

The Chelating Ligand 1,3-Bis(pyrazol-1'-yl)propane (Bpp) Enforces a Tetrahedral Geometry in Both Cu^{II} and Cu^I Species

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The ligand 1,3-bis(pyrazol-1'-yl)propane (bpp) has been prepared by reacting 1,3-dichloropropane with two equivalents of pyrazole. After reaction of bpp with copper(II) tetrafluoroborate, three different compounds were obtained, two with Cu^{II} and one with Cu^I as cation, depending on the preparative method. The formation of single crystals of these compounds was only observed when 1-(3-chloropropyl)pyrazole (ppc) was present in the solution. The single-crystal X-ray structures of [Cu(bpp)₂](BF₄)₂ and [Cu(bpp)₂](BF₄) show that bpp acts as a didentate chelating ligand to form an uncom-

mon eight-atom chelate ring with the copper ion. Two polymorphs of the Cu^{II} complex were characterized. In each of them, the metal atoms possess a distorted tetrahedral geometry. In the copper(I) complex the metal center is present in a less-distorted tetrahedral coordination sphere. The spectroscopic properties of the compounds are in agreement with the structural data. Cyclic voltammetry measurements showed a redox wave at 0.92 V vs. Ag/AgCl.

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Introduction

Didentate ligands may either form chelates or bridges between two different metal ions depending on the number of atoms between the donor atoms. However, they frequently form chelates, coordinating to one metal ion in a chelate ring.^[1] Chelate rings of different sizes have been the subject of intensive research in the past. For instance, five- to thirteen-membered rings are formed with 2,2'-bipyridine,^[2] bis(2-benzimidazolyl)ethanes,^[3,4] bis(2-benzimidazolyl)propanes^[3,5,6] 1,3-bis(pyrazol-1'-yl)propane and derivatives^[7] and 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane.^[8] Five-membered chelate rings are generally the most stable.^[9]

The metal ion used also influences the stability of a complex. Although Cu^I is very unstable in protic solutions with respect to disproportionation [2 Cu⁺(aq) → Cu²⁺(aq) + Cu⁰(s)],^[1] the Cu^I ion can be stabilized by coordination with ligands having a π -acceptor character.

Generally, Cu^I ions in coordination complexes have a (distorted) tetrahedral geometry. A few examples are complexes formed with bipyridine derivatives,^[10] thiocyanate,^[11] adiponitriles,^[12] pyridines^[13,14] and indole-containing ligands.^[15] In rare cases, Cu^I can have other coordination environments, including linear,^[1] trigonal,^[1] and trigonal pyramidal.^[16]

Cu^{II} ions in coordination complexes display several geometries; (distorted) octahedral,^[17–19] distorted trigonal bipyramidal,^[10] square pyramidal,^[11] (distorted) square-planar^[8,20] and (distorted) tetrahedral^[4,5] complexes have been observed. However, because of the influence of the Jahn–Teller effect square-planar-based geometries are usually preferred^[1] by four-coordinate Cu^{II}. Steric constraints are known to generate tetrahedral geometries. Coordination complexes of Cu^{II} and Cu^I sharing the same molecular formula and (distorted) tetrahedral geometry are therefore very rare. The previously reported^[21] Cu^{II} and Cu^I compounds formed with the ligand 2,2'-bis(2-imidazolyl)biphenyl are examples of such complexes.

In this paper, Cu^{II} and Cu^I complexes with 1,3-bis(pyrazol-1'-yl)propane (bpp) that display similar (distorted) tetrahedral geometries are described. In these complexes, the bpp ligands act as didentate chelating ligands to form uncommon eight-atom chelate rings. In earlier work^[7] metal complexes with the general formula [M(bpp)X₂] (M = Cu²⁺, Zn²⁺ or Co²⁺ and X = Cl[−] or NO₃[−]) have been reported.

The complexes described in this paper are the first containing two bpp ligands coordinated to one metal center. The best single crystals were grown from solutions of 1,3-bis(pyrazol-1'-yl)propane and Cu^{II} tetrafluoroborate, in which an excess of 1-(3-chloropropyl)pyrazole (ppc) was also present.

Two red polymorphic forms of the compound [Cu(bpp)₂](BF₄)₂ were obtained: orthorhombic α -[Cu(bpp)₂](BF₄)₂ (**1**) crystallized from ethanol, and triclinic β -[Cu(bpp)₂](BF₄)₂ (**2**) crystallized from methanol. In addi-

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tion, the light yellow Cu^{I} complex $[\text{Cu}(\text{bpp})_2](\text{BF}_4)$ (**3**) was isolated. This complex also formed from Cu^{II} tetrafluoroborate, upon standing, by auto-reduction.

The X-ray crystal structures of the two forms of $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ and $[\text{Cu}(\text{bpp})_2](\text{BF}_4)$ will be presented and discussed. Furthermore, the spectroscopic properties of $[\text{Cu}(\text{bpp})_2](\text{BF}_4)$, and spectroscopic and magnetic properties of $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ will be presented. Finally, the results of cyclic voltammetry measurements performed with $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ will be discussed.

Results and Discussion

General Complex Synthesis

When crystallization attempts were performed with the ligand ppc, complexes containing the ligand bpp, which was present as a contamination in ppc, were isolated instead. These experiments were repeated using different Cu:bpp ratios and ppc in a large excess. In each case, independent of the Cu:bpp ratio, complexes in which Cu and bpp are present in a 1:2 ratio were formed. When crystallizations were performed without ppc, red solids formed which were shown by elemental analysis also to possess a Cu:bpp ratio of 1:2, as for the complexes formed in the presence of ppc. However, no single crystals could be obtained when ppc was not present in the solution. A possible reason for this is that ppc keeps the bpp complexes in solution longer, thus allowing slower crystallization and therefore the growth of high-quality single crystals. This theory is supported by the fact that the copper(I) complex $[\text{Cu}(\text{bpp})_2](\text{BF}_4)$ does not form at all without the presence of ppc. Because the complex does not spend enough time in solution, formation by slow auto-reduction does not take place.

Molecular Structures of α - $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ (**1**) and β - $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ (**2**)

The Cu^{II} complex $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ crystallizes in two polymorphs: orthorhombic α - $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ (**1**), formed in ethanol, and triclinic β - $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ (**2**), formed in methanol. The formation of **1** and **2** in different solvents is probably caused by a solvent effect. The presence of both polymorphs in the preparations is unlikely because several crystals were used for structure determination and each time only one polymorph was observed. Selected geometric parameters for **1** and **2** are listed in Table 1 and 2, respectively. The asymmetric unit of **1** contains one unique quarter of a cation with D_2 symmetry (Figure 1). In **2**, three independent cations are present in the asymmetric unit, all of which adopt similar conformations with approximate (noncrystallographic) D_2 symmetry (Figure 2). The cations in both structures are oriented such that one of their (pseudo) C_2 -axes is parallel to a short a axis [**1**: $a = 7.9532(1)$ Å; **2**: $a = 7.9557(15)$ Å]. Translation-related cations are stacked into columns along the [100] direction (Figure 3). These columns, separated by the (disordered) BF_4^- anions, are arranged in different patterns in the two

polymorphs. In **1**, all of the cations are parallel with their three C_2 -axes aligned with the three cell axes, as required by the orthorhombic symmetry (Figure 4). In the triclinic polymorph **2**, the cations centered by Cu(2) and Cu(3) are nearly parallel and together with the BF_4^- anions they form two-column-wide layers within which the packing is similar to that in **1**. Columns of Cu(1)-centered cations, rotated by approximately 60° (about [100]) with respect to the other cations, fit efficiently between these layers (Figure 5). The higher calculated density of **2** (1.590 g cm^{-3}) in comparison to that of **1** (1.563 g cm^{-3}) reflects its more compact packing.

Table 1. Selected bond lengths (Å) and bond angles ($^\circ$) in α - $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ (**1**) and $[\text{Cu}(\text{bpp})_2](\text{BF}_4)$ (**3**)

α - $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ Bond lengths (Å)		$[\text{Cu}(\text{bpp})_2](\text{BF}_4)$ Bond lengths (Å)	
Cu(1)–N(2)	1.948(3)	Cu(1)–N(2)	2.0344(15)
		Cu(1)–N(4)	2.0207(15)
		Cu(1)–N(6)	2.0246(15)
		Cu(1)–N(8)	2.0458(15)
Bond angles ($^\circ$)		Bond angles ($^\circ$)	
N(2)–Cu(1)–N(2)a	107.71(13)	N(2)–Cu(1)–N(4)	113.00(6)
N(2)–Cu(1)–N(2)b	127.20(13)	N(2)–Cu(1)–N(6)	106.91(6)
N(2)–Cu(1)–N(2)c	95.23(13)	N(2)–Cu(1)–N(8)	103.33(6)
		N(4)–Cu(1)–N(6)	114.18(6)
		N(4)–Cu(1)–N(8)	107.65(6)
		N(6)–Cu(1)–N(8)	111.26(6)

Table 2. Selected bond lengths (Å) and bond angles ($^\circ$) in β - $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ (**2**)

Bond lengths (Å)		Bond angles (°)	
Residue 1			
Cu(1)–N(2)	1.973(3)	N(2)–Cu(1)–N(4)	104.49(11)
Cu(1)–N(4)	1.982(3)	N(6)–Cu(1)–N(8)	104.32(10)
Cu(1)–N(6)	1.975(3)	N(2)–Cu(1)–N(8)	135.66(10)
Cu(1)–N(8)	1.981(3)	N(4)–Cu(1)–N(6)	135.65(11)
		N(2)–Cu(1)–N(6)	91.34(10)
		N(4)–Cu(1)–N(8)	92.80(10)
Residue 2			
Cu(2)–N(10)	1.961(3)	N(10)–Cu(2)–N(12)	105.58(11)
Cu(2)–N(12)	1.957(3)	N(14)–Cu(2)–N(16)	105.08(11)
Cu(2)–N(14)	1.967(3)	N(10)–Cu(2)–N(14)	134.25(11)
Cu(2)–N(16)	1.963(3)	N(12)–Cu(2)–N(16)	130.34(11)
		N(10)–Cu(2)–N(16)	93.96(10)
		N(12)–Cu(2)–N(14)	93.16(11)
Residue 3			
Cu(3)–N(18)	1.959(2)	N(18)–Cu(3)–N(20)	105.76(10)
Cu(3)–N(20)	1.966(3)	N(22)–Cu(3)–N(24)	105.61(11)
Cu(3)–N(22)	1.963(3)	N(18)–Cu(3)–N(22)	130.47(10)
Cu(3)–N(24)	1.967(3)	N(20)–Cu(3)–N(24)	132.15(11)
		N(18)–Cu(3)–N(24)	94.24(10)
		N(20)–Cu(3)–N(22)	93.71(10)

As shown in Figure 1 and 2, the Cu^{II} ions in both structures are each coordinated to two didentate bpp ligands via the N2 atoms of the pyrazole rings [**1**: Cu–N 1.948(3) Å; **2**: Cu–N 1.957(3)–1.982(3) Å], forming eight-membered

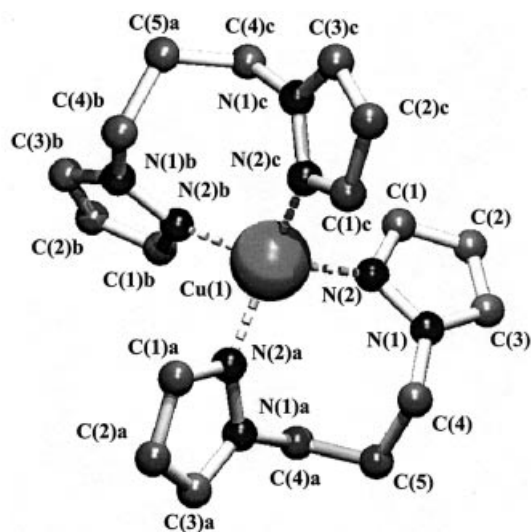


Figure 1. PLATON/POVRAY representation^[27,28] of the molecular structure of the cation in α -[Cu(bpp)₂](BF₄)₂ (**1**); hydrogen atoms and counterions have been omitted for clarity

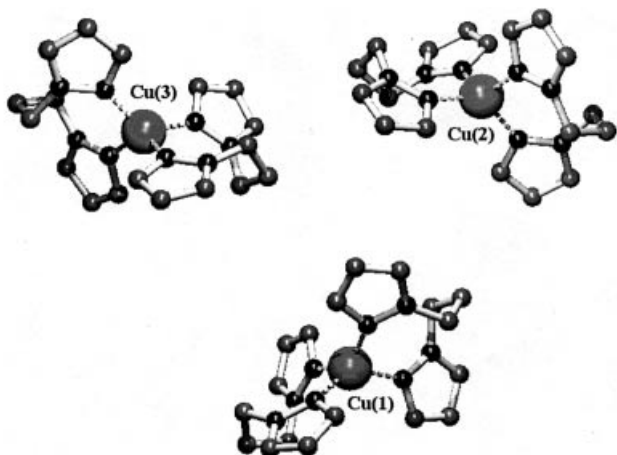


Figure 2. PLATON/POVRAY representation^[27,28] of the molecular structure of the three independent cations in β -[Cu(bpp)₂](BF₄)₂ (**2**); hydrogen atoms and counterions have been omitted for clarity

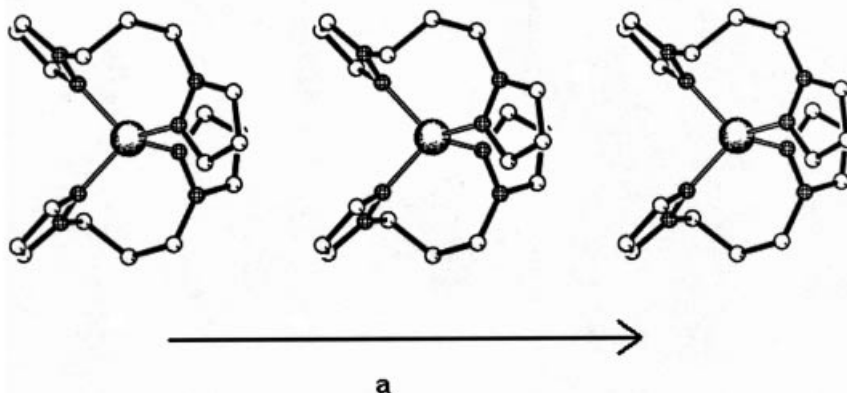


Figure 3. PLATON/POVRAY representation^[27,28] of translation-related cations stacked into columns parallel to the *a* axis, in α -[Cu(bpp)₂](BF₄)₂ (**1**) and β -[Cu(bpp)₂](BF₄)₂ (**2**)

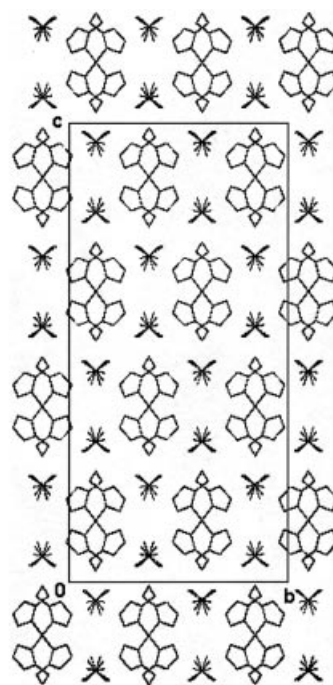


Figure 4. PLATON/POVRAY representation^[27,28] of the crystal packing of α -[Cu(bpp)₂](BF₄)₂ (**1**), seen in a view down the *a* axis

chelate rings. The coordination geometry at the metal centers is distorted tetrahedral. Although the ligand bite angles are close to 109° [**1**: N–Cu–N 107.71(13)°; **2**: N–Cu–N 104.32(10)–105.76(10)°], the other N–Cu–N angles deviate by up to 18° (**1**) or 27° (**2**) from the ideal tetrahedral value. The dihedral angles between the N–Cu–N planes of the chelate rings in each complex cation [**1**: 66.8(2)°; **2**: 57.05(15)–62.30(15)°] also indicate a flattening of the CuN₄ tetrahedrons for which a value of 90° would be expected.

Molecular Structure of [Cu(bpp)₂](BF₄) (**3**)

In the crystal structure of the Cu^I complex [Cu(bpp)₂](BF₄) (**3**), the asymmetric unit contains one inde-

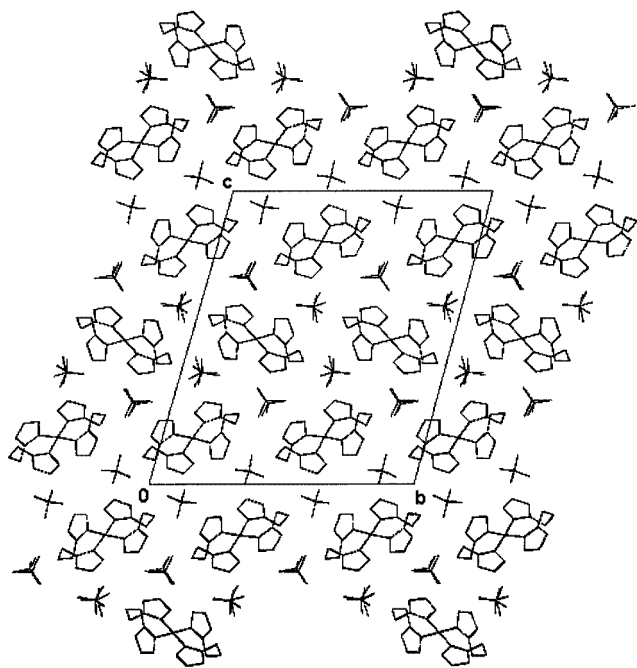


Figure 5. PLATON/POVRAY representation^[27,28] of the crystal packing of β -[Cu(bpp)₂](BF₄)₂ (**2**), seen in a view down the *a* axis

pendent cation possessing (noncrystallographic) *S*₄-based symmetry, as shown in Figure 6. The relevant geometric parameters for **3** are given in Table 1. The Cu^I ion of **3** is coordinated to two bpp ligands, but at Cu–N distances of 2.0207(15)–2.0458(15) Å which, as expected, are longer than those found in the Cu^{II} complex. Similar Cu^I–N [2.029(6)–2.053(6) Å] and Cu^{II}–N [1.941(9)–1.977(8) Å] bond lengths have been reported for the nearly tetrahedral complexes [CuL₂](ClO₄) and [CuL₂](ClO₄)₂ [L = 2,2'-bis(2-imidazolyl)biphenyl].^[21] In **3**, the Cu-centered coordination environment is a slightly distorted tetrahedron; the N–Cu–N angles range from 103.33(6)–114.18(6)°, and the dihedral angle between the N–Cu–N planes of the chelate rings is 89.58(9)°.

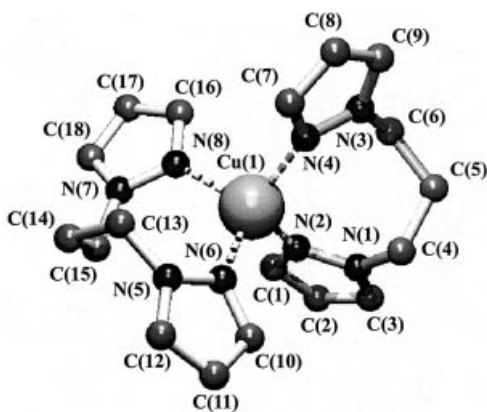


Figure 6. PLATON/POVRAY representation^[27,28] of the molecular structure of the cation in [Cu(bpp)₂](BF₄) (**3**); hydrogen atoms and counterions have been omitted for clarity

Spectroscopic and Magnetic Properties

Ligand field spectra have been recorded for both [Cu(bpp)₂](BF₄)₂ and [Cu(bpp)₂](BF₄) in the solid state. The spectrum of α -[Cu(bpp)₂](BF₄)₂ (**1**) consists of broad signals at $39.2 \times 10^3 \text{ cm}^{-1}$ and $22.7 \times 10^3 \text{ cm}^{-1}$, which are attributed to LMCT transitions. In the spectrum of β -[Cu(bpp)₂](BF₄)₂ (**2**), these signals are present at $40.2 \times 10^3 \text{ cm}^{-1}$ and $21.5 \times 10^3 \text{ cm}^{-1}$. Furthermore, in the spectrum of **1** a weak signal is present at $14.5 \times 10^3 \text{ cm}^{-1}$, in the normal range for d–d transitions in slightly distorted tetrahedrally coordinated Cu^{II} complexes.^[7,22] This signal is not visible in the spectrum of **2**, where the LMCT transition dominates.

The diffuse reflectance spectrum of [Cu(bpp)₂](BF₄) consists of one broad signal at $37.9 \times 10^3 \text{ cm}^{-1}$, with a shoulder at $25.0 \times 10^3 \text{ cm}^{-1}$, which is ascribed to MLCT transitions. No d–d transition signals are present, as is expected for Cu^I.

The X-band EPR spectra of a polycrystalline powder of α -[Cu(bpp)₂](BF₄)₂ (**1**) were recorded at room temperature and 77 K. The resolution did not improve upon cooling to 77 K. The spectra show an axial *S* = 1/2 signal with *g* values that are normal for Cu^{II} in a slightly distorted tetrahedral environment: *g*_⊥ = 2.11, *g*_{||} = 2.32 and *A*_{||} = 13.0 mT.^[7] The spectrum of α -[Cu(bpp)₂](BF₄)₂ in a frozen solution of ethanol was also recorded. This spectrum shows *g* values that are similar to the *g* values of the powder spectra, which indicates that the complex is stable in solution. The same spectra were recorded for β -[Cu(bpp)₂](BF₄)₂ (**2**). These spectra show an axial *S* = 1/2 signal with *g*_⊥ = 2.13, *g*_{||} = 2.38 and *A*_{||} = 12.0 mT.

Magnetic susceptibility measurements were also performed on [Cu(bpp)₂](BF₄)₂ to detect any possible magnetic exchange. A plot of χ^{-1} vs. *T* fits a straight line through zero, with a value of the Curie constant *C* of 0.44 cm³·K·mol^{−1}, which corresponds to a μ_{eff} of 1.88.

Cyclic Voltammetry

The cyclic voltammogram of [Cu(bpp)₂](BF₄)₂ (Figure 7) shows an irreversible wave at 0.92 V vs. Ag/AgCl, ascribed to the couple Cu^{II}/Cu^I (*E*_{pc} at 0.83 V, *E*_{pa} at 1.01 V). At scan rates between 30–80 mV/s, *I*_{pc}/*I*_{pa} = 1 and *I*_p/ν^{1/2} is independent of ν, but at higher and lower scan rates this reversibility is lost. In the Cu^{II} and Cu^I complexes with the ligand 2,2'-bis(2-imidazolyl)biphenyl mentioned above,^[21] the Cu^{II}/Cu^I reduction wave occurs at 0.08 V vs. SCE (−0.052 V vs. Ag/AgCl) in acetonitrile.^[23] Upon comparison, the reduction of [Cu(bpp)₂]²⁺ to [Cu(bpp)₂]⁺ takes place at an unusually high potential, confirming the high stability of the Cu^I complex [Cu(bpp)₂](BF₄), and also explaining the easy reduction of the Cu^{II} species in ethanol solution. Such a stabilisation of Cu^I by π-donor ligands such as azoles is well known. After reduction of Cu^I to Cu(0) at *E*_{pc} = −0.55 V, a stripping peak appears at *E*_{pa} = −0.28 V, as a result of the deposition of Cu(0) on the electrode surface. The Cu^{II}/Cu^I reduction wave becomes less prominent at scan rates higher and lower than 60 mV/s.

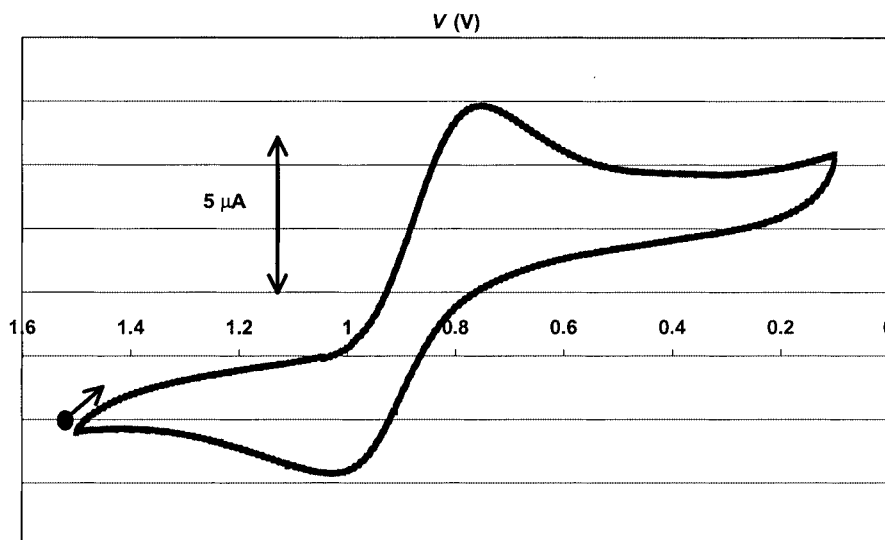


Figure 7. Cyclic voltammogram of $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ in acetonitrile (10^{-3} M) at a scan rate of 60 mV/s

Conclusion

The ligand 1,3-bis(pyrazol-1'-yl)propane (bpp) has been synthesized from 1,3-dichloropropane and pyrazole. Attempts to obtain coordination complexes of bpp with both Cu^{II} and Cu^{I} succeeded. The complexes that were obtained are the first to contain copper ions surrounded by two — rather than only one — bpp ligands forming eight-atom chelate rings with the metal ion.^[7] The best single crystals were grown from solutions of 1,3-bis(pyrazol-1'-yl)propane and Cu^{II} tetrafluoroborate, in which an excess of 1-(3-chloropropyl)pyrazole (ppc) was also present. A possible reason for this behavior is that the complexes stay in solution longer when ppc is present. The slower crystal growth yields higher quality single crystals. All attempts to obtain crystalline Cu^{II} complexes with only ppc were unsuccessful. The Cu^{II} ions in the two polymorphs of the $[\text{Cu}(\text{bpp})_2](\text{BF}_4)_2$ complex are surrounded by a distorted tetrahedral coordination environment. This is remarkable because Cu^{II} has a strong preference for a square-planar geometry when it is surrounded by four monodentate ligands or two didentate ligands.^[1] Tetrahedral geometries are much more common for Cu^{I} than for Cu^{II} . When the Cu^{II} complexes were found to be stable in a distorted tetrahedral geometry, it was expected that a tetrahedral Cu^{I} complex should also be stable, as is indeed the case. However, this complex was not expected to form from a Cu^{II} solution. The large redox potential for the copper ion in the complexes (0.92 V vs. Ag/AgCl) indicates the stability of the Cu^{I} complex.

Experimental Section

General Remarks

^1H NMR spectra were obtained with a Bruker 300 MHz spectrometer. X-band powder EPR spectra were obtained with a Jeol

RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. FTIR spectra were obtained with a Perkin–Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the diffuse reflectance technique ($4000\text{--}300\text{ cm}^{-1}$, res. 4 cm^{-1}). Magnetic susceptibility measurements ($2\text{--}300\text{ K}$) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for the magnetization of the sample holder and for the sample diamagnetism, which was estimated from the Pascal constants.^[24] Cyclic voltammetry measurements were performed with an Autolab PGSTAT 10 cyclic voltameter, using a Pt working electrode, a Pt auxiliary electrode and a Ag/AgCl reference electrode in acetonitrile (10^{-3} M), with tetrabutylammonium hexafluorophosphate as electrolyte, at a scan rate of 60 mV/s. C, H, N determinations were performed with a Perkin–Elmer 2400 Series II analyzer.

Synthesis of the Ligands

1,3-Bis(pyrazol-1'-yl)propane (bpp; Figure 8) was prepared by adding 0.2 mol (13.6 g) of pyrazole and 0.4 mol (45.2 g) of 1,3-dichloropropane dissolved in 80 mL of toluene to a solution of 0.1 mol (4 g) of sodium hydroxide in 80 mL of water. After addition of 0.2 g of tetrabutylammonium bromide to increase the rate of charge transfer between the layers, the solution was refluxed at 100°C for four days. The two layers were separated and the water layer was extracted with dichloromethane. All organic layers were combined, then dried with magnesium sulfate, and filtered. After evaporation of the solvents, the product was obtained as a yellow oil. The yield was 17% (2.99 g). ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 7.70(\text{d}, \text{a})$, $6.23(\text{dd}, \text{b})$, $7.44(\text{d}, \text{c})$, $4.07(\text{t}, \text{d})$, $2.17(\text{q}, \text{e})$.

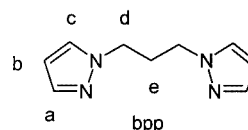


Figure 8. The ligand bpp

Table 3. Crystallographic data for α -[Cu(bpp)₂](BF₄)₂, β -[Cu(bpp)₂](BF₄)₂ and [Cu(bpp)₂](BF₄)

	α -[Cu(bpp) ₂](BF ₄) ₂	β -[Cu(bpp) ₂](BF ₄) ₂	[Cu(bpp) ₂](BF ₄)
Formula	C ₁₈ H ₂₄ B ₂ CuF ₈ N ₈	C ₁₈ H ₂₄ B ₂ CuF ₈ N ₈	C ₁₈ H ₂₄ BF ₄ CuN ₈
Molecular weight	589.61	589.61	502.80
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	Fddd (No. 70)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> (Å)	7.9532(1)	7.9557(15)	9.6773(2)
<i>b</i> (Å)	17.0680(3)	20.485(4)	23.9139(4)
<i>c</i> (Å)	36.9087(8)	23.835(4)	9.5287(1)
α (°)		74.406(16)	
β (°)		81.178(15)	90.4560(10)
γ (°)		89.381(14)	
<i>V</i> (Å ³)	5010.18(15)	3695.3(12)	2205.08(6)
<i>Z</i>	8	6	4
<i>D</i> _{calc} (g·cm ⁻³)	1.563	1.590	1.515
μ (Mo- <i>K</i> α) (mm ⁻¹)	0.955	0.972	1.047
<i>F</i> (000)	2392	1794	1032
Crystal size (mm)	0.06 × 0.12 × 0.21	0.09 × 0.30 × 0.45	0.09 × 0.15 × 0.30
<i>T</i> (K)	150	150	150
λ (Å)	Mo- <i>K</i> α 0.71073	Mo- <i>K</i> α 0.71073	Mo- <i>K</i> α 0.71073
θ range (°)	2.2 to 27.5	1.5 to 27.5	1.7 to 26.0
Data collected	14882	44203	15999
Data unique	1448	16786	4243
Data observed [<i>I</i> > 2 σ (<i>I</i>)]	1167	12647	3624
<i>R</i> _{int}	0.046	0.051	0.032
No. of parameters	123	1160	289
No. of restraints	84	566	0
<i>R</i> (<i>F</i>), [<i>I</i> > 2 σ (<i>I</i>)]	0.0548	0.0466	0.0280
$\omega R(F^2)$	0.1470	0.1041	0.0706
<i>S</i>	1.03	1.08	1.04
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ (e·Å ⁻³)	−0.41, 0.88	−0.52, 0.70	−0.35, 0.25

1-(3-Chloropropyl)pyrazole (ppc) was prepared using the same procedure, but in this case only 0.1 mol (6.8 g) of pyrazole was added to the reaction mixture.

Synthesis of the Complexes

α -[Cu(bpp)₂](BF₄)₂ (1): This complex was obtained by adding a solution of 1.0 mmol (0.31 g) of Cu(BF₄)₂·4H₂O in 8 mL of ethanol to a solution of 1.0 mmol (0.15 g) of ppc and 0.1 mmol (0.02 g) of bpp in 8 mL ethanol. The compound crystallized from the green solution as red plates that were isolated by filtration and dried for several hours in air. C₁₈H₂₄B₂CuF₈N₈ (589.6): calcd. C 36.7, H 4.1, N 19.0; found C 36.7, H 4.3, N 19.0.

β -[Cu(bpp)₂](BF₄)₂ (2): This complex was obtained by adding a solution of 1.0 mmol (0.31 g) of Cu(BF₄)₂·4H₂O in 3 mL of methanol to a solution of 1.0 mmol (0.15 g) of ppc and 0.1 mmol (0.02 g) of bpp in 3 mL of methanol. The compound crystallized from the green solution as red plates that were isolated by filtration and dried for several hours in air. C₁₈H₂₄B₂CuF₈N₈ (589.6): calcd. C 36.7, H 4.1, N 19.0; found C 36.5, H 4.0, N 18.5.

[Cu(bpp)₂](BF₄) (3): This complex was obtained by adding a solution of 1.0 mmol (0.31 g) of Cu(BF₄)₂·4H₂O in 12 mL of ethanol to a solution of 10.5 mmol (2.16 g) of ppc and 3.0 mmol (0.54 g) of bpp in 12 mL of ethanol. The resulting solution was heated to boiling and immediately filtered. After two weeks, colorless blocks crystallized from the green solution and these were isolated by filtration, then dried for several hours in air. C₁₈H₂₄BCuF₄N₈ (502.8): calcd. C 43.0, H 4.8, N 22.3; found C 42.7, H 5.0, N 22.5.

X-ray Crystallographic Study: Intensity data for each of the structures were collected on a Nonius KappaCCD diffractometer with rotating anode (Mo-*K* α , λ = 0.71073 Å) at 150 K. Correction for absorption was considered unnecessary in all cases. The structures were solved by automated Patterson methods using DIRDIF99,^[25] and refined on *F*² by least-squares procedures using SHELXL-97.^[26] Structure validation and molecular graphics preparation were performed with the PLATON package.^[27]

The BF₄[−] anion in **1**, and four of the six independent anions in **2**, are disordered over two sets of atomic positions. All non-hydrogen atoms were refined with anisotropic displacement parameters, but the displacement parameters of the disordered atoms, as well as the ligand alkyl C atoms in complex **1**, were restrained to be approximately isotropic. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The BF₄[−] anions were restrained to approximately tetrahedral geometries. Crystal data and further details of the data collections are given in Table 3.

CCDC-184550 (**1**), -184551 (**2**), and -184552 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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