Low-dimensional compounds containing cyano groups. XII.[1] Bis(1,3-diaminopropane-$\kappa^2 N,N'$)-(dicyanamido-κN^1)copper(II) perchlorate

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The title compound, $[Cu(C_2N_3)(C_3H_{10}N_2)_2]ClO_4$, is made up of $[Cu(tn)_2\{N(CN)_2\}]^+$ complex cations (tn is 1,3-diaminopropane) and ClO_4^- anions. The Cu^{II} atom is coordinated by four N atoms of two equatorial tn ligands, with an average distance of 2.041 (7) Å, and one nitrile N atom of the dicyanamide anion in an axial position, at a distance of 2.236 (3) Å, in a manner approaching square-planar coordination geometry. The complex has C_s symmetry, with the mirror plane lying through the central C atoms of both tn ligands and the dca ligand. The ClO_4^- anion might be considered as very weakly coordinated in the opposite axial position [Cu—O = 2.705 (3) Å], thus completing the Cu^{II} coordination to asymmetric elongated octahedral (4+1+1*). The Cu atom and the perchlorate anion both lie on mirror planes.

Comment

Understanding the shape of coordination polyhedra (SCP) in the case of five-coordination is a current problem in coordination chemistry. A number of different structural approaches have been used in the past to describe the geometries of five-coordinated compounds (Potočňák *et al.*, 2001). With the aim of finding out possible reasons for different SCP in related compounds, we have previously studied the structures of five-coordinate Cu^{II} coordination compounds of the general formula $[Cu(L)_2X]Y$, where L is a bidentate chelate ligand, such as 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy), X is an N-donor pseudohalide anion and Y is the tricyanomethanide anion, $[C(CN)_3]^-$ (Potočňák *et al.*, 2001). In more recent work, we have changed our focus from compounds with

the same counter-anion to compounds with the same coordinated anionic ligand, having the general formula $[Cu(dca)(L)_2]Y$, where dca is the dicyanamide anion $[N(CN)_2]^-$ and Y is an anion of charge 1−. The SCP in these compounds, as well as that in compounds with the $[C(CN)_3]^-$ counter-anion, is more or less distorted trigonal–bipyramidal,

(I)
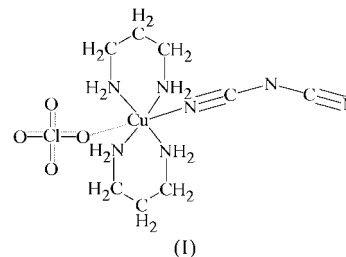
but we have observed that the SCP in compounds with bpy molecules is more distorted than in compounds with phen molecules. We postulate that the reason could be a different rigidity between the highly rigid phen and the less rigid bpy ligand. While the two outer pyridine rings in a phen molecule are connected by a benzene ring, making the whole molecule planar, the two pyridine rings in a bpy molecule can rotate around their common C—C single bond. To verify this idea, we have decided to use even more flexible ligands L than bpy, namely aliphatic diamines, such as ethylenediamine, 1,2-diaminopropane or 1,3-diaminopropane (tn), in the desired $[Cu(dca)(L)_2]Y$ compounds. To avoid the possible effect of anion Y on the SCP, we have used the same anion in our study, in this case a perchlorate anion. To date, we have succeeded in the preparation of the title compound with tn, $[Cu(dca)(tn)_2]ClO_4$, (I), the structure of which is presented here and compared with the previously prepared $[Cu(dca)(L)_2]ClO_4$ compounds containing bpy [(II)] or phen ligands [(III)].

Fig. 1 shows the structure and atom-labelling scheme of one formula unit of (I). The Cu atom is mainly coordinated by two
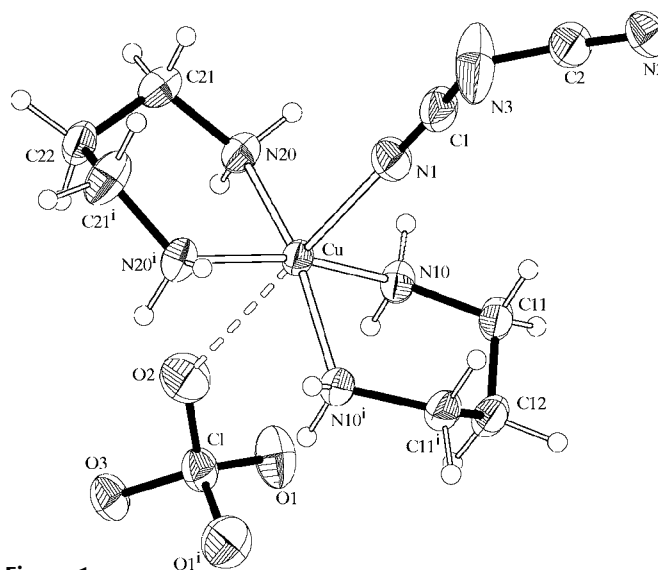

Figure 1
The structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) x, $\frac{1}{2} - y$, z.]

[1] Part XI: Potočňák, Burčák, Baran & Jäger (2005).

chelate-like bound tn molecules and by one terminal N atom of the dca ligand (Table 1). The complex has C_s symmetry, with the mirror plane lying through the central C atoms of both tn ligands and the dca ligand. The four N atoms of the tn ligands are thus coplanar by symmetry and form the base of a distorted square pyramid [average Cu—N = 2.041 (7) Å]. Owing to the Jahn–Teller effect, the axial bond to the dca ligand is elongated [2.236 (3) Å].

Using the criteria of Harrison & Hathaway (1980), the angles N1—Cu—N20, N1—Cu—N10[i] and N20—Cu—N10[i] [symmetry code: (i) $x, \frac{1}{2} - y, z$] can be labelled α_1, α_2 and α_3, respectively (Table 2). The large angle α_3, which is opposite to the Cu—N1 bond (N1 from dca), and the small difference of 0.35° between α_1 and α_2, clearly classify the coordination polyhedron around the Cu[II] atom as square pyramidal. The same result is obtained, of course, when using the τ parameter of Addison *et al.* (1984) as a criterion, which is zero by symmetry in (I) (the τ parameter is 100 for an ideal trigonal bipyramid and 0 for an ideal tetragonal pyramid). Table 2 also lists the values of selected bond distances and angles, and the τ parameters for compounds (II) and (III). One can see from this table that the SCP gradually changes from distorted square pyramidal in (I) through intermediate in (II) to distorted trigonal bipyramidal in (III). This may be seen as a confirmation of our hypothesis on the dependence of the SCP on the different rigidity of the chelate *L* ligands used.

The very weakly coordinated ClO_4^- anion [Cu—O = 2.705 (3) Å] supplements the coordination sphere of the Cu[II] atom to an asymmetrically elongated octahedron (4+1+1*). Atoms Cl, O2 and O3 lie on the same mirror plane as the Cu[II] atom and the dca anion. Although the displacement ellipsoids of the O atoms are larger than the ellipsoids for other atoms, they are not disordered. The Cu[II] atom is displaced by 0.2556 (2) Å from the equatorial plane towards atom N1. To the best of our knowledge, only eight structures of copper(II) compounds with a comparable CuN_5O chromophore containing coordinated perchlorate anions are known to date (Cambridge Structural Database, Version 5.26, update of February 2005; Allen, 2002). The Cu—O$_{axial}$ and Cu—N$_{axial}$

bond distances in these compounds are in the ranges 2.383 (3)–2.732 (3) [mean 2.59 (11) Å] and 2.323 (3)–2.842 (61) Å [mean 2.51 (18) Å], respectively, which are close to the corresponding bond distances in (I). In contrast with (I), the maximum deviation of the Cu atoms from the equatorial plane in these compounds is only 0.088 (2) Å (Lee *et al.*, 1997) and, moreover, the Cu—N and Cu—O bond distances are much more symmetric than in (I). In the title compound, (I), the perchlorate anion is thus the weakest coordinated moiety and the coordination mode of the Cu[II] atom is much closer to a deformed square pyramid than a distorted octahedron.

According to the definition of Zelewsky (1995), both tn molecules in (I) are in chair forms, as also observed in other copper compounds with two tn molecules [*e.g.* Wang *et al.* (2002) and Thetiot *et al.* (2003)]. The bond distances in both molecules are normal for single C—C and C—N bonds, while the C—C—C and C—C—N angles adopt slightly higher values than tetrahedral.

There are three canonical formulae describing the bonding mode in the dicyanamide ligand (Golub *et al.*, 1986). Inspection of the bond lengths in (I) (Table 1) shows that the third canonical formula, with single and triple C—N bonds only, can be used for a proper description of the bonding mode in this particular case. Both cyano N≡C bonds (C1≡N1 and C2≡N2) are normal for an N≡C triple bond and both amide N—C distances (N3—C1 and N3—C2) are only slightly shorter than a single bond between an N atom and an *sp*-hybridized C atom (Jolly, 1991). The N1—C1—N3 and N3—C2—N2 angles are slightly bent from linearity, while the value of the C1—N3—C2 angle is close to the expected value of 120°. Nevertheless, the reliability of the geometric parameters involving atoms N3, C1 and C2 may be reduced by the observed disorder over two positions related by the mirror plane [the distances from this plane are 0.43 (1), 0.20 (1) and 0.21 (1) Å, respectively]. In accordance with Golub *et al.* (1986), the bonding mode of dicyanamide to the Cu[II] atom can be considered as almost linear [C1—N1—Cu = 169.9 (4)°].

Besides ionic forces, the crystal structure of (I) is stabilized by weak N—H⋯*X* hydrogen bonds (*X* is O or N); those with an N—H⋯*X* angle greater than 120° and an H⋯*X* distance less than 2.6 Å are given in Table 3. Two of them, N10—H10*A*⋯O1 and its symmetry equivalent, are 'intramolecular' in the sense that the hydrogen bonds connect cation and anion within the asymmetric part of the structure. The others are intermolecular. The non-coordinated atom N2 of the dicyanamide ligand acts as fourfold acceptor for N—H⋯N hydrogen bonds. Through these intermolecular bonds, cations and anions are interconnected to form sheets along the (101) plane, as shown in Fig. 2.

Figure 2
Hydrogen bonds (dashed lines) connecting the cations and anions of (I) into layers parallel to (101). [Symmetry codes: (ii) $-x, -y, 2 - z$; (iii) $-x, y - \frac{1}{2}, 2 - z$; (iv) $1 - x, y - \frac{1}{2}, 1 - z$.]

Experimental

Crystals of (I) were prepared by mixing a 0.1 *M* aqueous solution of $Cu(ClO_4)_2$ (5 ml) with a 0.1 *M* aqueous solution of $Na[N(CN)_2]$ (10 ml). To the resulting solution, a 1 *M* aqueous solution of tn (1 ml) was added (all solutions were warmed before mixing). Blue crystals of the title complex appeared in two weeks. The crystals were filtered off and dried in air.
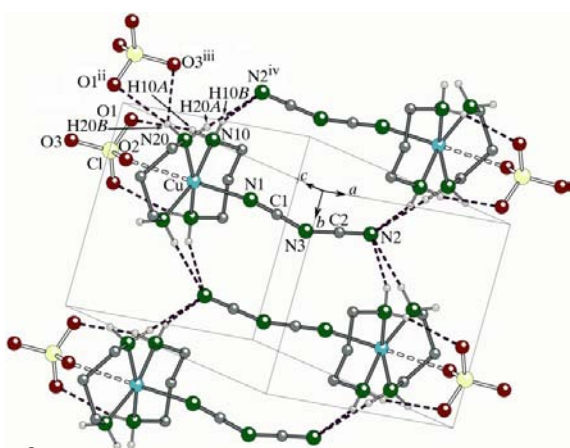
Crystal data

[Cu(C$_2$N$_3$)(C$_3$H$_{10}$N$_2$)$_2$]ClO$_4$
$M_r = 377.30$
Monoclinic, $P2_1/m$
$a = 8.4715 (17)$ Å
$b = 7.5679 (15)$ Å
$c = 11.953 (2)$ Å
$\beta = 92.56 (3)°$
$V = 765.5 (3)$ Å^3
$Z = 2$

$D_x = 1.637$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9435
    reflections
$\theta = 1.7–29.4°$
$\mu = 1.63$ mm^{-1}
$T = 193 (2)$ K
Platelet, blue
$0.24 \times 0.22 \times 0.06$ mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: numerical
    (*XPREP* in *SHELXTL*;
    Sheldrick, 1997*b*)
    $T_{min} = 0.722$, $T_{max} = 0.900$
9279 measured reflections

2268 independent reflections
2018 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 29.5°$
$h = -11 \rightarrow 11$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.109$
$S = 1.03$
2268 reflections
122 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 0.3495P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}
Extinction correction: *SHELXL97*
    (Sheldrick, 1997*a*)
Extinction coefficient: 0.030 (6)

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

Cu—N20	2.0349 (19)	C1—N1	1.139 (5)
Cu—N10	2.0468 (18)	C1—N3	1.280 (6)
Cu—N1	2.236 (3)	N3—C2	1.272 (6)
Cu—O2	2.705 (3)	C2—N2	1.157 (5)
N20—Cu—N20^v	93.91 (12)	N10—Cu—O2	82.76 (7)
N20—Cu—N10^v	165.49 (8)	N1—Cu—O2	179.70 (10)
N20—Cu—N10	86.06 (8)	N1—C1—N3	173.9 (5)
N10^v—Cu—N10	90.37 (11)	C1—N1—Cu	169.9 (4)
N20—Cu—N1	97.37 (8)	C2—N3—C1	128.3 (5)
N10—Cu—N1	97.02 (8)	N2—C2—N3	173.0 (5)
N20—Cu—O2	82.84 (8)		

Symmetry code: (v) $x, \frac{1}{2} - y, z$.

Table 2
A comparison of molecular geometry parameters (Å, °) for some [Cu(*L*)$_2$(dca)]$^+$ species.

Parameter^a	(I)	(II)	(III)
Cu—N10	2.0468 (18)	2.0024 (17)	2.001 (5)
Cu—N30		1.9916 (17)	1.996 (5)
Cu—N20	2.0349 (19)	2.1456 (19)	2.087 (5)
Cu—N40		2.0395 (19)	2.086 (4)
Cu—N1	2.236 (3)	1.995 (2)	2.033 (6)
N10—Cu—N30	165.5 (8)	177.16 (9)	179.14 (19)
α_1	97.37 (8)	146.66 (8)	118.41 (19)
α_2	97.02 (8)	108.46 (8)	115.19 (1)
α_3	165.49 (8)	104.87 (8)	126.40 (1)
τ	0.0	50.8	87.9

Notes: (I) is [Cu(dca)(tn)$_2$]ClO$_4$ (this work); (II) is [Cu(dca)(bpy)$_2$]ClO$_4$ (Potočňák *et al.*, 2002); (III) is [Cu(dca)(phen)$_2$]ClO$_4$ (Burčák *et al.*, 2004); (*a*) numbering schemes have been standardized as for (II).

Table 3
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N10—H10$A\cdots$O1	0.92	2.45	3.352 (3)	166
N10—H10$B\cdots$N2^{iii}	0.92	2.33	3.198 (3)	158
N20—H20$B\cdots$O1^i	0.92	2.39	3.292 (3)	166
N20—H20$B\cdots$O3^{ii}	0.92	2.42	3.117 (3)	132
N20—H20$A\cdots$N2^{iii}	0.92	2.38	3.261 (3)	161

Symmetry codes: (i) $-x, -y, 2 - z$; (ii) $-x, y - \frac{1}{2}, 2 - z$; (iii) $1 - x, y - \frac{1}{2}, 1 - z$.

All H-atom positions were calculated using the appropriate riding model, with C—H distances of 0.99 Å and N—H distances of 0.92 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$. Geometric analysis was performed using *PARST* (Nardelli, 1983) and *SHELXL97* (Sheldrick, 1997*a*).

Data collection: *WinXPOSE* in *X-AREA* (Stoe & Cie, 2002); cell refinement: *RECIPE* in *X-AREA*; data reduction: *INTEGRATE* in *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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