Two novel bis(2,9-dimethyl-1,10-phenanthroline)copper(I) complexes: [Cu(dmp)$_2$]$_2$(PF$_6$)$_2$·0.5(bpmh)·CH$_3$CN and [Cu(dmp)$_2$][N(CN)$_2$]

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Two new salts of the cation [Cu^I(dmp)$_2$]$^+$ (dmp is 2,9-dimethyl-1,10-phenanthroline, C$_{14}$H$_{12}$N$_2$), namely bis[bis(2,9-dimethyl-1,10-phenanthroline-$\kappa^2 N,N'$)copper(I)] bis(hexafluorophosphate) hemi[bis(4-pyridylmethylidene)hydrazine] acetonitrile solvate, [Cu(C$_{14}$H$_{12}$N$_2$)$_2$]$_2$(PF$_6$)$_2$·0.5C$_{12}$H$_{10}$N$_4$·C$_2$H$_3$N or [Cu(dmp)$_2$]$_2$(PF$_6$)$_2$·0.5(bpmh)·CH$_3$CN [bpmh is bis(4-pyridylmethylidene)hydrazine, C$_{12}$H$_{10}$N$_4$], (I), and bis(2,9-dimethyl-1,10-phenanthroline-$\kappa^2 N,N'$)copper(I) dicyanamide, [Cu(C$_{14}$H$_{12}$N$_2$)$_2$](C$_2$N$_3$) or [Cu(dmp)$_2$][N(CN)$_2$], (II), are reported. The Cu—N bond lengths and the distortion from idealized tetrahedral geometry of the dmp ligands are discussed and compared with related compounds. The bpmh molecule in (I) is π–π stacked with a dmp ligand at a distance of 3.4 Å, rather than coordinated to the metal atom. The molecule lies across an inversion center in the crystal. In (II), the normally coordinated dicyanamide molecule is present as an uncoordinated counter-ion.

Comment

Complexes of copper chelated with 2,9-dimethyl-1,10-phenanthroline (dmp) have attracted attention due to their long-lived excited states and potential use in solar energy conversion (Blake *et al.*, 1998; Kuang *et al.*, 2002; Chen *et al.*, 2002; Morpurgo *et al.*, 1984; Cuttell *et al.*, 2002). Such compounds absorb light in the visible range to undergo a metal-to-ligand charge transfer (MLCT). Upon excitation, the molecules are known to undergo a geometry change, and this change has been observed in one such compound through time-resolved X-ray diffraction (Coppens *et al.*, 2004). Kovalevsky *et al.* (2003, 2004) have recently reported on a series of [Cu^I(dmp)$_2$]$^+$ salts with varying counter-ions in an attempt to correlate the ground-state structure and spectroscopic properties. Much attention has been focused on the distortion of the [Cu^I(dmp)$_2$]$^+$ cation from its idealized tetrahedral geometry. Understanding the effects of packing forces on the geometry of the cation is a necessary preliminary step for

understanding the geometry changes associated with photo-excitation. We report here the crystal structures of two new [Cu^I(dmp)$_2$]$^+$ compounds.

Crystals of [Cu(dmp)$_2$]$_2$(PF$_6$)$_2$·0.5(bpmh)·CH$_3$CN, (I) (Figs. 1 and 2), contain two [Cu^I(dmp)$_2$]$^+$ cations, two PF$_6^-$ anions, one acetonitrile solvent molecule, and one half-molecule of bpmh (residing on an inversion center) in the asymmetric unit. All bond lengths and angles are within their expected ranges. Two F atoms of one of the PF$_6^-$ anions are disordered. The pyridyl ring (N9/C57–O61) of the bpmh ligand at (x, y, z) is almost coplanar with the dmp N7/C43–C46/C54 ring and stabilized by π–π stacking; the centroid–centroid separation is 3.62 Å and the shortest atom–atom separation is 3.263 (2) Å (C60···C45). Dmp rings C18–C21/C25/C26 at (x, y, z) and $(-x, -y, -z)$ are separated by 3.378 (1) Å, with a shortest atom–atom separation of 3.360 (2) Å (C19···C25).

(I)

(II)
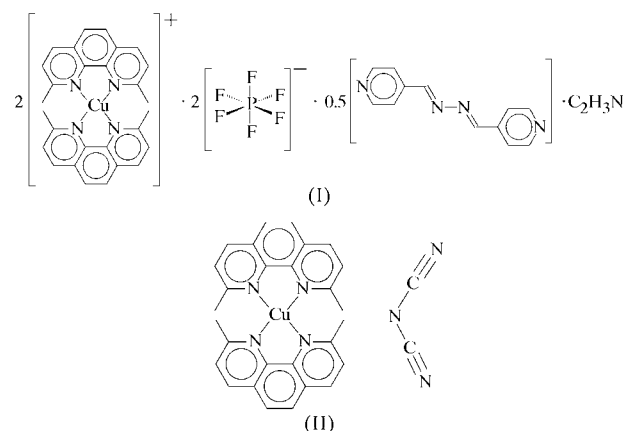
Crystals of (I) (Figs. 1 and 2) were prepared in an attempt to link the two Cu atoms through a bpmh linkage. While the bpmh molecule has often been utilized as a linker in the
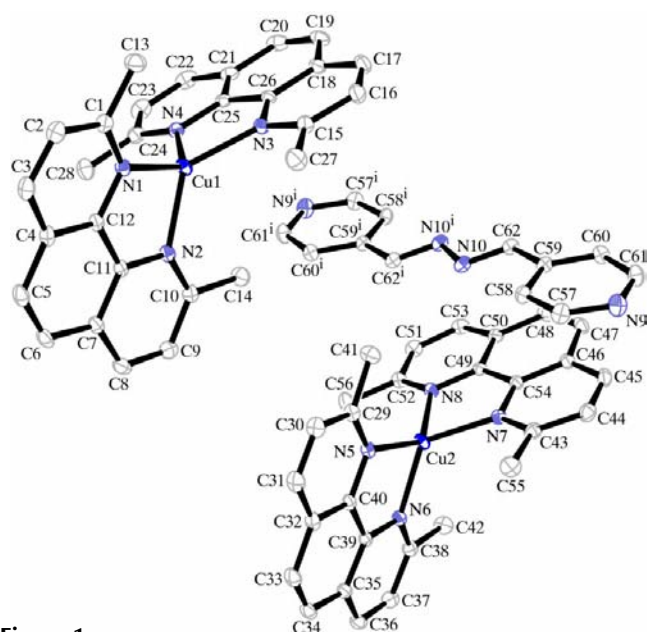

Figure 1
The two cations and the bpmh molecule in (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $1 - x, 1 - y, -z$.]

construction of supramolecular frameworks (Ma & Coppens, 2003) and in metal polymers (Ag, Co, Mn, Ni, Pb, Zn), to date no examples of a Cu complex with a bridging bpmh are known. Several examples of Cu compounds with similar bridging ligands, but containing a heterocyclic five-membered ring rather than the dimethylhydrazine group, are known (Du *et al.*, 2002, 2004; Dong *et al.*, 2003; Huang *et al.*, 2004). Even though an excess of the ligand was used during the synthesis of (I), the bpmh was incorporated into the crystal in an unco-ordinated arrangement. Goodgame *et al.* (2001) reported another crystal in which a molecule which usually acts as a linker, namely 1-(4-pyridyl)pyridin-4-one, co-crystallizes in a Cu complex instead. Kovalevsky *et al.* (2003) reported an example in which an uncoordinated dmp molecule is π–π stacked with a coordinated dmp ligand.
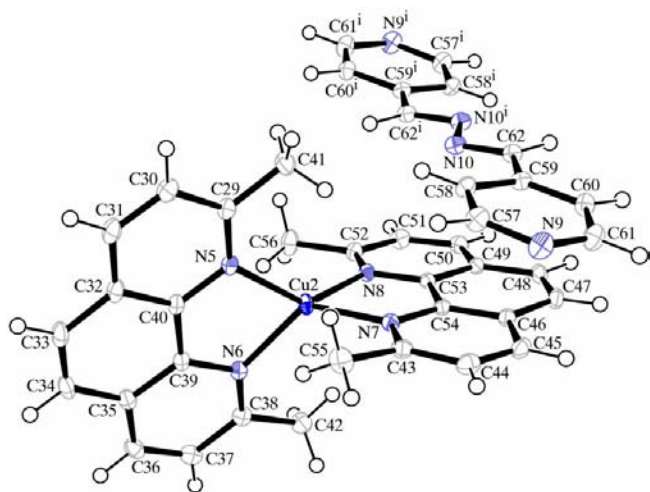

Figure 2
The stacking involving the bpmh molecule and a dmp ligand of cation *A* in (I). Displacement ellipsoids are drawn at the 50% probability level. The full bpmh molecule is depicted for clarity. [Symmetry code: (i) $1 - x, 1 - y, -z$.]
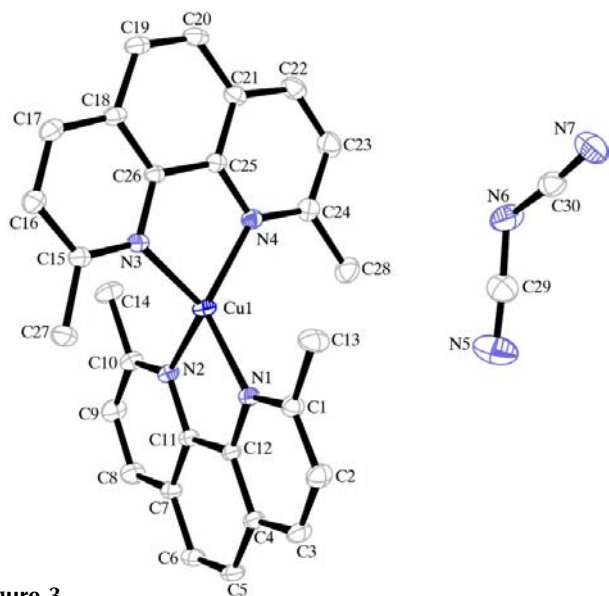

Figure 3
Compound (II), with H atoms omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

The rocking, wagging, and flattening distortions of the cations were calculated using a method described previously by Dobson *et al.* (1984). For cation *A*, the flattening distortion is rather large at $\theta z = 79.6°$, whereas the rocking and wagging distortions are $\theta x = 87.8°$ and $\theta y = 84.7°$, respectively. Cation *B* has slightly larger rocking and wagging distortions of $\theta x = 84.6°$ and $\theta y = 84.2°$, respectively, and a smaller flattening of $\theta z = 81.3°$. Kovalevsky *et al.* (2003, 2004) have reported two other hexafluorophosphate salts of this cation, one of which crystallizes with a 0.5-occupancy CH_2Cl_2 solvent molecule. The cations in the crystals of both these compounds are considerably more distorted than cations *A* or *B* in (I). The overall distortion of the cations in (I) is nearly the same and in the middle of the range of all previously reported salts of this cation (Kovalevsky *et al.*, 2003). In cation *A*, the Cu—N distances range from 2.026 (1) to 2.060 (1) Å; cation *B* has a similar Cu—N distance range of 2.018 (1)–2.059 (1) Å.

Compound (II) (Fig. 3), $[Cu(dmp)_2][N(CN)_2]$, crystallizes with one $[Cu^I(dmp)_2]^+$ cation and one $[N(CN)_2]^-$ anion in the asymmetric unit. All bond lengths and angles lie within their expected ranges. The Cu—N bond length range is 2.019 (1)–2.050 (1) Å. The rocking and wagging distortions in the cation are $\theta x = 88.2°$ and $\theta y = 86.9°$, with a flattening of $\theta z = 88.6°$. The overall distortion of the cation is quite small and comparable with that of the least distorted salt reported to date, with a *p*-tosylate counter-ion (Kovalevsky *et al.*, 2003). The C4–C7/C11/C12 ring is parallel to the inversion-related ring at $(2 - x, -y, -z)$, with a centroid–centroid separation of 3.50 Å.

The $[N(CN)_2]^-$ ion (dca) is a much-used ligand in Cu coordination chemistry. It has attracted recent attention because of its multiple coordination modes and interesting magnetic properties (Vangdal *et al.*, 2002). However, it is rarely found as an uncoordinated counterion. Two cases have been reported to date. In the first, the dca anion is semi-coordinated in $[Cu_2(tppz)(dca)_3(H_2O)](dca)\cdot H_2O$ [tppz is 2,3,5,6-tetrakis(2-pyridyl)pyrazine], with N—Cu 2.939 Å (Carranza *et al.*, 2003). However, in (II) the dca anion is completely uncoordinated, the shortest Cu···N distance being 4.641 Å. In the second case, dca is linked to a cation *via* an N—H···N hydrogen bond in the salt $[Cu(C_2N_3)(trien)](C_2N_3)$ (Luo *et al.*, 2003). In (II), only weaker C—H···N interactions exist, the shortest being 0.2 Å longer than the N—H···N bond linking the cation and anion in the compound prepared by Luo *et al.* The previously reported compounds also contain at least one coordinated dca anion. In (II), all dca atoms are coplanar, whereas the central C—N—C bond angle is 117.74 (14)°. The two terminal C—N bonds are bent slightly outwards, with N—C—N angles of 174.36 (17) and 175.3 (2)°.

Experimental

In attempting to synthesize polymeric copper(I)–dmp complexes, we found that $[Cu(dmp)_2]$ will often form even when it is not favored by the stoichiometry. Compound (I) was synthesized by dissolving $[Cu^I(CH_3CN)_4]PF_6$ (1.0 mmol), dmp (0.9 mmol), and bpmh (1.3 mmol) in CH_2Cl_2 (30 ml) and CH_3CN (20 ml). The bright-red solution was heated to 343 K and stirred for 3 h. The solid remaining

after the reaction was filtered off. Dark-red crystals were obtained by gas-phase ether diffusion into the solution. Compound (II) was synthesized by dissolving $Cu^{I}Cl$ (1.0 mmol), dmp (0.9 mmol), and $NaN(CN)_2$ (1.3 mmol) in ethanol (15 ml) and water (15 ml). The orange solution was stirred and heated to 343 K for 3 h. Orange crystals were grown by slow evaporation of the solution.

Compound (I)

Crystal data

$[Cu(C_{14}H_{12}N_2)_2]_2(PF_6)_2\cdot$ $0.5C_{12}H_{10}N_4\cdot C_2H_3N$	$Z = 2$
$M_r = 1396.24$	$D_x = 1.568$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 13.6775$ (5) Å	Cell parameters from 22 175
$b = 14.0221$ (5) Å	reflections
$c = 17.2879$ (6) Å	$\theta = 4.9$–$56.1°$
$\alpha = 111.776$ (1)°	$\mu = 0.86$ mm^{-1}
$\beta = 91.679$ (1)°	$T = 90$ (1) K
$\gamma = 104.212$ (1)°	Cubic, red
$V = 2957.96$ (18) Å^3	$0.20 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	14 342 independent reflections
φ and ω scans	12 664 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.023$
$T_{min} = 0.782$, $T_{max} = 0.919$	$\theta_{max} = 28.1°$
45 314 measured reflections	$h = -18 \rightarrow 18$
	$k = -18 \rightarrow 18$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 2.1375P]$
$wR(F^2) = 0.082$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.002$
14342 reflections	$\Delta\rho_{max} = 1.03$ e Å^{-3}
849 parameters	$\Delta\rho_{min} = -0.69$ e Å^{-3}
H-atom parameters constrained	Extinction correction: SHELXL97 (Sheldrick, 1997)
	Extinction coefficient: 0.0133 (4)

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N1	2.0402 (12)	Cu2—N5	2.0259 (12)
Cu1—N2	2.0350 (12)	Cu2—N6	2.0587 (12)
Cu1—N3	2.0182 (12)	Cu2—N7	2.0602 (12)
Cu1—N4	2.0591 (12)	Cu2—N8	2.0261 (12)
N1—Cu1—N2	82.42 (5)	N5—Cu2—N6	82.24 (5)
N1—Cu1—N3	127.02 (5)	N5—Cu2—N7	117.54 (5)
N1—Cu1—N4	128.14 (5)	N5—Cu2—N8	134.81 (5)
N2—Cu1—N3	128.70 (5)	N6—Cu2—N7	125.71 (5)
N2—Cu1—N4	113.29 (5)	N6—Cu2—N8	120.45 (5)
N3—Cu1—N4	82.54 (5)	N7—Cu2—N8	82.30 (5)

Compound (II)

Crystal data

$[Cu(C_{14}H_{12}N_2)_2](C_2N_3)$	$D_x = 1.412$ Mg m^{-3}
$M_r = 546.12$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 19 294
$a = 15.0055$ (5) Å	reflections
$b = 10.3286$ (3) Å	$\theta = 4.7$–$56.5°$
$c = 16.8878$ (5) Å	$\mu = 0.88$ mm^{-1}
$\beta = 101.138$ (1)°	$T = 90$ (1) K
$V = 2568.1$ (1) Å^3	Parallelepiped, orange
$Z = 4$	$0.3 \times 0.2 \times 0.1$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	7446 independent reflections
φ and ω scans	6422 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.033$
$T_{min} = 0.719$, $T_{max} = 0.941$	$\theta_{max} = 30.0°$
44 252 measured reflections	$h = -21 \rightarrow 21$
	$k = -14 \rightarrow 14$
	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$+ 1.4111P]$
$wR(F^2) = 0.085$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
7446 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
348 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
H-atom parameters constrained	Extinction correction: SHELXL97 (Sheldrick, 1997)
	Extinction coefficient: 0.0108 (6)

Table 2
Selected geometric parameters (Å, °) for (II).

Cu1—N1	2.0185 (11)	Cu1—N3	2.0374 (11)
Cu1—N4	2.0251 (11)	Cu1—N2	2.0498 (11)
N1—Cu1—N4	126.72 (4)	N3—Cu1—N2	120.80 (4)
N1—Cu1—N3	125.85 (4)	C30—N6—C29	117.74 (14)
N4—Cu1—N3	82.39 (4)	N7—C30—N6	174.36 (17)
N1—Cu1—N2	82.44 (4)	N5—C29—N6	175.3 (2)
N4—Cu1—N2	124.34 (4)		

H atoms were located in difference maps and treated as riding for the aromatic and methylene H atoms, with C—H distances of 0.95 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$, and placed in idealized positions for CH$_3$ H atoms, with C—H distances of 0.98 Å and with $U_{iso}(H) = 1.5U_{eq}(C)$. Free isotropic refinement of H atoms did not lead to a significant improvment in the R factor.

For both compounds, data collection: SMART (Bruker, 1999); cell refinement: SMART; data reduction: SAINT (Bruker, 1999); structure solution: SHELXS97 (Sheldrick, 1997); structure refinement: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); publication software: SHELXTL.

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