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Synthesis and Characterization of the Multidentate Ligand 2,9-Bis(*N*-pyrazolylmethyl)-1,10-phenanthroline (bpmp) and Its Copper(I) and Copper(II) Complexes

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The synthesis of the novel nitrogen ligand 2,9-bis(*N*-pyrazolylmethyl)-1,10-phen (bpmp), $C_{20}H_{16}N_6$, and of the tetrafluoroborate and perchlorate salts of its copper(I) and copper(II) complexes, respectively, are reported. The structures of the free ligand and of the copper(II) complex have been determined by three-dimensional X-ray diffraction methods. The ligand crystallizes in the space group $P2_1$ of the monoclinic system with two molecules in a cell of dimensions $a = 5.979(2)$ Å, $b = 9.127(2)$ Å, $c = 15.637(3)$ Å, and $\beta = 98.59(3)°$. The structure has been refined to a final value for the crystallographic R factor of 0.0486 based on 1365 observed independent reflections. The ligand adopts a relatively extended conformation in the crystals, the torsion angles around the nominally single C–C bonds linking the phen and pyrazole rings being 163.6 and 164.4°, respectively. The copper(II) complex $[Cu(bpmp)(H_2O)](ClO_4)_2$ crystallizes in the space group $P\bar{1}$ of the triclinic system with two molecules in a cell of dimensions $a = 8.6040(10)$ Å, $b = 10.499(2)$ Å, $c = 13.405(3)$ Å, $\alpha = 89.080(10)°$, $\beta = 80.040(10)°$, and $\gamma = 84.380(10)°$. The structure has been refined to a final value for the crystallographic R factor of 0.0490 based on 3560 observed independent reflections. The cation adopts a five-coordinate geometry, the coordination being provided by two phen nitrogen atoms [N(1) and N(2)] and two pyrazole nitrogen atoms [N(3) and N(4)] from the ligand and by a water molecule. The geometry at copper is best described as trigonal bipyramidal, with one phenanthroline and one pyrazolyl nitrogen atom axial while the other phenanthroline and pyrazolyl nitrogen atoms and the water ligand are equatorial. The copper(II) complex $[Cu(bpmp)(H_2O)]^{2+}$ exhibits a reversible wave at 0.037 V *vs* Ag/AgCl, attributable to the $[Cu(bpmp)(H_2O)]^{2+/+}$ couple.

Introduction

2,2′-Bipyridine (bpy) and 1,10-phenanthroline (phen) have been extensively used as ligands in both analytical and preparative coordination chemistry.[1] It is only relatively recently, however, that systematic studies of substituted derivatives of bpy, phen, and other α-diimines were successfully undertaken;[2–4] as examples, recent reports demonstrate that these ligand systems have now been incorporated into macrocycles.[5,6] Much of this work has been initiated by the intense current interest in the catalytic, redox, and photoredox properties of these ligands with various metals,[7] particularly with ruthenium.[2f,8] The key feature of these nitrogen heterocycles containing six-membered rings is their π-electron deficiency, making them excellent π acceptors; consequently, they have been used to stabilize various metal complexes in lower oxidation states.[3,6,9] On the other hand, the five-membered-ring heterocycles are much poorer π acceptors (and better π donors);[10] if they were assembled on the bpy and phen framework, a fine tuning could be attained in the properties of their complexes, since the ligands would now contain both soft and hard sites. A survey of the literature indicates that scarcely any data are available on such systems, with the exception of reports of ligands such as 2,6-bis(*N*-pyrazolyl)pyridine,[11] 2,6-bis(*N*-pyrazolylmethyl)pyridine,[12] and 6,6′-bis(3-methyl-5-phenyl-*N*-pyrazolyl)-2,2′-bipyridine.[13]

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(1) Reedijk, J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, p 73.

(2) (a) Chung, L. Y.; Constable, E. C.; Khan, M. S.; Lewis, J. *Inorg. Chim. Acta* **1991**, *185*, 93. (b) Newkome, G. R.; Kohli, D. K.; Fronczek, F. *J. Chem. Soc., Chem. Commun.* **1980**, 9. (c) Pyper, P. J.; Goot, H. V. D.; Timmerman, H.; Nauta, W. *Th. Eur. J. Med. Chem., Chim. Ther.* **1984**, *19*, 399. (d) Moran, D. B.; Morton, G. O.; Albright, D. J. *J. Heterocycl. Chem.* **1986**, *23*, 1071. (e) Rawle, S. C.; Moore, P.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1992**, 684. (f) Collin, J. P.; Beley, M.; Sauvage, J. P. *Inorg. Chim. Acta* **1991**, *186*, 91. (g) Constable, E. C.; Elder, S. M.; Healey, J.; Tocher, E. A. *J. Chem. Soc., Dalton Trans.* **1990**, 1669. (h) Constable, E. C.; Chotalia, R. *J. Chem. Soc., Chem. Commun.* **1992**, *64*. (i) Spahni, V. W.; Calzaferri, G. *Helv. Chim. Acta* **1984**, *67*, 450. (j) Antonini, I.; Claudi, F.; Cristalli, G.; Franchetti, P.; Grifantini, M.; Martelli, S. *J. Med. Chem.* **1981**, *24*, 1181. (k) Abushamleh, A. S.; Goodwin, H. A. *Aust. J. Chem.* **1988**, *41*, 873. (l) Chandler, C. J.; Deady, L. W.; Reiss, J. A. *J. Heterocycl. Chem.* **1981**, *18*, 599.

(3) Md. Athar Masood; Zacharias, P. S. *J. Chem. Soc., Dalton Trans.* **1991**, 111.

(4) Garber, Ty.; Wallendael, S. V.; Rillema, P. D.; Kirk, M.; Hatfield, W. E.; Welch, J. H.; Singh, P. *Inorg. Chem.* **1990**, *29*, 2863.

(5) (a) Sauvage, J. P. *Acc. Chem. Res.* **1990**, *23*, 319. (b) Buchecker, D. O.; Sauvage, J. P. *Chem. Rev.* **1987**, *87*, 795. (c) Chambron, J. C.; Heitz, V.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1992**, 1131. (d) Chambron, J. C.; Mitchell, D. K.; Sauvage, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 4625. (e) Cram, D. J.; Weiss, J.; Helgeson, R. C.; Knobler, C. B.; Dorigo, A. E.; Houk, K. N. *J. Chem. Soc., Chem. Commun.* **1988**, 407. (f) Keipert, S. J.; Knobler, C. B.; Cram, D. J. *Tetrahedron* **1987**, *43*, 4861. (g) Chandler, C. J.; Deady, L. W.; Reiss, J. A.; Tzimos, V. *J. Heterocycl. Chem.* **1982**, *19*, 1017. (h) Chandler, C. J.; Deady, L. W.; Reiss, J. A. *J. Heterocycl. Chem.* **1986**, *23*, 1327. (i) Alpha, B.; Lehn, J. M.; Mathis, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 266. (j) Lewis, J.; Donoghue, T. D. O.; Hague, Z. P.; Tasker, P. A. *J. Chem. Soc., Dalton. Trans.* **1980**, 1664. (k) Lüning, U.; Müller, M. *Liebigs Ann. Chem.* **1989**, 367.

(6) Buchecker, D. O.; Sauvage, J. P.; Kern, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 7791.

(7) (a) Palmer, C. E. A.; McMillin, D. R.; Kirmaier, C.; Holten, D. *Inorg. Chem.* **1987**, *26*, 3167. (b) Sakaki, S.; Koga, G.; Ohkubo, K. *Inorg. Chem.* **1986**, *25*, 2330. (c) Blaskie, M. W.; McMillin, D. R. *Inorg. Chem.* **1980**, *19*, 3519. (d) Ahn, B. T.; McMillin, D. R. *Inorg. Chem.* **1981**, *20*, 1427. (e) Marnot, P. A.; Ruppert, R. R.; Sauvage, J. P. *Nouv. J. Chim.* **1981**, *5*, 543.

(8) (a) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845. (b) Bierig, K.; Morgan, R. J.; Tysoe, S.; Gafney, H. D.; Strekas, T. C. *Inorg. Chem.* **1991**, *30*, 4898. (c) Elliot, M. C.; Freitag, R. A.; Blaney, D. D. *J. Am. Chem. Soc.* **1985**, *107*, 4647. (d) Takeuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407.

(9) Md. Athar Masood; Jagannathan, R.; Zacharias, P. S. *J. Chem. Soc., Dalton Trans.* **1991**, 2553.

(10) Constable, E. C. *Coord. Chem. Rev.* **1989**, *93*, 205.

(11) (a) Jameson, D. L.; Blaho, J. K.; Kruger, K. T.; Goldsby, K. A. *Inorg. Chem.* **1989**, *28*, 4312. (b) Jameson, D. L.; Goldsby, K. A. *J. Org. Chem.* **1990**, *55*, 4992.

(12) House, D. A.; Steel, P. J.; Watson, A. A. *Inorg. Chim. Acta* **1987**, *130*, 167.

(13) Lewis, J.; Wainwright, K. P. *J. Chem. Soc., Dalton Trans.* **1978**, 440.

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In an endeavor to extend the range of available chelating heteroatomic phen- and pyrazolyl-based ligands, we report the first synthesis of 2,9-bis(*N*-pyrazolylmethyl)-1,10-phenanthroline (bpmp), along with its crystal structure and the physical and chemical properties of its copper(II) and copper(I) complexes, including the crystal structure of the copper(II) complex.

Experimental Section

Syntheses. All starting materials were purchased from Aldrich; whenever required, solvents were distilled and dried according to standard laboratory procedures. The C, H, and N analyses were recorded by Atlantic Microlab, Inc.

(a) 1,10-Phenanthroline-2,9-dicarboxaldehyde was prepared according to the known procedure.[21] A modified synthesis is reported here. Selenium(IV) oxide, 20 g (180 mmol), was dissolved in 4% aqueous dioxane (500 mL), and then 10 g of 2,9-dimethyl-1,10-phenanthroline monohydrate (48 mmol) dissolved in 300 mL of 4% aqueous dioxane was slowly added while the mixture was stirred vigorously. After the addition was completed, the solution was refluxed for 4 h and then filtered hot through a water-jacketed Büchner funnel filled with a thick Celite pad, the funnel being kept hot by circulation of hot water. A significant amount of dialdehyde precipitated, and the filtration then was continued on another pad of Celite. The filtrates were combined, and the solvent was removed by rotary evaporation, taking utmost care that the solvent was not removed to dryness. The dialdehyde separated from the mixture as a yellow brown solid contaminated with white or red selenium. Additional dialdehyde can be obtained by collecting the Celite pads after scraping the surface off and then refluxing in 4% aqueous dioxane, filtering hot, and removing solvent as before.

The selenium-contaminated dialdehyde was purified according to the known procedure[5k] by dissolving it in dry dimethylformamide, cooling to 0 °C for a few hours, filtering, and adding distilled water to the filtrate until precipitation was complete. The white solid was collected by filtration and dried to give a total yield of 8.0 g.

(b) 2,9-Bis(bromomethyl)-1,10-phenanthroline. This was prepared according to the literature method.[21] The solid was purified by eluting on a silica gel column using $CH_2Cl_2/CH_3COOC_2H_5/C_2H_5OH$ (5/1/0.25 v/v) and collecting the first pale yellow fraction. Removal of the solvent by rotary evaporation gave a light yellow solid.

(c) 2,9-Bis(*N*-pyrazolylmethyl)-1,10-phenanthroline (bpmp). A 560-mg sample of 2,9-bis(bromomethyl)-1,10-phenanthroline (1.53 mmol) was dissolved in ethanol (10 mL). Dichloromethane (25 mL) and then benzene (200 mL) were added. To this solution was added a 40% solution of NaOH (20 mL). The solution immediately changed color from yellow to light yellow. Then 600 mg of pyrazole (8.8 mmol) was added, followed by the addition of 40% tetrabutylammonium hydroxide (TBAH) solution (0.25 mL). After refluxing vigorously for 36 h, the solution was cooled and the organic fraction was collected and dried over 2 g of anhydrous $MgSO_4$. It was then filtered, and the solvent was removed by rotary evaporation to give a slightly sticky yellow solid. Column chromatography on silica gel with $CH_3COOC_2H_5/C_2H_5OH$ (20/1 v/v) gave a light yellow solid. The ligand was then purified over preparative silica gel plates with ethyl acetate as the eluent. NMR spectroscopy demonstrated that the product was still impure. The ligand was again purified by preparative alumina plates using ethyl acetate as the eluent. Final purification was attained by recrystallization from benzene/dichloromethane (5/1 v/v) to give 325 mg (62%) of colorless thin needles, mp 205 °C. ^1H NMR: singlet (4H), 5.95 ppm; split singlet (2H), 6.42 ppm; three singlets (3H), 7.12–7.3 ppm; twinned doublet and a singlet (5H), 7.6–7.85 ppm; doublet (2H), 8.2 ppm. ^{13}C depth NMR: $-CH_2-$, 58.5 ppm; $-CH-$, 107, 121, 127, 131, 138, 140 ppm; $-C-$, 128, 147, 159 ppm. Anal. Calcd for $C_{20}H_{16}N_6$: C, 70.58; H, 4.71; N, 24.71. Found: C, 70.55; H, 4.76; N, 24.60. IR: 1716, 1623, 1589, 1547, 1496, 1395, 1370, 1285, 1209, 1108, 1083, 1049, 964, 846, 753, 610 cm^{-1}.

Table I. Crystallographic Details for the Structures

	ligand	complex
formula	$C_{20}H_{16}N_6$	$[CuC_{20}H_{18}N_6O](ClO_4)_2$
fw	340.4	618.8
a, Å	5.979(2)	8.6040(10)
b, Å	9.127(2)	10.499(2)
c, Å	15.637(3)	13.405(2)
α, deg	90	89.080(10)
β, deg	98.59(3)	80.040(10)
γ, deg	90	84.380(10)
V, Å^3	843.7(4)	1186.9(3)
Z	2	2
ρ_{calc}, g cm^{-3}	1.340	1.731
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
T, K	295	294
λ, Å	0.710 69	0.710 69
μ, mm^{-1}	0.085	1.211
NO[a]	2061	5485
NO [$I > 3\sigma(I)$]	1365	3560
R[b]	0.0486	0.0490
R_w[c]	0.0650	0.0659

[a] NO = number of observed reflections. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]$.

(d) $[Cu(bpmp)(H_2O)](ClO_4)_2$. *Caution*! Perchlorate salts are potentially explosive. This complex, and all perchlorate salts, should be handled with great care and should not be synthesized in large quantities.

A solution containing 185 mg of copper(II) perchlorate hexahydrate (0.5 mmol) dissolved in methanol (10 mL) was added dropwise to a stirring solution containing 177 mg (0.52 mmol) of ligand dissolved in dichloromethane/methanol (10 mL, 1/1 v/v). A blue solution resulted, which was allowed to stir for 30 min, and then the volume of the solution was reduced at room temperature to give a blue powder, which was recrystallized from methanol/acetonitrile (1/3 v/v) to give dark blue rectangular crystals after 1 week. The yield was 250 mg (80%). Anal. Calcd for $CuC_{20}H_{18}N_6Cl_2O_9$: C, 38.68; H, 2.90; N, 13.54. Found: C, 38.70; H, 2.91; N, 13.59. IR: 3463, 1572, 1505, 1420, 1285, 1083, 872, 779, 762, 627 cm^{-1}.

(e) $[Cu(bpmp)](BF_4)$. A solution containing 157 mg (0.5 mmol) of $[Cu(CH_3CN)_4]BF_4$[14] dissolved in acetonitrile (10 mL) was added under nitrogen to a stirring solution containing 340 mg (1 mmol) of ligand dissolved in dichloromethane/acetonitrile (10 mL, 1/1 v/v). The red solution that resulted immediately was allowed to stir at room temperature for 30 min, and then the volume of the solution was reduced under a constant flow of nitrogen to give a deep red solid. IR: 1724, 1614, 1581, 1496, 1420, 1395, 1361, 1285, 1057, 855, 753, 610 cm^{-1}. Regrettably, no consistent analysis could be obtained for samples of this material.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Magnetic susceptibility was determined at 22 °C on a JME magnetic susceptibility balance; $HgCo(SCN)_4$ was used as calibrant. ^1H and ^{13}C NMR spectra were recorded on a JEOL 270 spectrometer. Chemical shifts are listed in ppm relative to tetramethylsilane. Electronic spectra were obtained by using 1×10^{-3} mol dm^{-3} solutions in acetonitrile on a Perkin-Elmer Lambda 17 spectrometer, and diffuse reflectance spectra were obtained on the same instrument fitted with a diffuse reflectance accessory. Cyclic voltammograms were obtained with a BAS 100A electrochemical analyzer. A three-electrode cell comprising a glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode was used. Solutions of copper(II) complex (1×10^{-3} mol dm^{-3}) in acetonitrile were used. The supporting electrolyte was 0.1 mol dm^{-3} tetraethylammonium perchlorate. All experiments were performed under a blanket of dry nitrogen at 22 ± 1 °C. All potentials are referred to Ag/AgCl.

X-ray Crystallography. The structures of the ligand (bpmp) and the perchlorate salt of the copper(II) complex $[Cu(bpmp)(H_2O)](ClO_4)_2$ were determined at 22 °C (295 K) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1) = 0.709\,26$ Å; $\lambda(K\alpha_2) = 0.713\,54$ Å] and graphite monochromator. The structures were solved by direct methods and refined by least-squares techniques, the programs being from the SHELXTL IRIS system. The data were corrected for Lorentz–polarization and absorption effects. Crystallographic details and cell constants for both compounds are found in Table I.

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(14) Meerwein, H.; Hederick, V.; Wunderlich, K. *Arch. Pharm.* **1958**, *63*, 541.

(15) Downard, A. J.; Honey, G. E.; Steel, P. J. *Inorg. Chem.* **1991**, *30*, 3733.

(16) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1961**, 3091.

(17) Figgis, B. N.; Lewis, J. In *Modern Coordination Chemistry*; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; Chapter 6, p 403.

(18) (a) McKenzie, E. D. *J. Chem. Soc. A* **1970**, 3095. (b) Yao, Y.; Perkovic, M. W.; Rillema, D. P.; Woods, C. *Inorg. Chem.* **1992**, *31*, 3956.

(19) (a) Ahn, B. T.; McMillin, D. R. *Inorg. Chem.* **1978**, *17*, 2213. (b) Ichinaga, A. K.; Kirchoff, J. R.; McMillin, D. R.; Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *Inorg. Chem.* **1987**, *26*, 4290.

(20) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 705.

(21) (a) Brown, G. M.; Hopf, F. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 5385. (b) Callahan, R. W.; Brown, G. M.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 1443.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $C_{20}H_{16}N_6$

	x	*y*	*z*	*U*(eq)[a]
C(1)	−1148(7)	4840(7)	7986(3)	41(1)
C(2)	−1882(8)	5778(8)	8592(3)	55(2)
C(3)	−991(8)	7141(7)	8689(3)	58(2)
C(4)	708(8)	7583(7)	8208(3)	47(1)
C(5)	1734(10)	8981(7)	8305(3)	58(2)
C(6)	3362(9)	9358(7)	7836(3)	60(2)
C(7)	4111(7)	8365(6)	7250(2)	44(1)
C(8)	5890(8)	8699(7)	6791(3)	51(2)
C(9)	6572(7)	7705(7)	6215(3)	48(1)
C(10)	5479(6)	6347(7)	6124(2)	40(1)
C(11)	3154(7)	6940(6)	7127(3)	37(1)
C(12)	1381(6)	6546(6)	7623(2)	36(1)
C(13)	−2144(8)	3338(7)	7795(3)	52(2)
C(14)	−2300(7)	2012(7)	9125(3)	57(2)
C(15)	−3887(11)	1797(10)	9633(3)	88(3)
C(16)	−5952(10)	2396(8)	9289(4)	71(2)
C(17)	8234(7)	7179(7)	3904(3)	49(1)
C(18)	10276(8)	6534(7)	4270(3)	53(2)
C(19)	9698(7)	5674(7)	4919(3)	50(1)
C(20)	6141(8)	5209(6)	5524(3)	49(1)
N(1)	430(5)	5193	7509(2)	38(1)
N(2)	3836(5)	5954(5)	6573(2)	39(1)
N(3)	6522(6)	6720(6)	4271(2)	49(1)
N(4)	−5574(7)	3042(7)	8538(3)	70(2)
N(5)	−3377(6)	2779(6)	8462(2)	44(1)
N(6)	7452(5)	5788(6)	4891(2)	42(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The ligand bpmp was crystallized from benzene/dichloromethane solutions (4/1 v/v) as a thin colorless needles. The crystals rapidly decompose in air, so a crystal of dimensions 0.82 × 0.42 × 0.16 mm was coated with an envelope of colorless nail polish gel and mounted immediately. Data were collected in the range $0 \leq h \leq 7$, $0 \leq k \leq 11$, $-20 \leq l \leq 20$. All hydrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å) while other atoms were refined anisotropically. Final values of the conventional *R* factors were $R = 0.0492$ and $R_w = 0.0654$ based on 1365 independent data with $I > 3\sigma(I)$. Final atomic positional parameters are presented in Table II.

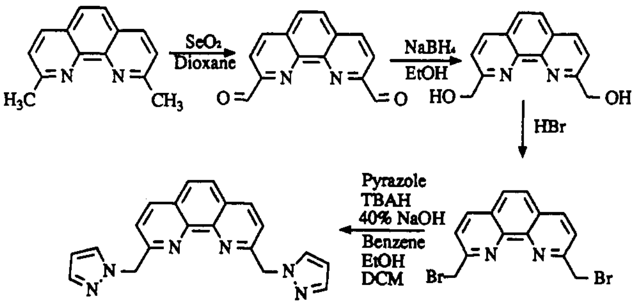
The complex $[Cu(bpmp)(H_2O)](ClO_4)_2$ was crystallized from MeOH/MeCN (1/1 v/v) as a blue rectangular prism. A crystal of dimensions 0.80 × 0.24 × 0.24 mm was used for data collection. Data were collected in the range $0 \leq h \leq 11$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$. All hydrogen atoms were located and refined isotropically while other atoms were refined anisotropically. The final values of the conventional *R* factors were $R = 0.0490$ and $R_w = 0.0659$ based on 3560 independent data with $I > 3\sigma(I)$. Final atomic positional parameters are presented in Table III.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $C_{20}H_{16}Cl_2CuN_6O_9$

	x	*y*	*z*	*U*(eq)[a]
Cu(1)	−1639(1)	2275(1)	2492(1)	38(1)
N(1)	27(4)	1020(3)	1740(3)	37(1)
N(2)	−1713(4)	930(3)	3557(3)	39(1)
N(3)	−2480(4)	3593(3)	3526(3)	41(1)
N(4)	−1611(5)	3418(3)	1323(3)	44(1)
C(1)	932(5)	1138(4)	841(3)	41(1)
C(2)	2083(6)	144(5)	443(4)	55(2)
C(3)	2307(6)	−942(5)	982(4)	57(2)
C(4)	1412(5)	−1079(4)	1949(4)	48(2)
C(5)	1558(7)	−2150(5)	2611(5)	60(2)
C(6)	648(7)	−2208(5)	3520(5)	56(2)
C(7)	−508(6)	−1178(4)	3905(4)	48(2)
C(8)	−1486(7)	−1129(5)	4846(4)	55(2)
C(9)	−2547(7)	−86(5)	5123(4)	54(2)
C(10)	−2655(6)	950(4)	4459(3)	42(1)
C(11)	−681(5)	−98(4)	3278(3)	40(1)
C(12)	276(5)	−63(4)	2292(3)	39(1)
C(13)	833(6)	2392(5)	291(4)	51(2)
C(14)	−1251(7)	3858(5)	−317(4)	52(2)
C(15)	−2576(7)	4582(5)	123(4)	56(2)
C(16)	−2756(7)	4275(5)	1133(4)	51(2)
C(17)	−2058(6)	4760(4)	3611(4)	48(2)
C(18)	−2482(6)	5217(5)	4587(4)	55(2)
C(19)	−3212(6)	4265(5)	5114(4)	48(2)
C(20)	−3866(6)	2083(5)	4684(4)	47(2)
N(5)	−681(5)	3140(3)	407(3)	42(1)
N(6)	−3197(4)	3292(3)	4476(3)	40(1)
Cl(1)	−3832(1)	−2136(1)	2325(1)	48(1)
O(1)	−2163(5)	−2457(5)	2194(3)	81(2)
O(2)	−4633(6)	−3162(4)	2792(4)	93(2)
O(3)	−4244(6)	−1923(7)	1371(4)	127(3)
O(4)	−4298(8)	−1063(5)	2960(4)	125(3)
Cl(2)	−7341(2)	3471(1)	2587(1)	52(1)
O(5)	−6509(6)	2916(5)	1638(3)	98(2)
O(6)	−8490(10)	2802(7)	3028(5)	162(4)
O(7)	−6277(8)	3561(8)	3244(5)	165(4)
O(8)	−7994(13)	4647(7)	2392(6)	216(5)
O(1W)	−3726(5)	1365(3)	1962(3)	64(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme I



Results and Discussion

Ligand Synthesis. The ligand 2,9-bis(*N*-pyrazolylmethyl)-1,10-phenanthroline (bpmp) was chosen because the π deficiency of the phen system would be supplemented by the π-excessive pyrazole rings and as a consequence there was the possibility of unusual chemical properties. In fact, it was found earlier that the π^* LUMO in compounds such as 2,6-bis(*N*-pyrazolyl)pyridine is significantly higher in energy than that of terpyridine.[11] bpmp was prepared from 2,9-dimethyl-1,10-phenanthroline (dmp) by a four-step sequence involving oxidation of dmp to the dialdehyde, reduction of the dialdehyde to its diol by sodium borohydride in ethanol, bromination of the diol by HBr, and a phase-transfer reaction[15] effected by refluxing 2,9-bis(bromomethyl)-1,10-phenanthroline with pyrazole in methylene chloride, ethanol, and benzene (which constitute one phase) and 40% NaOH solution (the second phase). A 40% solution of TBAH was used as a phase-transfer reagent. The reaction sequence is shown in Scheme I. We have found this procedure to be very much more convenient than the possible alternative which could involve the reaction of a hydrazine with a β-diketone,[13] a method which is usually used to obtain five-membered heterocyclic rings. This type of reaction needs a suitable metal ion as a template for cyclization, and it is frequently observed that obtaining the required pure hydrazine species and removing the template metal after cyclization are extremely difficult processes. Perhaps for these or other reasons, we failed to obtain bpmp by this method. Similarly, in our hands direct reaction of the dibromo species with appropriate pyrazolate in diglyme or of sodium pyrazolate in either dimethylformamide or tetrahydrofuran under various conditions of temperature as well as time did not give the required ligand. The phase-transfer procedure described above was successful, but the ligand was found to be highly contaminated. Hence, a complete cycle of purification was devised, consisting of passing the compound through a silica gel column, followed by chromatographic separation on a silica and then on an alumina preparative TLC column and finally recrystallization from benzene/dichloromethane. A similar reaction sequence designed to synthesize 2,9-bis(3,5-dimethyl-*N*-pyrazolyl)methyl)-1,10-phenanthroline has so far proved unsuccessful, but further attempts to prepare this latter ligand are continuing.

Complex Syntheses. The copper(II) complex was readily prepared by the addition of copper(II) perchlorate to the ligand. Good single crystals were obtained from methanol/acetonitrile solutions. If the ligand and metal salt were mixed in a 1/1 ratio, the formation of a copper(I) complex was prompt under anaerobic conditions, but under aerobic conditions the red solution of copper(I) that initially formed turned green after about 60 min of exposure to air. All efforts to grow single crystals of copper(I) complexes with a variety of counterions failed. If the ligand and metal salt were mixed in a 2/1 ratio, however, the copper(I) complex was formed even under aerobic conditions and the solution remained stable, the red color persisting even after days of exposure to air. The low-resolution mass spectrum, however, did not indicate that a complex with a bis(ligand) composition had formed. No *m/z* peaks could be observed that would correspond to the parent ion or to fragments containing one copper atom and two ligands. We have been unable to isolate a pure solid copper(I) complex.

Infrared Spectroscopy. The IR spectrum of the copper(II) exhibited a strong absorption band at 1083 cm^{-1}, indicative of an ionic perchlorate group.[16] The C=N stretching band that appeared at 1547 cm^{-1} for the free ligand was found at 1505 cm^{-1} for the copper(II) complex, indicating the coordination of the phen nitrogen atoms to the metal ion. Similarly, for the copper(I) complexes, a peak at 1496 cm^{-1} was due to the phen nitrogens coordinating to the copper(I) ion.

Magnetic Susceptibility. The room-temperature magnetic susceptibility of the copper(II) complex showed a room-temperature value of 1.86 μ_B. This value is slightly higher than the anticipated spin-only value of $\sqrt{3}\ \mu_B$, and is commonly observed in monomeric copper(II) complexes.[17]

Electronic Absorption Spectrum. The visible spectrum of the copper(II) complex showed a broad band centered at 650 nm (ϵ = 102 $M^{-1}\ cm^{-1}$) while that of the copper(I) complex showed an intermediate-intensity band at 437 nm (ϵ = 3625 $M^{-1}\ cm^{-1}$). In the UV region, intraligand $\pi \rightarrow \pi^*$ transitions were observed and were found to be consistent with coordinated ligand. The diffuse reflectance spectrum for the copper(II) complex similarly showed a broad band centered at 650 nm.

A square pyramidal copper(II) complex would be expected to show a single band between 555 and 665 nm while a trigonal bipyramidal complex should show two transitions which could be observed as two peaks or a peak and a shoulder between 550 and 1100 nm in their solid states.[18] The solution electronic spectrum exhibited a broad band in the range 510–750 nm centered at 650 nm in acetonitrile and 657 nm in DMF. A diffuse reflectance spectrum of the sample exhibited a similar single broad band; no second band, or a shoulder to the single band, could be observed. However the broadness of the spectrum and the observed energies of the transitions indicate the most probable geometry around the copper(II) ion to be trigonal bipyramidal.

The copper(I) complex formed in solution with a 1/2 metal/ligand ratio exhibited an intermediate-intensity band centered at 437 nm. This intermediate-intensity transition is assigned as a metal-to-ligand charge-transfer transition (MLCT); in the phen copper(I) complexes it is attributed to enhanced splitting among $d_{x^2-y^2}$, d_{xy}, and d_{yz} orbitals and arises due to $e(xz,yz) \rightarrow e(\psi^*)$ and $b(x^2-y^2) \rightarrow a_2(\chi^*)$ transitions.[3,19] Further, the low λ_{max} value observed here also indicates the π^* LUMO orbitals in the ligand must be significantly higher in energy than usually observed for 2,9-disubstituted phen copper(I) complexes; the molar absorption coefficient is also much lower than expected for 2,9-disubstituted phen complexes. This is perhaps due to the presence of pyrazolyl moieties on the ligand, but might also be due to the presence of only one phen moiety resulting in the reduced availability of π^* orbitals.

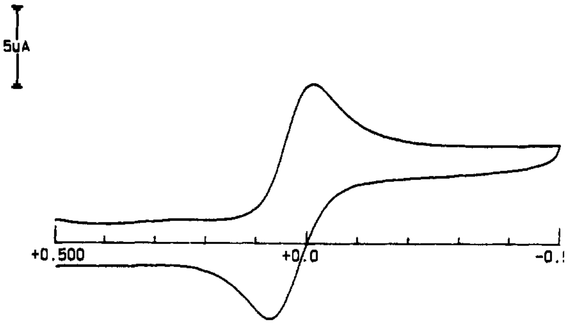


Figure 1. Cyclic voltammogram for $[Cu(bpmp)(H_2O)]^{2+}$ in acetonitrile with 0.1 M TEAP as supporting electrolyte (scan rate 20 mV/s).

The freshly prepared copper(I) complex in which a 1/1 metal/ligand ratio was used showed a similar band at 437 nm, but with the lapse of time, this MLCT band was found to diminish while a d–d transition band was found to appear. After 24 h, it was found that the ratio of d–d band to the MLCT band was almost 8/1, indicating significant formation of copper(II) species.

Electrochemistry. Redox processes were investigated by cyclic voltammetry in acetonitrile. The ligand was found to be electrochemically inactive in the working range. As is seen in Figure 1, at a scan rate of 20 mV/s, the copper(II) complex $[Cu(bpmp)(H_2O)]^{2+}$ exhibits a reversible wave at 0.037 V *vs* Ag/AgCl, attributable to the $[Cu(bpmp)(H_2O)]^{2+/+}$ couple. This assignment is consistent with the observations of approximately equal cathodic and anodic currents and a plot of the square root of the sweep rate *vs* ΔE_p, which had an intercept of 75 mV, somewhat larger than the 59 mV expected for a reversible, one-electron transfer.[20] Higher values are often encountered for measurements in nonaqueous solvents due to uncompensated solution resistance.[21] For $[Cu(Diphen)(H_2O)]^{2+}$, a trigonal bipyramidal complex, a quasi-reversible redox Cu(II/I) couple was observed[18b] at 0.19 V *vs* SCE in acetonitrile while for $[Cu(O\text{-}BPY)]^{2+}$, where O-BPY is 1,2-bis(2,2′-bipyridyl-6-yl)ethane,[4] a reversible peak at 0.24 V *vs* Ag^+/AgCl was observed [E(Ag/AgCl) = E(SCE) + 0.045 V]. The quasi-reversible behavior of $[Cu(Diphen)(H_2O)]^{2+}$ is somewhat similar to what is observed at higher scan rates for $[Cu(bpmp)(H_2O)]^{2+}$ (*vide infra*). The less positive potential in the present complex is an indication that the net basicity of the complex is higher, due to the presence of pyrazoles in the ligand, and that hence reduction to copper(I) is impeded. The shift to more negative redox potential for the Cu(I/II) couple could also be an indication that five-coordinate geometry is retained in the solution, consistent with the spectroscopic observations.

At higher scan rates, the peak-to-peak separation in the cyclic voltammetry scans increases, leading to quasi-reversible behavior. This may be indicative of a relatively slow structural transition between the copper(II) and copper(I) species. This behavior of the present complex is intermediate between that of highly sterically hindered bis chelate copper(II) complexes[6,22] or copper(II) macrocycles like $[Cu(TIM)]^{2+}$ where TIM = 2,3,9,10-Me_4-[14] = 1,3,8,10-tetraene-N_4[23] and $[Cu(catenate)]^{2+}$,[5a,b,6] which undergo reversible redox processes, and noncyclic complexes like $[Cu(phen)_2]^{2+}$ and $[Cu(bpy)_2]^{2+}$, which undergo irreversible redox processes.

For the present complex, no other redox processes such as Cu(III/II) or Cu(I/0) could be observed. However, systems for which such couples are observed generally feature either tetrahedral distortions or steric and/or macrocyclic effects, which are absent in the present system. However, because of the chelate stabilizing effect there is a reversible behavior at lower scan rates and a quasi-reversible behavior at a higher scan rate.

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(22) Md. Athar Masood; Zacharias, P. S. *Transition Met. Chem.* (*London*) **1992**, *17*, 563.

(23) Maroney, M. J.; Wicholas, M. *Inorg. Chim. Acta* **1983**, *77*, L237.

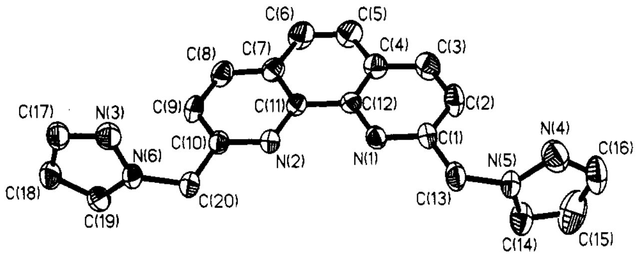

Figure 2. View of the structure of the bpmp ligand in the crystals. Hydrogen atoms are omitted for clarity.

Table IV. Bond Lengths (Å) for $C_{20}H_{16}N_6$

C(1)–C(2)	1.395(7)	C(1)–C(13)	1.506(8)
C(1)–N(1)	1.328(5)	C(2)–C(3)	1.353(9)
C(3)–C(4)	1.409(7)	C(4)–C(5)	1.414(8)
C(4)–C(12)	1.416(7)	C(5)–C(6)	1.349(8)
C(6)–C(7)	1.409(7)	C(7)–C(8)	1.403(7)
C(7)–C(11)	1.422(7)	C(8)–C(9)	1.382(7)
C(9)–C(10)	1.399(8)	C(10)–C(20)	1.492(7)
C(10)–N(2)	1.339(5)	C(11)–C(12)	1.450(6)
C(11)–N(2)	1.353(6)	C(12)–N(1)	1.360(5)
C(13)–N(5)	1.457(6)	C(14)–C(15)	1.340(8)
C(14)–N(5)	1.333(6)	C(15)–C(16)	1.384(9)
C(16)–N(4)	1.363(8)	C(17)–C(18)	1.399(6)
C(17)–N(3)	1.314(6)	C(18)–C(19)	1.367(8)
C(19)–N(6)	1.341(5)	C(20)–N(6)	1.450(6)
N(3)–N(6)	1.347(6)	N(4)–N(5)	1.358(6)

Table V. Bond Angles (deg) for $C_{20}H_{16}N_6$

C(2)–C(1)–C(13)	122.6(4)	C(2)–C(1)–N(1)	123.7(5)
C(13)–C(1)–N(1)	113.7(4)	C(1)–C(2)–C(3)	118.8(5)
C(2)–C(3)–C(4)	120.5(5)	C(3)–C(4)–C(5)	122.5(5)
C(3)–C(4)–C(12)	116.7(5)	C(5)–C(4)–C(12)	120.8(5)
C(4)–C(5)–C(6)	120.6(5)	C(5)–C(6)–C(7)	121.0(5)
C(6)–C(7)–C(8)	122.1(5)	C(6)–C(7)–C(11)	121.1(4)
C(8)–C(7)–C(11)	116.7(4)	C(7)–C(8)–C(9)	120.7(5)
C(8)–C(9)–C(10)	118.0(4)	C(9)–C(10)–C(20)	121.1(4)
C(9)–C(10)–N(2)	123.6(5)	C(20)–C(10)–N(2)	115.3(5)
C(7)–C(11)–C(12)	117.8(4)	C(7)–C(11)–N(2)	122.8(4)
C(12)–C(11)–N(2)	119.5(5)	C(4)–C(12)–C(11)	118.8(5)
C(4)–C(12)–N(1)	122.6(4)	C(11)–C(12)–N(1)	118.7(4)
C(1)–C(13)–N(5)	113.8(4)	C(15)–C(14)–N(5)	103.6(4)
C(14)–C(15)–C(16)	112.4(5)	C(15)–C(16)–N(4)	104.6(5)
C(18)–C(17)–N(3)	112.1(5)	C(17)–C(18)–C(19)	104.1(4)
C(18)–C(19)–N(6)	107.1(4)	C(10)–C(20)–N(6)	113.4(5)
C(1)–N(1)–C(12)	117.7(3)	C(10)–N(2)–C(11)	118.2(5)
C(17)–N(3)–N(6)	104.5(3)	C(16)–N(4)–N(5)	106.6(4)
C(13)–N(5)–C(14)	120.2(4)	C(13)–N(5)–N(4)	126.8(4)
C(14)–N(5)–N(4)	112.7(4)	C(19)–N(6)–C(20)	126.2(4)
C(19)–N(6)–N(3)	112.1(4)	C(20)–N(6)–N(3)	121.0(3)

The presence of a reversible or quasi-reversible Cu(II) ↔ Cu(I) couple in the copper(II) complex also suggests that a reduced copper(I) species could also be stable under anaerobic conditions, presumably requiring a significant structural rearrangement. However, no redox chemistry for the copper(I) complex [Cu(bpmp)]$^+$ could be observed. Bulk electrolysis of the copper(II) complex at −0.5 V in DMF/acetonitrile (1/3 v/v) indicates that one-electron reduction takes place. As was the case for the solution produced by chemical reduction, the reduced solution formed under these conditions exhibits an MLCT band at 437 nm, but cyclic voltammetry again exhibits no oxidation wave and no solid compound could be isolated. Consequently, we deduce that the Cu(I) complexes produced by either chemical or bulk electrochemical reduction are identical but are evidently structurally different from the copper(I) complex initially produced on the cyclic voltammetric time scale.

X-ray Crystal Structures. (a) Structure of the Free Ligand. A view of the free ligand as found in the crystals is depicted in Figure 2; bond lengths and angles in the structure are listed in Tables IV and V.

As is apparent from the figure, the ligand adopts a relatively extended conformation in the crystals. The N(1)–C(1)–C(13)–N(5) and N(2)–C(10)–C(20)–N(6) torsion angles around the nominally single C–C bonds linking the phen and pyrazole rings are 163.6 and 164.4°, respectively; in the copper(II) complex, of course, the pyrazole rings are rotated around these bonds so as to bring the nitrogen atoms N(3) and N(4) into contact with the metal (*vide infra*), the analogous torsion angles being −33.9 and −49.5°, respectively. The C(1)–C(13) and C(10)–C(20) bond lengths in the free ligand are 1.506(8) and 1.492(7) Å, respectively, indicative of some slight leakage of multiple bonding into these exocyclic bonds, as expected. The phen moiety is approximately planar, with no atom deviating from the 14-atom least-squares plane by more than 0.019 Å; the exocyclic atom C(20) lies in this plane, while C(13) lies 0.048 Å above the plane. Similarly, the five-membered pyrazole rings are also planar, with no atom deviating from the least-squares planes by more than 0.009 and 0.005 Å for the N(3) and N(4) rings, respectively. However, the pyrazole and phen moieties are not coplanar in the free ligand, the dihedral angles between the phen and pyrazole moieties being 76.5 and 80.4° for the N(3) and N(4) rings, respectively. The two pyrazole planes are inclined at an angle of 13.2°.

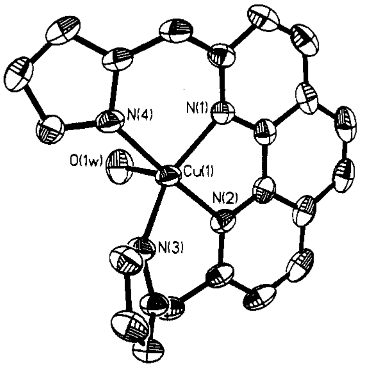

Figure 3. View of the structure of the cation [Cu(bpmp)(H_2O)]$^{2+}$ in the crystals of the perchlorate salt. Hydrogen atoms are omitted for clarity.

Table VI. Bond Lengths (Å) for $C_{20}H_{16}Cl_2CuN_6O_9$

Cu(1)–N(1)	1.995(3)	Cu(1)–N(2)	1.989(3)
Cu(1)–N(3)	1.970(3)	Cu(1)–N(4)	1.957(4)
Cu(1)–O(1W)	2.333(4)	N(1)–C(1)	1.328(5)
N(1)–C(12)	1.365(5)	N(2)–C(10)	1.333(5)
N(2)–C(11)	1.344(5)	N(3)–C(17)	1.323(6)
N(3)–N(6)	1.362(5)	N(4)–C(16)	1.323(7)
N(4)–N(5)	1.364(5)	C(1)–C(2)	1.410(6)
C(1)–C(13)	1.500(7)	C(2)–C(3)	1.356(8)
C(3)–C(4)	1.402(7)	C(4)–C(5)	1.430(8)
C(4)–C(12)	1.401(6)	C(5)–C(6)	1.333(9)
C(6)–C(7)	1.434(7)	C(7)–C(8)	1.389(7)
C(7)–C(11)	1.411(6)	C(8)–C(9)	1.368(7)
C(9)–C(10)	1.400(7)	C(10)–C(20)	1.501(6)
C(11)–C(12)	1.434(6)	C(13)–N(5)	1.440(6)
C(14)–C(15)	1.356(7)	C(14)–N(5)	1.348(6)
C(15)–C(16)	1.372(8)	C(17)–C(18)	1.377(7)
C(18)–C(19)	1.357(7)	C(19)–N(6)	1.341(6)
C(20)–N(6)	1.448(6)	Cl(1)–O(1)	1.424(4)
Cl(1)–O(2)	1.415(5)	Cl(1)–O(3)	1.394(5)
Cl(1)–O(4)	1.406(5)	Cl(2)–O(5)	1.448(5)
Cl(2)–O(6)	1.319(8)	Cl(2)–O(7)	1.387(7)
Cl(2)–O(8)	1.347(8)		

(b) Structure of the Copper(II) Complex. A view of the cation of the copper(II) complex as found in the crystals is depicted in Figure 3; bond lengths and angles in the structure are listed in Tables VI and VII.

The cation adopts a five-coordinate geometry, the coordination being provided by two phen nitrogen atoms [N(1) and N(2)] and two pyrazole nitrogen atoms [N(3) and N(4)] from the ligand and by a water molecule. As is invariably the case for five-coordinate copper(II) complexes, the observed geometry could be described as either a distorted trigonal bipyramid or a distorted tetragonal pyramid. In a tetragonal pyramidal description, the four nitrogen donors would be expected to be approximately

Table VII. Bond Angles (deg) for $C_{20}H_{16}Cl_2CuN_6O_9$

N(1)–Cu(1)–N(2)	82.8(1)	N(1)–Cu(1)–N(3)	154.7(2)
N(2)–Cu(1)–N(3)	90.4(1)	N(1)–Cu(1)–N(4)	92.7(1)
N(2)–Cu(1)–N(4)	172.4(2)	N(3)–Cu(1)–N(4)	96.2(1)
N(1)–Cu(1)–O(1W)	94.1(1)	N(2)–Cu(1)–O(1W)	86.8(1)
N(3)–Cu(1)–O(1W)	109.9(1)	N(4)–Cu(1)–O(1W)	87.4(2)
Cu(1)–N(1)–C(1)	129.2(3)	Cu(1)–N(1)–C(12)	112.0(2)
C(1)–N(1)–C(12)	118.7(3)	Cu(1)–N(2)–C(10)	127.7(3)
Cu(1)–N(2)–C(11)	112.5(3)	C(10)–N(2)–C(11)	119.8(4)
Cu(1)–N(3)–C(17)	129.4(3)	Cu(1)–N(3)–N(6)	122.1(3)
C(17)–N(3)–N(6)	104.8(4)	Cu(1)–N(4)–C(16)	127.6(3)
Cu(1)–N(4)–N(5)	122.9(3)	C(16)–N(4)–N(5)	105.5(4)
N(1)–C(1)–C(2)	120.7(4)	N(1)–C(1)–C(13)	119.3(4)
C(2)–C(1)–C(13)	119.6(4)	C(1)–C(2)–C(3)	120.5(5)
C(2)–C(3)–C(4)	120.2(4)	C(3)–C(4)–C(5)	126.2(4)
C(3)–C(4)–C(12)	116.3(4)	C(5)–C(4)–C(12)	117.5(4)
C(4)–C(5)–C(6)	122.4(5)	C(5)–C(6)–C(7)	121.7(5)
C(6)–C(7)–C(8)	126.3(5)	C(6)–C(7)–C(11)	117.7(4)
C(8)–C(7)–C(11)	116.0(4)	C(7)–C(8)–C(9)	120.6(5)
C(8)–C(9)–C(10)	120.2(5)	N(2)–C(10)–C(9)	120.2(4)
N(2)–C(10)–C(20)	116.8(4)	C(9)–C(10)–C(20)	123.0(4)
N(2)–C(11)–C(7)	123.2(4)	N(2)–C(11)–C(12)	116.8(4)
C(7)–C(11)–C(12)	120.0(4)	N(1)–C(12)–C(4)	123.5(4)
N(1)–C(12)–C(11)	115.9(3)	C(4)–C(12)–C(11)	120.6(4)
C(1)–C(13)–N(5)	118.0(4)	C(15)–C(14)–N(5)	108.4(4)
C(14)–C(15)–C(16)	105.1(5)	N(4)–C(16)–C(15)	111.6(4)
N(3)–C(17)–C(18)	111.9(4)	C(17)–C(18)–C(19)	104.8(5)
C(18)–C(19)–N(6)	108.2(4)	C(10)–C(20)–N(6)	112.9(4)
N(4)–N(5)–C(13)	123.4(4)	N(4)–N(5)–C(14)	109.4(4)
C(13)–N(5)–C(14)	126.0(4)	N(3)–N(6)–C(19)	110.3(4)
N(3)–N(6)–C(20)	121.3(3)	C(19)–N(6)–C(20)	128.4(4)
O(1)–Cl(1)–O(2)	110.0(3)	O(1)–Cl(1)–O(3)	108.2(3)
O(2)–Cl(1)–O(3)	108.8(4)	O(1)–Cl(1)–O(4)	111.0(3)
O(2)–Cl(1)–O(4)	107.1(3)	O(3)–Cl(1)–O(4)	111.7(4)
O(5)–Cl(2)–O(6)	112.9(4)	O(5)–Cl(2)–O(7)	109.5(3)
O(6)–Cl(2)–O(7)	108.8(5)	O(5)–Cl(2)–O(8)	107.9(4)
O(6)–Cl(2)–O(8)	107.9(6)	O(7)–Cl(2)–O(8)	109.8(6)

coplanar and form the base, while the copper atom would be above the plane toward the axial water ligand. In the present complex, the nitrogen atoms deviate markedly from coplanarity, with N(2) and N(4) disposed 0.265 and 0.233 Å, respectively, above the least-squares plane while N(1) and N(3) are 0.261 and 0.237 Å, respectively, below the plane. The copper atom lies 0.163 Å above the plane, on the same side as N(2). In the trigonal bipyramidal description, the nitrogen atoms N(2) and N(4) are axial while N(1), N(3), and the water ligand are equatorial. In this model, we expect that copper and the three equatorial ligands should be coplanar, while the axial ligands are disposed (at roughly equal distances) above and below the plane. The mean deviation from the four-atom least-squares plane through Cu, N(1), N(3), and O(1W) is 0.042 Å, with the three ligand atoms lying slightly on one side of the plane and Cu on the other. Hence, we believe that the trigonal bipyramidal description is the more appropriate one in the present case. Because of the steric constraints of the tetradentate ligand, the bond angles around copper do not approximate the idealized values. Thus, the N(1)–Cu(1)–O(1W), N(3)–Cu(1)–O(1W) and N(1)–Cu(1)–N(3) equatorial angles of 94.1, 109.9, and 154.7° deviate greatly from the idealized value of 120°, while the axial N(2)–Cu–N(4) angle of 172.4° is similar to the expected value of 180°. The fifth coordination site is occupied by a water molecule, as is also found in [Cu(Diphen)(H_2O)]$^{2+}$. The Cu(1)–O(1W) interatomic distance of 2.333 Å in the present complex is larger than that of 2.198 Å found in [Cu(Diphen)(H_2O)]$^{2+}$ but is indicative of a relatively strong bond between copper and the water molecule. This bond length would be very short for an apically coordinated water molecule in a five-coordinate tetragonal pyramidal copper(II) complex.[24]

The Cu–N(pyrazole) distances of 1.970(3) and 1.957(4) Å are significantly shorter than the Cu–N(phen) lengths of 1.995(3) and 1.989(3) Å, suggesting that the pyrazole nitrogen atoms are the better donors for copper(II). In the trigonal bipyramidal description, the axial Cu–N bonds [Cu–N(2) and Cu–N(4)] are shorter than the corresponding equatorial bonds [Cu–N(1) and Cu–N(3), respectively], as expected for a trigonal bipyramidal structure with four nitrogen donors.

There is some indication of an interaction between the cation and a perchlorate anion in the structure, the distance from copper to the closest oxygen atom [O(6)] of the perchlorate counterion being 3.023 Å.

Interestingly, the two sets of chemically nonequivalent nitrogen atoms in the ligand (phen and pyrazolyl nitrogen atoms) act as chemically equivalent donors to copper; *i.e.*, one of each acts as an axial and as an equatorial donor. In contrast to the case of [Cu(Diphen)(H_2O)]$^{2+}$, where trigonal bipyramidal geometry is forced on the system by the steric requirements of the ligand, in [Cu(bpmp)(H_2O)]$^{2+}$ the observed geometry must result primarily from electronic factors since the conformational flexibility of the ligand imposes no steric constraint on the complex.

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Supplementary Material Available: Tables S1–S4, listing hydrogen atom parameters and anisotropic thermal parameters for the free ligand and the complex (5 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure amplitudes for the free ligand and the complex are available from D.J.H. on request.

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(24) Marsh, W. E.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1982**, *21*, 2679.