1.344(5)
C12–C9	1.459(5)
N11–N10	1.343(5)
C13–C12	1.390(9)
N17–C12	1.350(5)
C14–C13	1.387(10)
C15–C14	1.371(11)
C16–C15	1.400(11)
N17–C16	1.342(6)
N1*–Cu–N17	107.7(2)
N11*–Cu–N10	91.7(2)
N1*–Cu–N11*	79.2(2)
N17–Cu–N10	79.8(2)
Cu–N17–C16	129.1(4)
Cu–N1–C2	128.5(4)
Cu–N10–N11	134.0(4)
Cu–N11–N10	133.8(4)

Symmetry code of all atoms marked with *: $\frac{5}{4}-x$, $\frac{1}{4}-y$, z.

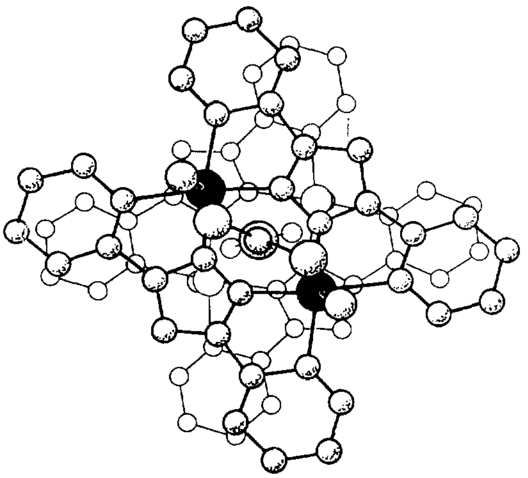

Fig. 3. Perspective view along the twofold axis parallel to [001] of tetrakis{[(3,5-bis(pyridine-2-yl)pyrazolate)(aqua)copper(II)] nitrate monohydrate}.

$\nu_1+\nu_4(E', D_{3h})$ combination band of the nitrate group. The presence of one single band in this region suggests an ionic character for the nitrate group in the complex [9]. In addition, the complex exhibits one single strong band in the ν_3 mode region at 1385 cm^{-1}, as is expected for an ionic nitrate group [10].

The electronic spectra of the copper compounds exhibit one single band at 610 (nitrate), 718 (chloride) and 684 (bromide) nm in the solid state (KBr pellets) or 614 (nitrate) and 596 (chloride) nm in 10^{-3} M methanolic solution (no satisfactory spectra were obtained for the bromide compound in methanolic solution due to its low solubility). These data suggest that the copper 'tetrameric' arrangement is preserved for the nitrate complex at least in recently prepared methanolic solutions, but not in the chloride and perhaps in the bromide complexes, in which a simple dimeric arrangement with halide coordination appears to be more reasonable.

Magnetic susceptibility measurements

Figures 4 and 5 show the temperature-dependent molar magnetic susceptibility (*) and magnetic moment (BM) (▲) of a powdered sample of the compound $[Cu_4(bpypz)_4(H_2O)_4](NO_3)_4\cdot 4H_2O$ with the calculated values (solid lines) assuming a dimer model and parameters in Table 3 and assuming a tetramer model and parameters in Table 4, respectively. The magnetic behaviour of the compound $[Cu_4(bpypz)_4(H_2O)_4](NO_3)_4\cdot 4H_2O$ was studied in the range 5.8–290.2 K. The susceptibility data show a maximum near to room temperature decreasing at lower temperatures with a minimum at 85 K. At lower temperatures the susceptibility increases again, probably due to paramagnetic impurities. The magnetic moment (per Cu atom) is 0.2 BM at 5.8 K and rises to 1.43 at 290.2 K. This behaviour is characteristic of an overall antiferromagnetic interaction with a singlet ground state.

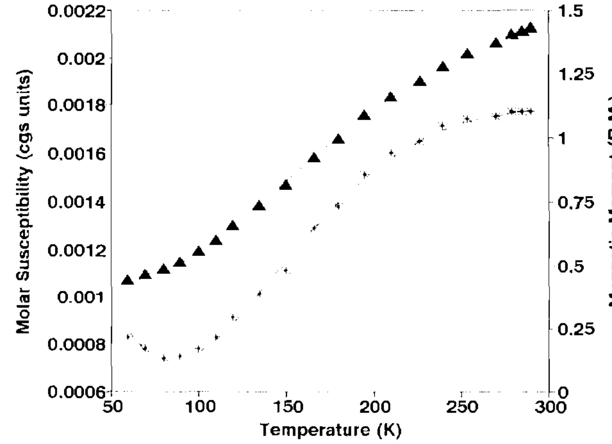

Fig. 4. Temperature-dependent molar magnetic susceptibility (*) and magnetic moment (BM) (▲) of a powdered sample of the compound $[Cu_4(bpypz)_4(H_2O)_4](NO_3)_4\cdot 4H_2O$ with the calculated values (solid lines) assuming a dimer model and parameters in Table 3.

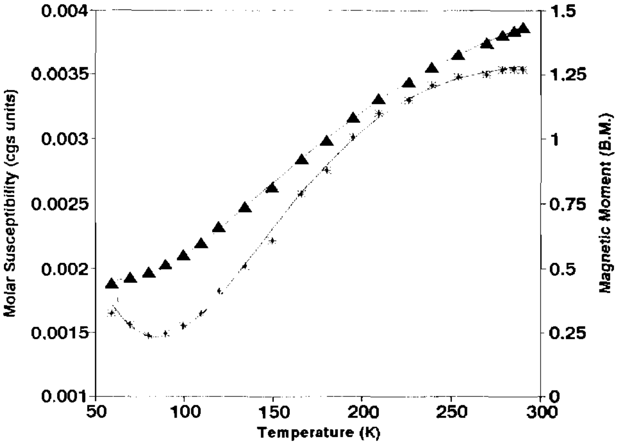

Fig. 5. Temperature-dependent molar magnetic susceptibility (*) and magnetic moment (BM) (▲) of a powdered sample of the compound $[Cu_4(bpypz)_4(H_2O)_4](NO_3)_4 \cdot 4H_2O$ with the calculated values (solid lines) assuming a tetramer model and parameters in Table 4.

TABLE 3. Fitting parameters for the title compounds assuming a magnetic dimer model

Compound	J (cm^{-1})	g	ρ	R^a
[CuLNO$_3$}	-180.9	2.34	0.042	3.2×10^{-10}
[CuLCl]	-169.2	2.34	0.052	9.4×10^{-10}
[CuLBr]	-178.1	2.28	0.038	7.9×10^{-10}

$^a R$ = reduced chi-squared.

TABLE 4. Fitting parameters for the title compounds assuming a magnetic trimer model

Compound	J_1	J_2	J_3	R^a
[CuLNO$_3$}	-180.9	1.5	1.5	2.5×10^{-8}
[CuLCl]	-169.2	3.9	3.9	1.2×10^{-6}
[CuLBr]	-178.1	-17.8	25.6	2.8×10^{-7}

$^a R$ = reduced chi-squared.

In a first approach, we interpret the magnetic behaviour in terms of a dinuclear formulation via a simple Bleaney–Bowers equation. The energy gap 2J between the singlet ground state and the triplet state is deduced from the magnetic data through the theoretical expression [11]

$$\chi_M = \frac{2Ng^2\beta^2}{kT}[3+\exp(-2J/kT)]^{-1}(1-\rho) + \rho\frac{2Ng^2\beta^2S(S+1)}{3kT} + 2N\alpha$$

where N, β, k and g have their usual meanings; ρ is the molar fraction of paramagnetic impurities and $N\alpha$ is the temperature independent paramagnetism (*TIP*) (60.0×10^{-6} cm^3 mol^{-1}/copper atom). The fitting was carried out by using a least-squares procedure allowing all the parameters, J, g and ρ to vary, using all the data from 50–300 K. The impurity is assumed to be Cu^{2+} ($S=1/2$), to have the same diamagnetic correction, molecular weight and g factor as the dinuclear complex, and to have a magnetic susceptibility that follows the Curie law [12]. The fit is excellent as can be seen in Table 3 and in Fig. 4, revealing strong antiferromagnetic interactions ($J = -180.9$ cm^{-1}) between copper(II) ions in the dimeric units.

In a second approach, the possible interaction between the two dinuclear units forming a tetrameric compound was considered. The X-ray crystal structure results reveal the presence of a C_2 axis through the center of the Cu–Cu distance in each dinuclear unit. Assuming a distorted C_2 tetrahedral arrangement for the Cu_4 core of the hypothetical tetranuclear complex, three parameters are needed to take into account the exchange interactions. J_1 is the parameter of the interaction within one dimeric unit, J_2 and J_3 are the parameters of the cross interactions. The latter parameters are not presumed equal due to two slightly different interdimer Cu–Cu distances in the tetramer complex, as shown by the X-ray solved molecular structure. A general magnetic susceptibility expression derived from the van Vlek equation was used as reported previously [13].

The observed data were therefore fitted to the aforementioned model, taking into account the fraction of monomeric impurities and the temperature independent paramagnetism (*TIP*) as was done in the dimer model. To avoid the problems of overparametrization, the g factor and the molar fraction of monomeric impurities ρ were assumed to be the same as the values calculated in the dimer model. Only J_1, J_2 and J_3 parameters were allowed to vary in the least-squares procedure. The starting J_1 value was taken to be the same as that found in the dimer model. In spite of the refinement, cycles finally converged giving a non-modified J_1 value. No better results were obtained when all the parameters in the least-squares procedure were allowed to vary. As can be seen in Fig. 5 and Table 4, the fit is excellent. The small values of the J_2 ($+1.5$ cm^{-1}) and J_3 ($+1.5$ cm^{-1}) parameters evidence small ferromagnetic interdimer interactions in the nitrate compound. However, the overall fit was not significantly improved assuming the tetramer model instead of the dimer one.

The large antiferromagnetic intradimer interaction could be attributed to the good overlap between the copper(II) and the ligand's magnetic orbitals in the strictly planar dinuclear moiety. It is well known that the Cu(II) ion in a square planar environment has its unpaired electron in a $d_{x^2-y^2}$ orbital [12], so any lost of planarity in the dimeric unit could negatively perturb the magnetic orbitals overlap. On the other hand, the small ferromagnetic interdimer interaction is in agreement with the large interdimer Cu–Cu distances and the consequent small overlap between copper(II) orbitals and the π-system orbitals of the pyrazole. This behaviour has also been found in several tetrameric cubane-like copper(II) complexes but with oxo or hydroxo bridges [11, 14–6] as reported in the literature.

The copper(II) chloride and bromide compounds behave in a similar fashion, as shown in Tables 3 (dimer model) and 4 (tetramer model). Only the bromide complex apparently has stronger interdimer interactions; at present the reason for this is not clear.

There are small differences in the J value (dimer model) between the nitrate, chloride and bromide complex. It is very difficult to rationalize them without knowledge of the three molecular structure. However, several examples of counteranion influence on the magnetic properties of the resulting compounds have been reported in the literature [11]. On the other hand, the chloride and bromide complexes probably exhibit only a dimeric arrangement with halide coordination in the solid state, according to their electronic spectra, and this fact makes the comparison with the behaviour of the associated pair of dimers of the nitrate complex more difficult.

Conclusions

Copper(II) ion forms a structurally tetramer complex with the bpypz ligand in the solid state. This compound can be considered as composed of two weakly associated pairs of dimers with $\pi(\eta^5)$ inter-dinuclear interactions, as is evidenced by magnetic susceptibility data analyses, long Cu–pyrazole distances and the observed electronic spectra.

Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre comprises bond angles, H-atom coordinates and thermal coefficients.

Acknowledgements

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References

1 S. Trofimenko, *Prog. Inorg. Chem., 34* (1986) 115.

2 L. A. Oro, D. Carmona, M. P. Lamata, M. C. Agreda, C. Foces-Foces, F. H. Cano and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.,* (1984) 1823.

3 G. López, G. García, J. Ruíz, G. Sánchez, J. García and C. Vicente, *J. Chem. Soc., Chem. Commun.,* (1989) 1045.

4 J. Casabó, J. Pons, K. S. Siddiqi, F. Teixidor, E. Molins and C. Miravitlles, *J. Chem. Soc., Dalton Trans.,* (1989) 1401.

5 J. Pons, F. J. Sánchez, X. López, F. Teixidor and J. Casabó, *Polyhedron, 9* (1990) 2839.

6 S. Trofimenko, *Chem. Rev., 72* (1972) 497.

7 J. Rius and C. Miravitlles, *Acta Crystallogr., Sect. A, 45* (1989) 490.

8 G. M. Sheldrick, *SHELX76,* program for crystal structure determination, University of Cambridge, UK, 1976.

9 A. B. P. Lever and E. Mantovani, *Inorg. Chem., 10* (1971) 817.

10 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 1978.

11 J. Sletten, A. Sørensen, M. Julve and Y. Journaux, *Inorg. Chem., 29* (1990) 5054.

12 G. Kolks, S. J. Lippard, J. V. Waszczak and H. R. Lilienthal, *J. Am. Chem. Soc., 104* (1982) 717.

13 J. W. Hall, W. E. Estes, E. D. Estes, R. P. Scaringe and W. E. Hatfield, *Inorg. Chem., 16* (1977) 1572.

14 W. Mazurek, K. J. Berry, K. S. Murray, M. J. O'Connor, M. R. Snow and A. G. Wedd, *Inorg. Chem., 21* (1982) 3071.

15 L. Merz and W. Haase, *J. Chem. Soc., Dalton Trans.,* (1978) 1594.

16 L. Schwabe and W. Haase, *J. Chem. Soc., Dalton Trans.,* (1985) 1909.