

Copper(II) coordination chemistry of 4,6-di-(2'-pyridylthio)-pyrimidine involving polymeric and metallocyclic structures

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Abstract

4,6-Di-(2'-pyridylthio)pyrimidine (DPP) forms 1:1 complexes with Cu(II) salts: $[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I), $([\text{Cu}(\text{DPP})(\text{H}_2\text{O})(\text{CH}_3\text{CN})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O})_x$ (II), $[\text{Cu}_2(\text{DPP})_2\text{Br}_4]$ (III), $[\text{Cu}_2(\text{DPP})_2(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ (IV). I crystallized in the monoclinic space group $P2_1/c$ ($Z=4$) with $a=7.841(2)$, $b=14.989(2)$, $c=13.851(1)$ Å, $\beta=90.22(1)^\circ$, $V=1627.8(4)$ Å³, $R=0.031$ for 2071 observed reflections. II crystallized in the monoclinic space group $P2_1/a$ ($Z=4$) with $a=12.632(6)$, $b=14.783(6)$, $c=14.480(5)$ Å, $\beta=98.42(3)^\circ$, $V=2675(1)$ Å³, $R=0.055$ for 1947 observed reflections. The Cu(II) ions in I have distorted square-pyramidal geometries and are bound to two pyridine nitrogens, one pyrimidine nitrogen and two chloride anions. Two DPP ligands act as tridentate donors and coordinate to two copper ions forming a large metallocyclic ring. In II DPP still acts as a tridentate ligand, but coordinates to two Cu(II) ions, linking the metal centers in a polymeric chain. Each copper ion has a square pyramidal geometry with three nitrogen donors from the DPP ligands and one coordinated acetonitrile and one coordinated water molecule. Room temperature magnetic moments for all complexes suggest that they have dilute copper(II) centers. I and III show a two-electron reduction at positive potentials (0.41–0.46 V versus SCE).

Introduction

The study of dinuclear complexes containing bridging heterocyclic ligands has been the subject of much recent attention, since they are of great significance as models for some biological systems [1–4]. The magnetic communication between the two metal centers via the π system of the heterocyclic ligand varies with the identity of the ligand. Tetradentate (N_4) and hexadentate (N_6) phthalazine and tetradentate (N_4) pyridazine ligands form predominantly binuclear copper(II) complexes, in which the two copper centers are bridged by a diazine group and in many cases by hydroxide and an additional exogenous bridge, e.g. Br, Cl, NO_3 , SO_4 , IO_3 [5–19]. The two copper ions usually experience moderate to strong antiferromagnetic coupling [12–15, 17–19]. In related dinuclear copper(II) complexes involving pyrazine bridges, where the heterocyclic nitrogen donor centers are arranged at the 1,4 ring positions [20–24], only very weak intramolecular antiferromagnetic interactions were observed. Some related pyrimidine ligands, which involve a 1,3 arrangement of nitrogen donors, have been studied. The doubly bidentate chelating ligand 2,2'-bipyrimidine forms homodinuclear Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes

involving two pyrimidine bridges [25–29]. In general the pyrimidine bridge results in weak antiferromagnetic coupling between two metal centers, although in a series of dinuclear copper(II) complexes moderate antiferromagnetic exchange was observed [28]. Ligands containing one potentially bridging pyrimidine group, such as 4,6-di(3,5-dimethylpyrazol-1-yl)pyrimidine can, in principle, bridge two metal centers, but so far this type of coordination behavior is rare, and only appears to occur in a di-rhodium complex [30]. The synthesis of 4,6-bis(2'-pyridylthio)pyrimidine (DPP), which would logically create two N_2 coordination sites separated by the 1,3 heterocyclic bridge, was carried out to complement the earlier work on N_4 diazine bridged complexes [5–19] and further explore the role of the 1,3 heterocyclic pyrimidine bridge as a spin exchange medium.

Experimental

Synthesis of ligands and copper complexes

4,6-Di-(2'-pyridylthio)pyrimidine (DPP) (Fig. 1)

Pyridine-2-thiol (4.46 g, 40 mmol) was added to anhydrous ethanol (30 ml) in which sodium metal (0.92 g, 40 mmol) had been dissolved and the resulting solution was stirred for 30 min. A solution of 4,6-dichloro-

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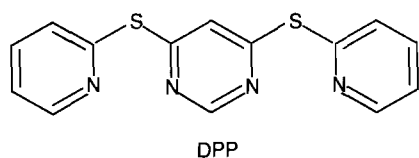


Fig. 1. Structural representation of the ligand DPP.

pyrimidine (2.98 g, 20 mmol) in 100 ml EtOH was added dropwise by using a pressure equalizing funnel, over a period of 2 h under reflux, during which time a white precipitate formed. The mixture was stirred overnight and the EtOH was evaporated to dryness. The residue was extracted with CHCl_3 , and dried with anhydrous Na_2SO_4 . The volume of the CHCl_3 solution was reduced to 40 ml, 100 ml hexane was then added and the mixture put in the refrigerator, until white crystals formed. Yield 5.5 g (92%); m.p. 67–69 °C. Mass spectrum: 298 (2%, parent), 220 (100%), 188 (27%), 160 (12%), 135 (13%), 78 (61%). ^1H NMR (δ ppm versus TMS, CDCl_3): 7.17 (doublet, 1H, pyrimidine), 7.30 (multiplet, 2H, pyridine), 7.61 (multiplet, 2H, pyridine), 7.73 (multiplet, 2H, pyridine), 8.57 (multiplet, 2H, pyridine), 8.70 (doublet, 1H, pyrimidine).

Anticipating that DPP would selectively bind two metal centers per ligand a ratio of metal:ligand of 2:1 or larger was used. In all cases, however, the complex stoichiometry turned out to be 1:1.

$[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I)

DPP (149 mg, 0.5 mmol) was dissolved in 15 ml methanol, added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (226 mg, 1.5 mmol) in 15 ml methanol and the resulting mixture filtered. The green colored filtrate was left at room temperature for several days and green crystals formed. Yield 162 mg (75%). *Anal.* Calc. for $\text{Cu}_2(\text{C}_{28}\text{H}_{20}\text{N}_8\text{S}_4)\text{Cl}_4$ (I): C, 38.85; H, 2.33; N, 12.94. Found: C, 38.81; H, 2.43; N, 12.87%.

$[\text{Cu}(\text{DPP})(\text{H}_2\text{O})(\text{CH}_3\text{CN})] \cdot (\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ (II)

DPP (149 mg, 0.5 mmol) was dissolved in 10 ml CH_3CN , added to a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (370.5 mg, 1.0 mmol) in 10 ml CH_3CN and the resulting solution filtered. The deep green filtrate was left at room temperature for several days and blue crystals formed. Yield 208 mg (63%). *Anal.* Calc. for $\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{S}_2)(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})(\text{ClO}_4)_2$ (II): C, 32.72; H, 2.75; N, 12.72. Found: C, 32.51; H, 2.74; N, 12.67%. The X-ray sample was chosen from the bulk sample and was shown to contain just one acetonitrile. Although the sample appeared to be uniform it must contain a proportion of crystals with more acetonitrile. On standing for an extended period of time crystals of the bulk sample crumble and lose solvent.

$[\text{Cu}_2(\text{DPP})_2\text{Br}_4]$ (III)

This compound was prepared in a similar manner to I by using CuBr_2 to give greenish brown crystals. Yield 190 mg (73%). *Anal.* Calc. for $\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{S}_2)\text{Br}_2$: C, 32.23; H, 1.93; N, 10.74. Found: C, 32.33; H, 2.18; N, 10.58%.

$[\text{Cu}_2(\text{DPP})_2(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ (IV)

This compound was prepared in a similar manner to I by using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and was isolated as blue crystals. Yield 66%. *Anal.* Calc. for $\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{S}_2)(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$: C, 33.97; H, 2.24; N, 16.98. Found: C, 33.89; H, 2.30; N, 16.71%.

Physical measurements

C, H, N analyses were carried out by Canadian Microanalytical Service, Delta, British Columbia.

Room temperature magnetic moments were measured by the Faraday method using a Cahn 7600 Faraday magnetic susceptibility system. NMR spectra were recorded using a GE 300 MHz instrument and mass spectra with a VG micromass 7070 HS spectrometer. IR spectra were recorded using a Mattson Polaris FTIR spectrometer and electronic spectra with a Cary 5E instrument. EPR spectra were recorded using a Bruker ESP 300 X-band spectrometer at room temperature and 77 K.

Electrochemical measurements were made with a BAS CV-27 voltammograph and a Hewlett-Packard X-Y recorder. The electrochemical cell consisted of a Pt wire auxiliary electrode, a SCE reference electrode and a glassy-carbon disk working electrode. All measurements were carried out in DMF (0.1 mol dm^{-3} TEAP), under a nitrogen atmosphere with 2×10^{-3} mol dm^{-3} complex concentrations.

Data collection and structure refinement

The diffraction intensities of a green parallelepiped crystal of $[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I) of approximate dimensions $0.400 \times 0.200 \times 0.150$ mm were collected using a Rigaku AFC6S diffractometer with graphite monochromatized $\text{Mo K}\alpha$ radiation. Cell constants and the orientation matrix were obtained by least-squares refinements of the setting angles of 21 carefully centered reflections in the range $44.56 < 2\theta < 48.82^\circ$. Based on a statistical analysis of the intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$. Machine and data collection parameters and crystal data are given in Table 1. The data were collected at 25 ± 1 °C using the ω - 2θ scan technique to a maximum 2θ value of 50.0° . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a take-off angle of 6.0° . Scans of $(1.78 + 0.30 \tan \theta)^\circ$ were made at a speed of $16.0^\circ/\text{min}$

TABLE 1. Crystal data for **I** and **II**

Compound	Cu ₂ (DPP) ₂ Cl ₄ (I)	[[Cu(DPP)(H ₂ O)(CH ₃ CN)](ClO ₄) ₂ ·2H ₂ O) _x (II)
Formula	C ₂₈ H ₂₀ N ₈ S ₄ Cu ₂ Cl ₄	C ₁₆ H ₁₉ N ₅ S ₂ CuCl ₂ O ₁₁
Formula weight	567.28	655.92
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> (Å)	7.841(2)	12.632(6)
<i>b</i> (Å)	14.989(2)	14.783(6)
<i>c</i> (Å)	13.851(1)	14.480(5)
β (°)	90.22(1)	98.42(3)
<i>V</i> (Å ³)	1627.8(4)	2675(1)
<i>Z</i>	4	4
ρ_{calc} (g cm ⁻³)	2.315	1.628
Crystal size (mm)	0.4 × 0.2 × 0.15	0.35 × 0.18 × 0.2
Crystal colour	green	blue
Radiation (λ , Å)	Mo K α (0.71069)	Cu K α (1.54178)
μ (cm ⁻¹)	35.40	50.18
2 θ Scan range (°)	44.6–48.8	43.7–47.6
Data collected	3222	4382
Unique data	2994	4171
With <i>I</i> > 3.00 σ (<i>I</i>)	2071	1947
L.S. parameters	209	335
Goodness of fit	1.59	1.84
<i>R</i>	0.031	0.055
<i>R</i> _w	0.029	0.047
Temperature (°C)	25	25

(in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of two rescans) and the counts were accumulated to assure good counting statistics. The ratio of peak counting time to background counting time was 2:1.

A total of 3222 reflections was collected. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection (no decay correction applied). An empirical absorption correction was applied, using the program DIFABS [31], which resulted in transmission factors ranging from 0.89 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods [32, 33]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2071 observed reflections ($I > 3.00\sigma(I)$) and 209 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.031$ and $R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2} = 0.029$. The standard deviation of an observation of unit weight was 1.59. The weighting scheme was based on counting statistics and included a factor ($\rho = 0.01$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to

0.32 and -0.30 electrons/Å³, respectively, and have no chemical significance. Neutral atom scattering factors [34] and anomalous dispersion terms [35, 36] were taken from the usual sources. All calculations were performed using the TEXSAN [37] crystallographic software package using a VAX 3100 workstation. Hydrogen atoms were placed in calculated positions with thermal parameters set at 1.2 times those of the bonded carbon atoms. Atomic positional parameters are given in Table 2 and selected bonded distances and angles are given in Table 3. See also 'Supplementary material'.

The diffraction intensities of a freshly prepared blue parallelepiped crystal of **II** of approximate dimensions $0.350 \times 0.180 \times 0.200$ mm were collected in a similar manner to **I**. The intensities of three representative reflections, measured after every 150 reflections, remained constant throughout the data collection indicating no apparent instability of the crystal due to solvent loss. Crystal data, intensity collection and refinement details are given in Table 1. Atomic positional parameters are given in Table 4 and selected bond distances and angles are given in Table 5. Hydrogen atoms on the water molecules were located in a difference map, while others were placed in calculated positions. Hydrogens were included in the last round of least-squares, but were not refined. See also 'Supplementary material'.

TABLE 2. Positional parameters and equivalent isotropic temperature factors for $[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Cu(1)	0.78202(6)	0.37724(3)	0.23084(3)	2.31(2)
Cl(1)	0.9917(1)	0.32602(8)	0.35158(7)	3.22(5)
Cl(2)	0.5141(1)	0.37753(8)	0.29176(8)	3.49(5)
S(1)	0.7182(1)	0.32929(8)	0.00145(7)	2.75(5)
S(2)	1.3539(1)	0.45317(8)	-0.10175(8)	2.95(5)
N(1)	0.7376(4)	0.2529(2)	0.1766(2)	2.3(2)
N(2)	0.9619(4)	0.3904(2)	0.1215(2)	2.2(1)
N(3)	1.1977(4)	0.4888(2)	-0.2699(2)	2.6(2)
N(4)	1.2355(4)	0.4406(2)	0.0721(2)	2.7(2)
C(1)	0.7254(5)	0.1830(3)	0.2369(3)	2.9(2)
C(2)	0.6826(6)	0.0985(3)	0.2059(3)	3.3(2)
C(3)	0.6522(6)	0.0840(3)	0.1104(4)	3.8(2)
C(4)	0.6654(6)	0.1547(3)	0.0464(3)	3.4(2)
C(5)	0.7084(5)	0.2381(3)	0.0821(3)	2.3(2)
C(6)	0.9246(5)	0.3703(3)	0.0288(3)	2.3(2)
C(7)	1.1190(5)	0.4218(3)	0.1382(3)	2.7(2)
C(8)	1.1949(5)	0.4220(3)	-0.0197(3)	2.4(2)
C(9)	1.0394(5)	0.3830(3)	-0.0448(3)	2.3(2)
C(10)	1.2631(5)	0.4223(3)	-0.2157(3)	2.7(2)
C(11)	1.2747(6)	0.3355(3)	-0.2469(3)	3.5(2)
C(12)	1.2176(6)	0.3151(3)	-0.3398(4)	4.2(3)
C(13)	1.1520(6)	0.3813(4)	-0.3960(3)	4.3(3)
C(14)	1.1433(6)	0.4666(3)	-0.3588(3)	3.7(2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_{i=1}^3\sum_{j=1}^3 U_{ij}a_i^*a_j^*\vec{a}_i\cdot\vec{a}_j.$$

TABLE 3. Selected bond lengths and angles in $[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I)

Cu(1)–Cl(1)	2.463(1)	Cl(1)–Cu(1)–Cl(2)	111.40(5)
Cu(1)–Cl(2)	2.267(1)	Cl(1)–Cu(1)–N(1)	94.48(9)
Cu(1)–N(1)	2.039(3)	Cl(1)–Cu(1)–N(2)	94.09(9)
Cu(1)–N(2)	2.083(3)	Cl(1)–Cu(1)–N(3)	94.2(1)
Cu(1)–N(3)	2.086(3)	Cl(2)–Cu(1)–N(1)	88.96(9)
		Cl(2)–Cu(1)–N(2)	154.35(9)
		Cl(2)–Cu(1)–N(3)	88.4(1)
		N(1)–Cu(1)–N(2)	86.2(1)
		N(1)–Cu(1)–N(3)	171.3(1)
		N(2)–Cu(1)–N(3)	92.7(1)

Results and discussion

Description of the structures

$[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I)

A structural representation of compound I is given in Fig. 2, together with the atomic labelling scheme, and bond lengths and bond angles relevant to the copper coordination spheres are given in Table 3. The structure consists of a very unusual arrangement of two tridentate ligands coordinated to two copper(II) centers in such a way as to create a large metallocycle, involving an alternating arrangement of ligands and metals. The copper–copper separation is 8.142(1) Å, and the distance between the pyrimidine rings is ap-

TABLE 4. Positional parameters and equivalent isotropic temperature factors (e.s.d.s) for $[(\text{Cu}(\text{DPP})(\text{H}_2\text{O})(\text{CH}_3\text{CN}))(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}]_x$ (II)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Cu(1)	0.3679(1)	0.4043(1)	0.7551(1)	3.06(6)
Cl(1)	0.3306(3)	0.7133(2)	0.9704(2)	5.1(2)
Cl(2)	0.4653(2)	0.0930(3)	0.7237(2)	5.5(2)
S(1)	0.0482(2)	0.0708(2)	0.6268(2)	4.4(1)
S(2)	0.2664(2)	0.3620(2)	0.5324(2)	4.7(1)
O(1)	0.3114(8)	0.6941(6)	0.8764(5)	8.6(6)
O(2)	0.234(1)	0.7323(9)	1.0004(7)	13.8(9)
O(3)	0.3805(6)	0.6389(5)	1.0223(5)	6.0(4)
O(4)	0.395(1)	0.7868(7)	0.9873(8)	14.4(9)
O(5)	0.489(1)	0.1295(7)	0.8100(7)	13.8(8)
O(6)	0.433(1)	0.1654(8)	0.6662(8)	13.5(9)
O(7)	0.3831(9)	0.0347(9)	0.716(1)	15(1)
O(8)	0.5473(8)	0.0490(8)	0.6950(9)	14(1)
O(9)	0.4501(5)	0.3116(5)	0.8357(4)	4.3(4)
O(10)	0.5178(7)	0.2805(9)	0.3516(8)	12.8(9)
O(11)	0.508(1)	0.192(1)	0.249(1)	22(2)
N(1)	0.2911(6)	0.4934(5)	0.6638(5)	3.1(4)
N(2)	0.2615(6)	0.3080(5)	0.7099(5)	3.0(4)
N(3)	0.1649(6)	0.1793(5)	0.7501(6)	3.5(4)
N(4)	-0.0069(6)	0.0100(5)	0.7882(5)	2.9(4)
N(5)	0.2787(7)	0.4502(6)	0.8713(6)	4.2(5)
C(1)	0.2749(8)	0.5772(7)	0.6923(7)	3.9(5)
C(2)	0.2174(9)	0.6422(7)	0.6394(8)	4.9(6)
C(3)	0.171(1)	0.6183(8)	0.552(1)	5.7(7)
C(4)	0.1844(9)	0.5321(8)	0.5186(8)	5.1(7)
C(5)	0.2447(8)	0.4715(7)	0.5777(7)	3.7(5)
C(6)	0.2242(7)	0.2926(6)	0.6197(6)	3.1(5)
C(7)	0.2281(7)	0.2502(7)	0.7705(6)	3.3(5)
C(8)	0.1315(8)	0.1643(7)	0.6603(7)	3.6(5)
C(9)	0.1569(8)	0.2227(7)	0.5908(7)	3.5(5)
C(10)	0.0689(8)	0.0060(6)	0.7322(7)	3.8(5)
C(11)	0.1591(8)	-0.0471(8)	0.7515(9)	5.1(6)
C(12)	0.1694(9)	-0.0987(8)	0.8321(9)	5.8(7)
C(13)	0.0941(8)	-0.0958(8)	0.8891(8)	5.0(6)
C(14)	0.0065(8)	-0.0404(7)	0.8646(7)	4.1(5)
C(15)	0.2172(8)	0.4743(7)	0.9143(7)	3.7(5)
C(16)	0.137(1)	0.5042(8)	0.9717(9)	6.7(8)

$$B_{\text{eq}} = (8\pi^2/3)\sum_{i=1}^3\sum_{j=1}^3 U_{ij}a_i^*a_j^*\vec{a}_i\cdot\vec{a}_j.$$

TABLE 5. Selected bond distances (Å) and angles (°) for $[(\text{Cu}(\text{DPP})(\text{H}_2\text{O})(\text{CH}_3\text{CN}))(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}]_x$ (II)

Cu(1)–O(9)	1.991(6)	O(9)–Cu(1)–N(1)	174.7(3)
Cu(1)–N(1)	2.012(7)	O(9)–Cu(1)–N(2)	88.2(3)
Cu(1)–N(2)	2.001(8)	O(9)–Cu(1)–N(4)	88.3(3)
Cu(1)–N(4)	2.027(7)	O(9)–Cu(1)–N(5)	92.6(3)
Cu(1)–N(5)	2.262(8)	N(1)–Cu(1)–N(2)	90.8(3)
		N(1)–Cu(1)–N(4)	91.8(3)
		N(1)–Cu(1)–N(5)	92.7(3)
		N(2)–Cu(1)–N(4)	170.0(3)
		N(2)–Cu(1)–N(5)	94.2(3)
		N(4)–Cu(1)–N(5)	95.4(3)

proximately 3.3 Å (distance from C(9) to the mean plane of the other pyrimidine ring is 3.279(4) Å). This structural feature is reminiscent of some binuclear

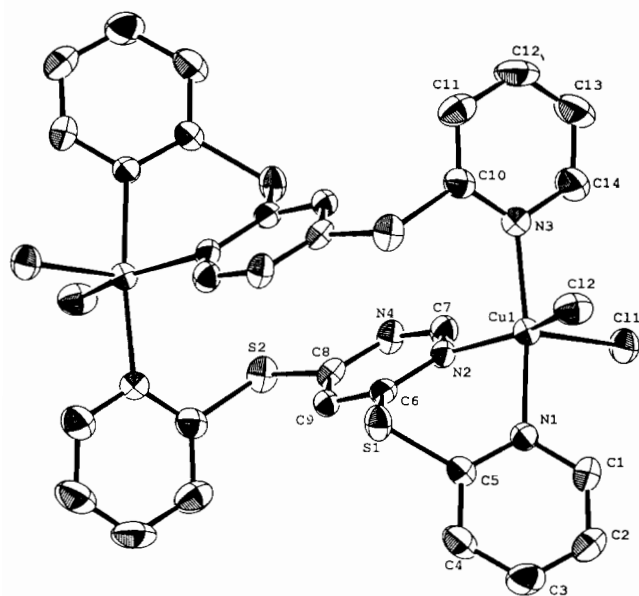


Fig. 2. Structural representation of $[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I) with hydrogen atoms omitted (40% probability thermal ellipsoids).

metallocyclic Cu(II) and Co(II) complexes of the ligand 1,2,4,5-tetrakis(4,5-dihydroimidazol-2-yl)benzene, in which metal-metal separations are approximately 7.6 Å, with a distance of about 4 Å between the parallel benzene rings [38, 39]. Although DPP is potentially a tetradentate ligand, it coordinates to the copper(II) ion, at least in the examples studied in this report, in a tridentate fashion. This may be associated, in part, with steric interactions between other potential copper ligands and hydrogen atoms on the pyrimidine 2-position and the pyridine 6-positions, as a result of the formation of six-membered chelate rings. This could lead to a severe twisting of the ligand itself possibly rendering one pyrimidine nitrogen inaccessible to the copper. The structure of a di-ruthenium(II) complex with 2,4,6-tri(2-pyridyl)-1,3,5-triazine, which involves a pyrimidine like 1,3,6-bridge [40], demonstrates that with ligands of this sort, which generate five-membered chelate rings, bis-bidentate chelation is possible. Each copper atom in I has a distorted five-coordinate geometry and is surrounded by two pyridine and one pyrimidine nitrogens and two chlorine atoms. The large angle N(2)-Cu(1)-Cl(2) of $154.35(9)^\circ$ suggests that the stereochemistry is best described as a distorted square pyramid, rather than a trigonal bipyramid, with three nitrogens and Cl(2) in the basal plane and Cl(1) in the apical site. The nitrogen-copper distances Cu(1)-N(1), Cu(1)-N(2) and Cu(1)-N(3) are 2.039(3), 2.083(3) and 2.086(3) Å, respectively, and quite normal for ligands of this sort. The copper-chlorine distances are 2.463(1) and 2.267(1) Å for Cl(1) and Cl(2), respectively, with the apical distance being much longer,

as expected. The copper atom is displaced by 0.368(3) Å from the mean plane of the basal donor set, towards the apical chlorine.

$[\text{Cu}(\text{DPP})(\text{CH}_3\text{CN})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (II)

The composition of the X-ray sample is slightly different from the complex formulation based on the bulk sample analysis. However it is assumed that the polymeric cations in both samples have the same structure. This is supported by the solid state ESR spectrum of II, which shows a unique axial signal. The structure of the cation $[\text{Cu}(\text{DPP})(\text{CH}_3\text{CN})(\text{H}_2\text{O})]^{2+}$ is represented in Fig. 3, together with the atomic labelling scheme. The overall structure is that of an infinite polymeric chain, in which DPP still acts as a tridentate ligand. The copper(II) ions are coordinated by two pyridine nitrogens and a pyrimidine nitrogen, one acetonitrile, and one water molecule in a square-pyramidal geometry with the acetonitrile nitrogen at the apex. The presence of coordinated acetonitrile is unusual, and illustrates how the metal evaluates potential ligands in the formation of a complex. Perchlorate is usually a poor choice and since no better ligands, e.g. chlorine, are present, solvent molecules are pressed into duty. It is interesting also that DPP itself does not provide a fourth nitrogen from the pyrimidine ring as a donor group, thus supporting the notion that steric factors are forcing the ligand again to behave as a tridentate donor. Short basal contacts exist to the three nitrogens (Cu(1)-N(1) 2.012(7), Cu(1)-N(2) 2.001(8), Cu(1)-N(4) 2.027(7) Å), and the water (Cu(1)-O(9) 1.991(6) Å), with a longer distance to the apical acetonitrile (Cu(1)-N(5) 2.262(8) Å). The copper center is displaced by 0.224(7) Å from the mean plane of the basal donor set, towards the acetonitrile.

Spectroscopic results

The IR spectra of $[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I) and $[\text{Cu}_2(\text{DPP})\text{Br}_4]$ (III) are identical in the range 4000-

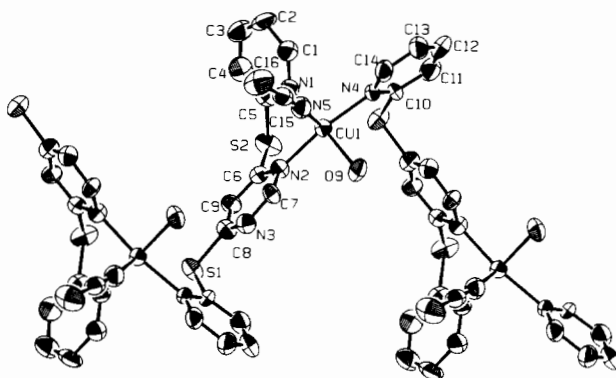


Fig. 3. Structural representation of a portion of the polymeric cation in $[\text{Cu}(\text{DPP})(\text{H}_2\text{O})(\text{CH}_3\text{CN})] \cdot (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (II) with hydrogen atoms omitted (40% probability thermal ellipsoids).

500 cm^{-1} , indicating an identical dimeric structure. Far-IR bands at 308 cm^{-1} in **I** and 252 cm^{-1} in **III** (Table 6) can be assigned to copper halogen stretch. For $([\text{Cu}(\text{DPP})(\text{CH}_3\text{CN})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN})_x$ (**II**), three moderately strong, sharp bands are observed for a freshly prepared sample at 2301, 2273 and 2247 cm^{-1} indicating the presence of more than one type of acetonitrile. Coordinated acetonitrile exhibits a single sharp peak in the range 2290–2295 cm^{-1} in a series of octahedral nickel(II) complexes [41], and a single peak at 2270 cm^{-1} in $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ [42]. The peak at 2273 cm^{-1} is therefore tentatively assigned to coordinated acetonitrile, and the other peaks to lattice acetonitrile. Re-examination of the IR spectrum of the same sample stored for about one year under ambient conditions revealed that all the acetonitrile bands disappeared. Enhanced absorption in the range 3400–3600 cm^{-1} suggests displacement of acetonitrile by water. A very strong, broad band at 1105 cm^{-1} , which remains essentially unchanged on standing, is indicative of non-coordinated perchlorate [41]. **IV** has a complicated combination ($\nu_1 + \nu_4$) nitrate spectral region with bands at 1759, 1747, 1731, 1721 cm^{-1} [43] suggesting two different monodentate nitrates. General similarities between the spectra of **I**, **III** and **IV** suggest a dimeric metalocyclic structure for **IV** also, with slightly different monodentate nitrates bound to the copper centers.

Electronic spectra (mull transmittance) for **I** and **III** show d–d bands at 770 and 810 nm, respectively (Table 6) consistent with square-pyramidal CuN_3X_2 ($\text{X} = \text{Cl}, \text{Br}$) chromophores. **II** and **IV** exhibit broad, solid state d–d bands at 655 and 610 nm, respectively, consistent with five-coordinate CuN_4O and CuN_3O_2 centers. The solid state ESR spectra of **I–IV** were recorded at room temperature (Table 6) and at 77 K, with no appreciable difference at the lower temperature. The spectra of **I** and **II** show typical axial signals, in keeping with structural and other spectroscopic data, while **III** has an

uninformative isotropic spectrum. **IV** displays three discernible signals, associated with a distorted square-pyramidal species.

Room temperature magnetic moments for compounds **I–IV** (Table 6) all exceed the spin-only value for a one unpaired electron system and suggest the presence of dilute copper(II) centers in all cases, with no spin exchange. The large distances separating the copper centers in **I**, and the long ligand molecular pathways (seven atoms involving two heterocyclic rings linked by a sulfur) in between the metals, would suggest that spin exchange would be most unlikely.

The electrochemical properties of compounds **I** and **III** were studied by cyclic voltammetry in DMF solution containing 0.1 M TEAP as supporting electrolyte (**II** and **IV** are not sufficiently soluble in suitable solvents). Cyclic voltammograms for these two compounds are very similar and involve two-electron, quasi-reversible reduction processes at positive potentials ($E_{1/2} = 0.41$ and 0.46 V, respectively), due to a one-step reduction of the dinuclear copper(II) species to dinuclear copper(I) species. ΔE_p values (Table 6) are compared with the reversible ferrocene/ferrocenium couple ($\Delta E_p = 90$ mV at 100 mV s^{-1}) under identical conditions. Controlled potential electrolysis experiments at 0.15 V (versus SCE) in DMF solution show that the reduction process is associated with a two-electron transfer. During electrolysis, the color of the solution changed from green to colorless indicating the reduction of the dinuclear copper(II) species to dinuclear copper(I) species. Re-oxidation of the fully reduced solutions at +0.55 V (versus SCE) restored the original green color and required two equivalents of charge, thus demonstrating the reversible nature of this redox process.

Supplementary material

Anisotropic thermal parameters, positional parameters for the hydrogen atoms, angles and distances

TABLE 6. Spectral, magnetic and electrochemical data

Compound	IR (cm^{-1})	μ_{eff} (BM) (r.t.)	UV–Vis (nm) ^a	ESR ^b (r.t.)	$E_{1/2}$ (V) ^c (vs. SCE)	ΔE_p (mV) ^c
$[\text{Cu}_2(\text{DPP})_2\text{Cl}_4]$ (I)	308 ($\nu(\text{Cu–Cl})$)	1.88	880, 765, 380	$g_{\parallel} = 2.25$ $g_{\perp} = 2.09$	0.41	120
$([\text{Cu}(\text{DPP})(\text{H}_2\text{O})(\text{CH}_3\text{CN})](\text{ClO}_4)_2 \cdot (\text{CH}_3\text{CN})_x$ (II)	3359, 3226 (H_2O); 2301, 2273, 2247 (CH_3CN); 1105 (ClO_4)	1.89	655, 405	$g_{\parallel} = 2.20$ $g_{\perp} = 2.06$		
$[\text{Cu}_2(\text{DPP})_2\text{Br}_4]$ (III)	252 ($\nu(\text{Cu–Br})$)	1.80	810, [435]	$g_{\text{av}} = 2.13$	0.46	120
$[\text{Cu}_2(\text{DPP})_2(\text{NO}_3)_4] \cdot (\text{H}_2\text{O})$ (IV)	3542, 3496 (H_2O); 1759, 1747, 1731, 1721 (NO_3 , $\nu_1 + \nu_4$)	1.83	610	$g_1 = 2.06$ $g_2 = 2.10$ $g_3 = 2.22$		
Ferrocene					0.455	90

^aMull transmittance [shoulder]. ^bSolid (r.t.). ^cScan rate 100 mV/s 2×10^{-3} to 5×10^{-4} mol dm^{-3} complex in DMF, 0.1 M tetraethylammonium perchlorate, glassy-carbon working electrode, and saturated calomel reference electrode.

pertaining to the ligand, least-squares planes data, calculated and observed structure factors are available from the authors (63 pages).

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