

Low-dimensional compounds containing cyano groups. IV. Bis(2,2'-bipyridine- κ^2N,N^1)(dicyan-amido- $\kappa N'$)copper(II) perchlorate and μ -dicyanamido- $\kappa^2N^1:N^5$ -bis[bis(2,2'-bipyridine- κ^2N,N')-copper(II)] triperchlorate ethanol hemisolvate, complexes with unusual dicyanamide coordination

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From reaction mixtures containing the same reagents, the two novel title complexes, with unusual coordination modes of the dicyanamide (dca) ligand, have been prepared. The first compound, $[\text{Cu}(\text{C}_2\text{N}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{ClO}_4$, represents a relatively rare class of compounds, with the dca ligand coordinated in a monodentate manner. Its structure is formed by the $[\text{Cu}(\text{bpy})_2\{\text{N}(\text{CN})_2\}]^+$ complex cation (bpy is 2,2'-bipyridine) and a ClO_4^- anion, which does not enter the inner coordination sphere. The Cu centre is five-coordinate within a strongly distorted trigonal bipyramid to two bpy molecules and one dca ligand, which is coordinated through one nitrile N atom in the equatorial plane. The second compound, $[\text{Cu}_2(\text{C}_2\text{N}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_4](\text{ClO}_4)_3 \cdot 0.5\text{C}_2\text{H}_6\text{O}$, contains dca coordinated in the more common bidentate manner, but instead of a chain structure, a unique binuclear complex is formed. The asymmetric unit consists of the $[\text{Cu}(\text{bpy})_2\{\text{N}(\text{CN})_2\}(\text{bpy})_2\text{-Cu}]^{3+}$ binuclear complex cation, the charge of which is neutralized by three uncoordinated perchlorate anions, and a half-molecule of ethanol. Both Cu centres in the cation are five-coordinate, adopting a slightly distorted trigonal-bipyramidal environment.

Comment

The dicyanamide (dca) anion, $[\text{N}(\text{CN})_2]^-$, exhibits a rich variety of bonding modes. It can coordinate either in a monodentate manner or, more typically, in a bidentate,

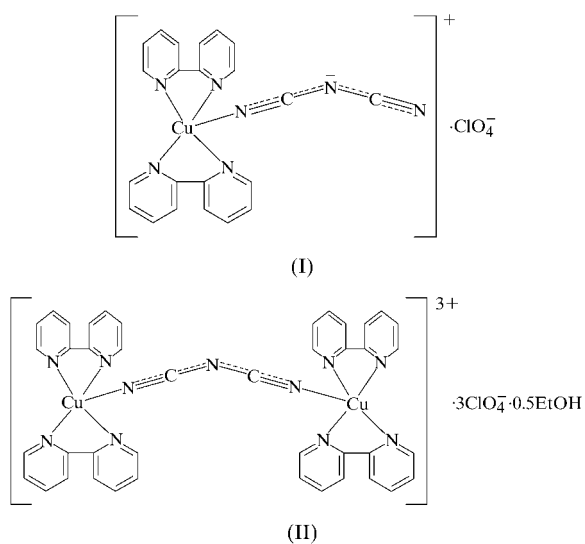
tridentate or even tetradentate manner, with participation of two or three N donor atoms. Nevertheless, monodentate coordination of dca through the amide N atom is rather improbable and, to date, no crystal structure of such a compound is known (Kohout *et al.*, 2000). On the other hand, the structures of several molecular and ionic compounds with dca coordinated in a monodentate manner through a nitrile N atom have been reported. These compounds contain either six-coordinate central atoms and are of the general formula $[\text{ML}_4(\text{dca})_2]$, e.g. $[\text{Ni}(\text{teta})(\text{dca})_2]$ (teta is triethylenetetramine; Březina *et al.*, 1999), $[\text{Ni}(4\text{-Meim})_4(\text{dca})_2]$ (4-Meim is 4-methylimidazole; Kožíšek *et al.*, 1996), $[\text{Cu}(\text{phen})_2(\text{dca})_2]$ (phen is 1,10-phenanthroline; Potočňák *et al.*, 1995) and $[\text{Cu}(\text{NITpPy})_2(\text{H}_2\text{O})_2(\text{dca})_2]$ (NITpPy is the nitronyl nitroxide radical; Dasna *et al.*, 2001), or exhibit five-coordination and have the general formula $[\text{ML}_4(\text{dca})]\text{X}$, e.g. $[\text{Cu}(\text{phen})_2(\text{dca})]\text{C}(\text{CN})_3$ (Potočňák *et al.*, 1996), $[\text{Cu}(\text{bpy})_2(\text{dca})]\text{C}(\text{CN})_3$ (bpy is 2,2'-bipyridine; Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001) and $[\text{Cu}(\text{bpy})_2(\text{dca})]\text{BF}_4$ (Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001), in which L_4 may be one tetradentate, two bidentate or four monodentate ligands, and X is a monoanion.

As a consequence of the possible bridging function of dca, there has been an unusual level of interest in this ligand in recent years, especially in connection with the preparation of magnetic materials. Among them, weak ferromagnets of the general formula $\alpha\text{-}[M(\text{dca})_2]$, with a three-dimensional rutile-type structure, have attracted much attention because of the ability of dca to act as a molecular-based magnet precursor, with several transition metal ions octahedrally coordinated by tridentate dca ligands (Batten *et al.*, 1998; Jensen *et al.*, 1999; Kurmoo & Kepert, 1998; Manson *et al.*, 1998). If the two dca ligands are tetrahedrally coordinated only through the nitrile N atoms, β -isomers of these compounds occur in the form of sheet-like structures (Jensen *et al.*, 1999). When two coordination sites of hexacoordinate metallic centres are occupied by additional blocking ligands, dca acts as a bidentate bridging ligand coordinated through the nitrile N atoms and the resulting compounds contain $[\text{ML}_2(\text{dca})_2]$ units (L_2 is one bidentate or two monodentate ligands; Manson *et al.*, 1999; Escuer *et al.*, 2000; van Albada *et al.*, 2000; Jäger *et al.*, 2001; Dasna *et al.*, 2001; Sun *et al.*, 2001). All these compounds are one-dimensional and contain chains in which two metallic centres are connected by a pair of dca ligands, forming double bridges. Moreover, if the ligands L can serve as additional bridges between central atoms, the above chains are connected by these ligands, giving two-dimensional sheets (Jensen *et al.*, 1999, 2001).

The $[\text{ML}_2(\text{dca})_2]$ units are also present in another type of structure, which was previously observed in $[M(\text{bpym})\text{-}(\text{dca})_2]\cdot\text{H}_2\text{O}$ (M is Mn, Fe or Co, and bpym is 2,2'-bipyrimidine; Marshall *et al.*, 2000) and consists of chains in which two hexacoordinate metallic centres are connected by only one bridging dca ligand, while the second remains monodentate. The same type of one-dimensional structure, but with five-coordinate metal atoms, has been observed in the recently published structures of $[\text{Cu}(\text{dmbpy})(\text{dca})_2]$ (dmbpy is

5,5'-dimethyl-2,2'-bipyridine; Kooijman *et al.*, 2002), [Cu(phen)(dca)₂] (Luo *et al.*, 2002) and [Cu(bpy)(dca)₂] (Potočňák *et al.*, 2002; Vangdal *et al.*, 2002).

As part of our study on low-dimensional magnetic materials (Černák *et al.*, 2002), and with the aim of finding possible reasons for the different shapes of the coordination polyhedra in related five-coordinate compounds, we present here the structures of two new complexes containing dca which were prepared from reaction mixtures containing the same reagents. The [Cu(bpy)₂(dca)]ClO₄ complex, (I), belongs to the class of compounds with dca coordinated in a relatively unusual monodentate manner. On the other hand, the [Cu(bpy)₂(dca)(bpy)₂Cu](ClO₄)₃·0.5EtOH complex, (II), contains dca coordinated in a bidentate manner, which is the most common coordination mode for dca. However, the propagation of the polymeric structure is broken at the two neighbouring central atoms and, instead of a chain structure, only binuclear units arise. As far as we are aware, complex (II) represents the first example of this type of structure containing bridging dca. Structures (I) and (II) are both ionic.



The structure of (I) (Fig. 1) consists of the [Cu(bpy)₂(N(CN)₂)]⁺ complex cation and a ClO₄⁻ anion, which does not enter the inner coordination sphere. The copper centre is five-coordinated, within a distorted trigonal bipyramid, to two bpy molecules and one dca ligand coordinated through one nitrile N atom in the equatorial plane. In the trigonal bipyramid, the two out-of-plane Cu1–N10 and Cu1–N30 bonds have nearly the same values and are almost collinear (Table 1). The two in-plane distances (Cu1–N20 and Cu1–N40) are, on average, longer by 0.096 Å than the out-of-plane Cu–N distances; this is a common feature for this kind of compound. The third in-plane Cu1–N2 [N from the N(CN)₂ ligand] distance is shorter than the other two but is comparable with the out-of-plane distances. This is different from the compound where the non-coordinating out-of-sphere anion *X* is [C(CN)₃]⁻, (III) (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001), where this is the shortest Cu–N bond, but the same trends in bond

distances were observed in the compound where *X* is [BF₄]⁻, (IV) (Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001), and in the related compound [Cu(phen)₂N(CN)₂][C(CN)₃], (V), where this bond has the same length (within 1σ) as the two out-of-plane bonds (Potočňák *et al.*, 1996); Table 2 gives details of these comparisons.

The out-of-plane angles in (I) lie within the range 78.78 (7)–96.84 (7)°, similar to the values observed in (III)–(V). The bond angles in the equatorial plane of (I) differ considerably from the ideal trigonal angle of 120°, with one wide angle of 146.66 (8)° (α₁ = N2–Cu1–N40) and two narrow angles of 108.46 (8)° (α₂ = N2–Cu1–N20) and 104.87 (8)° (α₃ = N20–Cu1–N40). Corresponding values for (III)–(V) are given in Table 2. Thus the angle α₃, which is opposite the Cu1–N2 bond, is narrower than the ideal angle of 120° by 15.13°, and there is a difference of 38.20° between α₁ and α₂.

According to the criteria of Harrison & Hathaway (1980), the coordination polyhedron around the Cu atom can be best described as distorted trigonal-bipyramidal with a distortion toward square-pyramidal, similar to (III) and (IV). On the other hand, according to the values of the angles α₁, α₂ and α₃, the coordination polyhedron of (V) can be best described as trigonal-bipyramidal with approximate C_{2v} symmetry. The difference in the shape of the coordination polyhedra is in accordance with the values of the τ parameter [Table 2; the τ parameter is 100 for an ideal trigonal bipyramid and 0 for an ideal tetragonal pyramid (Addison *et al.*, 1984)]. This difference in the shape of the coordination polyhedron of (I), (III) and (IV) on one hand and of (V) on the other can be explained by the lower rigidity of the bpy ligand compared with the phen ligand. While the two outer pyridine rings in a phen molecule are connected by a phenyl ring making the whole molecule planar, the two pyridine rings in a bpy molecule can rotate around their common C–C single bond.

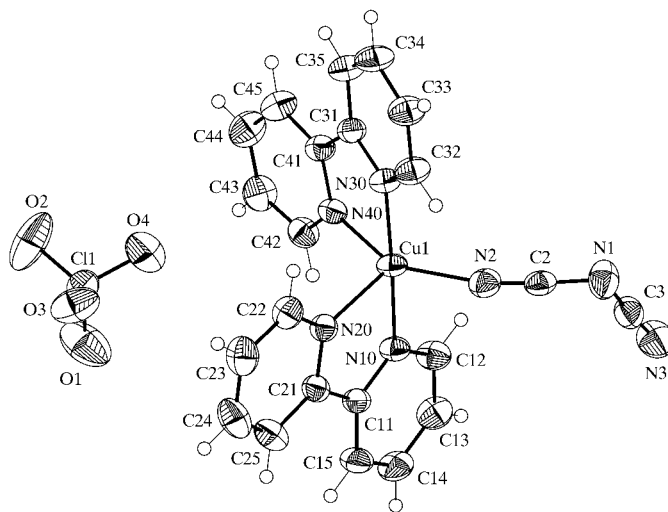


Figure 1
The structure of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The angles between the two pyridine rings are $2.54(7)$ and $8.35(7)^\circ$ for the first (N10–N20) and the second (N30–N40) bpy molecules in (I), respectively. Consequently, the first bpy molecule is almost planar [the largest deviation of atoms from the mean plane is $0.036(3)$ Å for atom C24], while the planarity of the second is less [the largest deviation from the mean plane is $0.112(3)$ Å for atom C43]. The sum of the bond angles in the equatorial plane of (I) (359.99°) indicates coplanarity of atom Cu1 with the three equatorial atoms [it is displaced from the N2/N20/N40 plane by $0.0092(3)$ Å towards atom N10].

The dca anion in (I) is ligated in the unusual monodentate manner. Inspection of the bond lengths (Table 1) shows that none of the three possible canonical formulae (Golub *et al.*, 1986) adequately describes the bonding mode of the dicyanamide. Both the nitrile $\text{N}\equiv\text{C}$ and amide $\text{N}=\text{C}$ distances have values close to those of $\text{N}\equiv\text{C}$ (1.15 Å) and $\text{N}=\text{C}$ bonds (1.27 Å), respectively. The N(amide)–C \equiv N(nitrile) angles are almost linear, while the C2–N1–C3 angle adopts a value of $119.4(2)^\circ$, close to the ideal value of 120° . The dca ligand is planar, the largest deviation from the mean plane being $0.003(2)$ Å for atom C2, and its bonding mode to atom Cu1 (C2 \equiv N2–Cu1) can be considered as angular.

The asymmetric unit of (II) (Fig. 2) contains one binuclear $[\text{Cu}(\text{bpy})_2\{\text{N}(\text{CN})_2\}(\text{bpy})_2\text{Cu}]^{3+}$ complex cation, the charge of which is balanced by three uncoordinated perchlorate anions, and half a molecule of ethanol. Formally, we can consider the cation as two $[\text{Cu}(\text{bpy})_2\{\text{N}(\text{CN})_2\}]^+$ complex cations, in which both Cu centres are five-coordinated within a slightly distorted trigonal bipyramid to two bpy molecules and one bridging dca ligand, which is coordinated equatorially to the two Cu centres

via different nitrile N atoms. Inspection of Tables 2 and 3 indicates that, from this point of view, there is no major difference between the complex cation in (I) and the 'two cations' in (II).

The two out-of-plane bonds around the Cu1 and Cu2 centres have the same length to within 2σ and are almost collinear. The two in-plane Cu–N_{phen} distances are of almost the same value and are longer on average than the out-of-plane Cu–N distances, by 0.093 Å for Cu1 and 0.100 Å for Cu2. The in-plane Cu–N(dca) distances are shorter than the other two, but, unlike the corresponding bond in (I), they are somewhat longer than the out-of-plane distances.

Although the corresponding bond distances around atoms Cu1 and Cu2 in (II) are very similar and all equatorial angles are close to the ideal value of 120° , the equatorial angles around Cu1 and Cu2 are nevertheless quite different. The α_1 angles are almost equal, but the α_2 and α_3 angles differ. Thus, there is a difference [of 8.54° for Cu1 and 1.49° for Cu2] between α_1 and α_2 , and both polyhedra can, according to the criteria of Harrison & Hathaway (1980), be best described as trigonal-bipyramidal with approximate C_{2v} symmetry. The high values of the τ parameter for the polyhedra around Cu1 and Cu2 confirm that the distortions of the polyhedra from the ideal trigonal-bipyramidal shape are small.

Although, in comparison with (I), the dicyanamide is ligated differently in (II), there are no significant differences in ligand molecular geometry in the two structures. Nevertheless, due to its bridging function in (II), the ligand is more symmetrical in this compound, and this manifests itself in almost identical values for the corresponding bond distances (Table 3). Moreover, probably due to internal repulsions within the

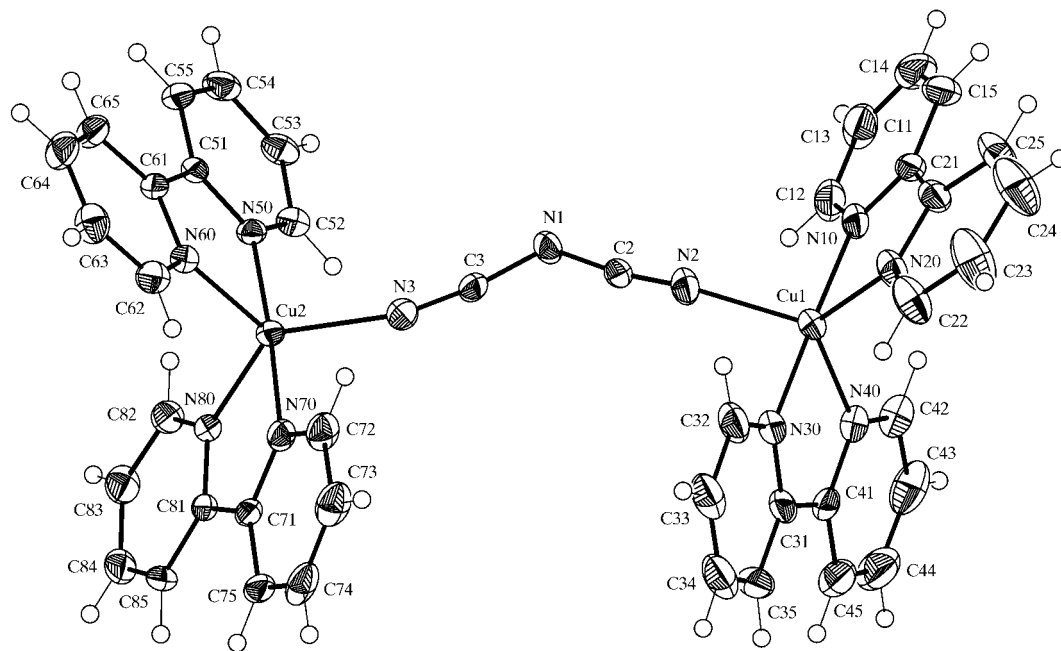


Figure 2

The structure of the dinuclear cation in (II) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

dinuclear cation, both the C3–N1–C2 and the two C≡N(nitrile)–Cu angles adopt higher values in (II), increasing the distance between the two Cu centres in the cation and thus decreasing the intra-cation repulsion.

The O6···C11 distance in (II) is shorter than the sum of the corresponding van der Waals radii, and the O6···C11ⁱ–C15ⁱ, O6···C11ⁱ–C21ⁱ and O6···C11ⁱ–N10ⁱ [symmetry code: (i) 1 – x, 1 – y, –z] angles have values of 90.2 (1), 85.3 (1) and 94.0 (1)°, respectively, which are all close to 90°. The O6···C11 contact is therefore almost perpendicular to the plane of the bipyridine molecule and may be considered as an intermolecular interaction between a free electron pair on the O atom and the delocalized π-electron system of the bipyridine molecule.

Experimental

Crystals of (I) were prepared by mixing a 0.1 M aqueous solution of Cu(ClO₄)₂ (5 ml) with a 0.1 M ethanol solution of bpy (10 ml). To the resulting blue solution, a 0.1 M aqueous ethanol solution of KN(CN)₂ (6 ml) was added (all solutions were warmed before mixing). Blue sheet-like crystals appeared within 1 h. The crystals were filtered off and dissolved in a mixture of ethanol and water (1:1). After two weeks, blue hexagonal plate-like crystals of (I) were filtered off and dried in air. Crystals of (II) were prepared by mixing a 0.1 M aqueous solution of Cu(ClO₄)₂ (5 ml) with a 0.1 M ethanol solution of bpy (10 ml). To the resulting blue solution, a 0.1 M aqueous ethanol solution of KN(CN)₂ (5 ml) was added (all solutions were warmed before mixing). Blue crystals of (II) appeared within one week. The crystals were filtered off and dried in air.

Compound (I)

Crystal data

[Cu(C₂N₃)(C₁₀H₈N₂)₂]ClO₄
M_r = 541.41
 Orthorhombic, *Pbca*
a = 8.7343 (4) Å
b = 17.9450 (9) Å
c = 28.7230 (17) Å
V = 4502.0 (4) Å³
Z = 8
D_x = 1.598 Mg m^{–3}

Mo *K*α radiation
 Cell parameters from 8000 reflections
 θ = 14.3–28.0°
 μ = 1.14 mm^{–1}
T = 193 (2) K
 Hexagonal plate, blue
 0.60 × 0.46 × 0.22 mm

Data collection

Stoe IPDS image-plate diffractometer
 φ scans
 Absorption correction: numerical, face-indexed
*T*_{min} = 0.627, *T*_{max} = 0.792
 40 361 measured reflections

5308 independent reflections
 3430 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.062
 θ _{max} = 28.1°
h = –10 → 11
k = –23 → 23
l = –37 → 37

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.036
wR(*F*²) = 0.091
S = 0.97
 5308 reflections
 316 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.050P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 $\Delta\rho$ _{max} = 0.53 e Å^{–3}
 $\Delta\rho$ _{min} = –0.43 e Å^{–3}

Table 1

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

Cu1–N30	1.9916 (18)	N10–C11	1.347 (3)
Cu1–N40	2.0396 (18)	N10–C12	1.339 (3)
Cu1–N10	2.0025 (18)	N20–C21	1.346 (3)
Cu1–N20	2.1457 (18)	N20–C22	1.337 (3)
Cu1–N2	1.995 (3)	N30–C31	1.349 (3)
N1–C2	1.291 (4)	N30–C32	1.340 (3)
N1–C3	1.323 (4)	N40–C41	1.352 (3)
N2–C2	1.145 (4)	N40–C42	1.336 (3)
N3–C3	1.138 (4)		
N30–Cu1–N40	80.52 (7)	Cu1–N30–C32	124.66 (15)
N2–Cu1–N30	92.51 (8)	C31–N30–C32	119.66 (19)
N2–Cu1–N40	146.67 (8)	Cu1–N40–C41	114.17 (14)
N10–Cu1–N20	78.78 (7)	Cu1–N40–C42	127.33 (15)
N10–Cu1–N30	177.17 (7)	C41–N40–C42	118.40 (19)
N10–Cu1–N40	96.85 (7)	N1–C2–N2	174.1 (3)
N2–Cu1–N10	90.27 (8)	N1–C3–N3	174.4 (3)
N2–Cu1–N20	108.46 (8)	N10–C11–C15	120.2 (2)
N20–Cu1–N40	104.87 (7)	N10–C11–C21	115.35 (18)
N20–Cu1–N30	100.81 (7)	N10–C12–C13	122.2 (2)
C2–N1–C3	119.4 (2)	N20–C21–C11	115.3 (2)
Cu1–N2–C2	143.5 (2)	N20–C21–C25	121.1 (2)
Cu1–N10–C11	117.65 (14)	N20–C22–C23	123.0 (2)
Cu1–N10–C12	122.71 (15)	N30–C31–C35	120.7 (2)
C11–N10–C12	119.62 (19)	N30–C31–C41	114.88 (18)
Cu1–N20–C21	112.91 (14)	N30–C32–C33	122.1 (2)
Cu1–N20–C22	128.26 (16)	N40–C41–C31	114.55 (19)
C21–N20–C22	118.7 (2)	N40–C41–C45	121.7 (2)
Cu1–N30–C31	115.66 (14)	N40–C42–C43	122.5 (2)

Compound (II)

Crystal data

[Cu₂(C₂N₃)(C₁₀H₈N₂)₄]
 (ClO₄)₃·0.5C₂H₆O
M_r = 1139.25
 Triclinic, *P* $\bar{1}$
a = 10.2999 (9) Å
b = 14.3808 (12) Å
c = 16.4311 (16) Å
 α = 74.120 (10)°
 β = 83.371 (11)°
 γ = 80.046 (10)°
V = 2299.7 (4) Å³

Z = 2
D_x = 1.645 Mg m^{–3}
 Mo *K*α radiation
 Cell parameters from 7998 reflections
 θ = 2.3–28.0°
 μ = 1.18 mm^{–1}
T = 193 (2) K
 Block, blue
 0.33 × 0.24 × 0.14 mm

Data collection

Stoe IPDS image-plate diffractometer
 φ scans
 Absorption correction: numerical, face-indexed
*T*_{min} = 0.790, *T*_{max} = 0.869
 27 918 measured reflections

10 314 independent reflections
 5455 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.072
 θ _{max} = 28.2°
h = –13 → 13
k = –17 → 17
l = –21 → 21

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.046
wR(*F*²) = 0.113
S = 0.84
 10 314 reflections
 658 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0564P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 $\Delta\rho$ _{max} = 0.99 e Å^{–3}
 $\Delta\rho$ _{min} = –0.67 e Å^{–3}

The aromatic H atoms in (I) were placed in calculated positions and refined as riding on their parent C atoms, with C–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). In (II), these H atoms were placed geometrically and refined as riding, with C–H = 0.95 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C), while the solvent H atoms were found in difference Fourier syntheses and refined as part of rigid rotating groups, with O–H = 0.84 Å,

Table 2A comparison of molecular geometry parameters (Å, °) for some [CuL₄(dca)]⁺ species.

Parameter†	(I)	(II), atom Cu1	(II), atom Cu2	(III)	(IV)	(V)
Cu1—N10	2.0024 (17)	1.979 (3)	1.979 (3)	1.998 (4)	2.006 (3)	1.981 (3)
Cu1—N30	1.9916 (17)	1.973 (3)	1.974 (3)	1.975 (4)	1.998 (3)	1.977 (4)
Cu1—N20	2.1456 (19)	2.063 (3)	2.086 (3)	2.116 (4)	2.142 (3)	2.112 (4)
Cu1—N40	2.0395 (19)	2.074 (4)	2.067 (3)	2.027 (4)	2.043 (3)	2.064 (3)
Cu1—N2	1.995 (2)	2.034 (3)	2.027 (3)	1.973 (5)	2.015 (3)	1.982 (4)
N10—Cu1—N30	177.16 (9)	178.41 (13)	176.73 (12)	175.3 (2)	177.52 (12)	175.12 (14)
α ₁	146.66 (8)	123.02 (15)	123.88 (13)	140.0 (2)	145.00 (13)	133.6 (2)
α ₂	108.46 (8)	114.48 (13)	122.39 (13)	112.4 (2)	108.54 (12)	115.7 (2)
α ₃	104.87 (8)	122.50 (13)	113.72 (11)	107.6 (2)	106.45 (11)	110.70 (13)
τ	50.8	92.3	88.1	58.8	54.2	69.2

† The numbering schemes have been standardized as for (I). Notes: (I) is [Cu(bpy)₂(dca)]ClO₄ (this work); (II) is [Cu(bpy)₂(dca)(bpy)₂Cu](ClO₄)₃·0.5EtOH (this work); (III) is [Cu(bpy)₂(dca)]C(CN)₃ (Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001); (IV) is [Cu(bpy)₂(dca)]BF₄ (Potočňák, Dunaj-Jurčo, Mikloš, Massa & Jäger, 2001); (V) is [Cu(phen)₂{N(CN)₂}C(CN)₃] (Potočňák *et al.*, 1996).

Table 3

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

Cu1—N2	2.034 (4)	N10—C11	1.344 (5)
Cu1—N10	1.980 (4)	N20—C21	1.360 (5)
Cu1—N20	2.063 (3)	N20—C22	1.331 (6)
Cu1—N30	1.973 (4)	N30—C31	1.342 (6)
Cu1—N40	2.073 (4)	N30—C32	1.337 (5)
Cu2—N3	2.027 (3)	N40—C42	1.343 (6)
Cu2—N50	1.979 (3)	N40—C41	1.350 (6)
Cu2—N60	2.086 (3)	N50—C52	1.343 (4)
Cu2—N70	1.974 (3)	N50—C51	1.341 (5)
Cu2—N80	2.067 (3)	N60—C62	1.332 (5)
O13—C5	1.392 (10)	N60—C61	1.360 (5)
N1—C2	1.302 (5)	N70—C72	1.341 (5)
N1—C3	1.291 (4)	N70—C71	1.350 (5)
N2—C2	1.152 (5)	N80—C82	1.339 (5)
N3—C3	1.153 (5)	N80—C81	1.345 (5)
N10—C12	1.339 (6)		
N2—Cu1—N10	90.91 (15)	Cu2—N50—C51	116.7 (2)
N2—Cu1—N20	123.00 (15)	Cu2—N60—C61	112.5 (2)
N2—Cu1—N30	90.56 (15)	C61—N60—C62	118.8 (3)
N2—Cu1—N40	114.49 (14)	Cu2—N60—C62	128.6 (3)
N10—Cu1—N20	80.70 (14)	C71—N70—C72	119.8 (3)
N10—Cu1—N30	178.42 (14)	Cu2—N70—C72	123.4 (3)
N10—Cu1—N40	99.58 (15)	Cu2—N70—C71	116.7 (2)
N20—Cu1—N30	98.01 (14)	Cu2—N80—C82	127.4 (3)
N20—Cu1—N40	122.51 (14)	C81—N80—C82	119.0 (3)
N30—Cu1—N40	80.31 (15)	Cu2—N80—C81	113.6 (3)
N3—Cu2—N50	91.82 (14)	N1—C2—N2	171.6 (4)
N3—Cu2—N60	122.38 (14)	N1—C3—N3	171.2 (4)
N3—Cu2—N70	91.44 (14)	N10—C11—C15	120.6 (4)
N3—Cu2—N80	123.90 (14)	N10—C11—C21	115.3 (3)
N50—Cu2—N60	80.24 (12)	N10—C12—C13	122.2 (4)
N50—Cu2—N70	176.73 (12)	N20—C21—C11	115.2 (3)
N50—Cu2—N80	98.27 (12)	N20—C21—C25	121.1 (4)
N60—Cu2—N70	97.73 (12)	N20—C22—C23	122.6 (5)
N60—Cu2—N80	113.71 (12)	N30—C31—C41	115.0 (4)
N70—Cu2—N80	80.15 (12)	N30—C31—C35	120.3 (4)
C2—N1—C3	125.3 (3)	N30—C32—C33	122.7 (5)
Cu1—N2—C2	161.4 (3)	N40—C41—C45	122.0 (4)
Cu2—N3—C3	167.0 (4)	N40—C41—C31	114.8 (4)
Cu1—N10—C11	116.0 (3)	N40—C42—C43	122.0 (5)
C11—N10—C12	119.5 (4)	N50—C51—C61	115.3 (3)
Cu1—N10—C12	124.4 (3)	N50—C51—C55	120.7 (3)
C21—N20—C22	118.4 (4)	N50—C52—C53	122.2 (4)
Cu1—N20—C21	112.6 (3)	N60—C61—C51	115.0 (3)
Cu1—N20—C22	128.8 (3)	N60—C61—C65	121.3 (3)
C31—N30—C32	119.4 (4)	N60—C62—C63	122.6 (4)
Cu1—N30—C32	124.1 (4)	N70—C71—C81	114.5 (3)
Cu1—N30—C31	116.5 (3)	N70—C71—C75	120.1 (3)
C41—N40—C42	118.8 (4)	N70—C72—C73	122.0 (4)
Cu1—N40—C41	112.8 (3)	N80—C81—C71	115.0 (3)
Cu1—N40—C42	128.0 (4)	N80—C81—C85	121.7 (4)
Cu2—N50—C52	123.6 (3)	N80—C82—C83	122.0 (4)
C51—N50—C52	119.7 (3)	O13—C5—C4	122.8 (7)

methylene C—H = 0.99 Å and methyl C—H = 0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$.

For both compounds, data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1508). Services for accessing these data are described at the back of the journal.

References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Albada, G. A. van, Quiroz-Castro, M. E., Mutikainen, I., Turpeinen, U. & Reedijk, J. (2000). *Inorg. Chim. Acta*, **298**, 221–225.
- Batten, S. R., Jensen, P., Moubaraki, B., Murray, K. S. & Robson, R. (1998). *Chem. Commun.* pp. 439–440.
- Březina, F., Trávníček, Z., Šindelář, Z., Pastorek, R. & Marek, J. (1999). *Transition Met. Chem.* **24**, 459–462.
- Černák, J., Orendáč, M., Potočňák, I., Chomič, J., Orendáčová, A., Skoršepa, J. & Feher, A. (2002). *Coord. Chem. Rev.* **224**, 51–66.
- Crystal Impact (1999). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
- Dasna, I., Golhen, S., Ouahab, L., Fettouhi, M., Pena, O., Daro, N. & Sutter, J.-P. (2001). *Inorg. Chim. Acta*, **326**, 37–46.
- Escuer, A., Mautner, F. A., Sanz, N. & Vicente, R. (2000). *Inorg. Chim. Acta*, **39**, 1668–1673.
- Golub, A. M., Köhler, H. & Skopenko, V. V. (1986). *Chemistry of Pseudohalides*, edited by R. J. H. Clark, p. 436. Amsterdam: Elsevier.
- Harrison, W. D. & Hathaway, B. J. (1980). *Acta Cryst.* **B36**, 1069–1074.
- Jäger, L., Wagner, C., Korabik, M., Zygumt, A. & Mroziński, J. (2001). *J. Mol. Struct.* **570**, 159–164.
- Jensen, P., Batten, S. R., Fallon, G. D., Moubaraki, B., Murray, K. S. & Price, D. J. (1999). *Chem. Commun.* pp. 177–178.
- Jensen, P., Batten, S. R., Moubaraki, B. & Murray, K. S. (2001). *J. Solid State Chem.* **159**, 352–361.
- Kohout, J., Jäger, L., Hvastijová, M. & Kožíšek, J. (2000). *J. Coord. Chem.* **51**, 169–218.
- Kooijman, H., Spek, A. L., van Albada, G. A. & Reedijk, J. (2002). *Acta Cryst.* **C58**, m124–m126.
- Kožíšek, J., Paulus, H., Danková, M. & Hvastijová, M. (1996). *Acta Cryst.* **C52**, 3019–3020.
- Kurmo, M. & Kepert, C. J. (1998). *New J. Chem.* **22**, 1515–1524.

- Luo, J., Hong, M., Weng, J., Zhao, Y. & Cao, R. (2002). *Inorg. Chim. Acta*, **329**, 59–65.
- Manson, J. L., Arif, A. M., Incarvito, C. D., Liable-Sands, L. M., Rheingold, A. L. & Miller, J. S. (1999). *J. Solid State Chem.* **145**, 369–378.
- Manson, J. L., Kmety, C. R., Huang, Q.-Z., Lynn, J. W., Bendele, G. M., Pagola, S., Stephens, P. W., Liable-Sands, L. M., Rheingold, A. L., Epstein, A. J. & Miller, J. S. (1998). *Chem. Mater.* **10**, 2552–2560.
- Marshall, S. R., Incarvito, C. D., Manson, J. L., Rheingold, A. L. & Miller, J. S. (2000). *Inorg. Chem.* **39**, 1969–1973.
- Potočňák, I., Burčák, M., Wagner, C. & Jäger, L. (2002). *Acta Cryst.* **C58**, m327–m329.
- Potočňák, I., Dunaj-Jurčo, M., Mikloš, D. & Jäger, L. (1996). *Acta Cryst.* **C52**, 1653–1655.
- Potočňák, I., Dunaj-Jurčo, M., Mikloš, D. & Jäger, L. (2001). *Monatsh. Chem.* **132**, 315–327.
- Potočňák, I., Dunaj-Jurčo, M., Mikloš, D., Kabešová, M. & Jäger, L. (1995). *Acta Cryst.* **C51**, 600–602.
- Potočňák, I., Dunaj-Jurčo, M., Mikloš, D., Massa, W. & Jäger, L. (2001). *Acta Cryst.* **C57**, 363–365.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (1999). *IPDS*. Version 2.90. Stoe & Cie, Darmstadt, Germany.
- Sun, B.-W., Gao, S., Ma, B.-Q. & Wang, Z.-M. (2001). *Inorg. Chem. Commun.* **4**, 72–75.
- Vangdal, B., Carranza, J., Lloret, F., Julve, M. & Sletten, J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 566–574.