metal-organic compounds

The one-dimensional structure of Cu(dmen)₂Pd(CN)₄ (dmen is N,N-dimethylethylenediamine)

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The title compound, *catena*-poly[[μ-cyano-1:2$\kappa^2 C$:N-dicyano-1$\kappa^2 C$-bis(N,N-dimethylethylenediamine-2$\kappa^2 N,N'$)-palladium(II)copper(II)]-μ-cyano-1:2'$\kappa^2 C$:N], [CuPd(CN)₄(C₄H₁₂N₂)₂]$_n$, consists of infinite quasi-linear chains with all metal positions on centers of symmetry. The paramagnetic [Cu(dmen)₂]²⁺ cations are linked by diamagnetic [Pd(CN)₄]²⁻ anions *via* bridging cyano groups, which occupy *trans* positions in both cation and anion, giving rise to 2,2-*TT*-type chains. The coordination polyhedron of the paramagnetic Cu atom is an octahedron exhibiting typical elongation due to the Jahn–Teller effect, with two longer Cu—N(≡C) bonds in the axial positions [2.5528 (13) Å] and four shorter Cu—N$_{dmen}$ bonds (dmen is N,N-dimethylethylenediamine) in the equatorial plane [1.9926 (11) and 2.1149 (12) Å]. The Cu—N≡C angle is 138.03 (12)°. Neighboring chains form weak N—H···NC hydrogen bonds.

Comment

Low-temperature magnetic and thermodynamic studies of Cu(en)₂Ni(CN)₄ (CENC; en is ethylenediamine) indicate that this compound behaves as a two-dimensional magnet (Orendáč *et al.*, 1995). From a structural point of view, this compound is one-dimensional: 2,2-*TT* chains [for the nomenclature, see Černák *et al.* (2002)] are built up of [Cu(en)₂]²⁺ cations and [Ni(CN)₄]²⁻ anions linked by bridging cyano groups in *trans* positions in both the cation and the anion. Several studies indicate that hydrogen bonds can mediate magnetic exchange interactions (Goodson *et al.*, 1994; Zhang *et al.*, 1997; Kopinga *et al.*, 1982). It is suggested that in the case of CENC, N—H···N hydrogen bonds may serve as paths of magnetic exchange interactions and thus may be responsible for the enhanced magnetic dimensionality of this material. In order to modify the hydrogen-bonding scheme in CENC and thus obtain a better insight into the magnetostructural correlation in this class of compounds, Cu(L$_n$)₂-Ni(CN)₄, where L$_n$ is N,N-dimethylethylenediamine (dmen),

N-methylethylenediamine and N,N'-dimethylethylenediamine, were prepared and structurally characterized (Kuchár *et al.*, 2003). Afterwards, the Ni[II] atom was replaced by Pd[II] in all of the above-mentioned compounds. The structure and magnetic properties of Cu(en)₂Pd(CN)₂ (CEPC) are described in Černák *et al.* (2001), and the preparation, identification and crystal structure of Cu(dmen)₂Pd(CN)₄ (CDPC) are reported here.
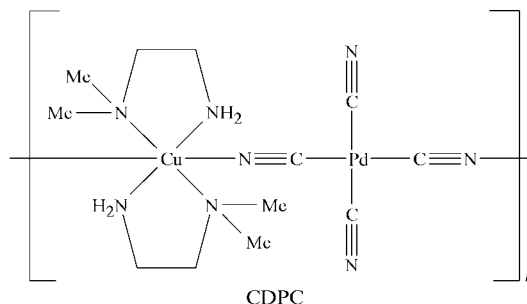
CDPC

The structure of CDPC has 2,2-*TT*-type chains of composition [–Cu(dmen)₂–NC–Pd(CN)₂–CN–]$_n$ (Fig. 1), and thus this compound is isostructural with the parent CDNC compound and analogous to CENC. The Cu-atom coordination sphere displays the usual axial deformation due to the Jahn–Teller effect, with longer axial bonds (Table 1). The dmen molecule is coordinated as an N-donor chelating ligand. Among the two independent Cu—N$_{dmen}$ coordination bonds, the Cu—N1 bond is significantly shorter than the Cu—N2 bond; this difference may be a consequence of the steric effect of the bulky methyl groups bonded to atom N2. The same difference was observed in Cu(dmen)Cu(CN)₃ (Colacio *et al.*, 2002) and the analogous CDNC compounds (Kuchár *et al.*, 2003). The corresponding values in CENC are 1.998 (1) and 2.001 (1) Å, respectively (Seitz *et al.*, 2001). The Ni atom in the anion lies on a symmetry center, so the NiC₄ chromophore is exactly planar. Among the four cyano groups, two in *trans* positions exhibit bridging character. The Cu—N4≡C6 angle is less bent than the corresponding angle in CENC [123.1 (1)°].
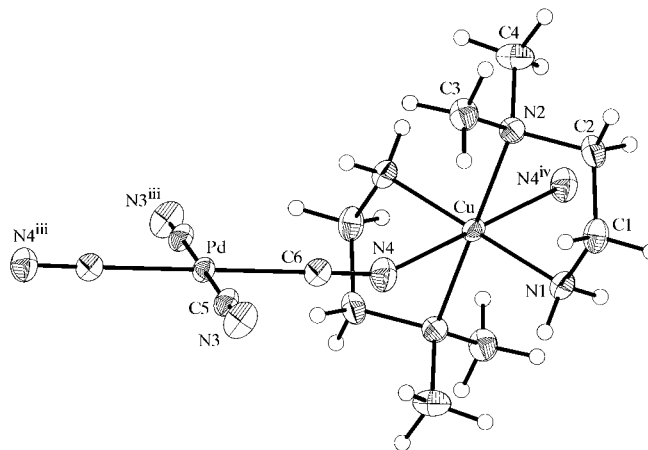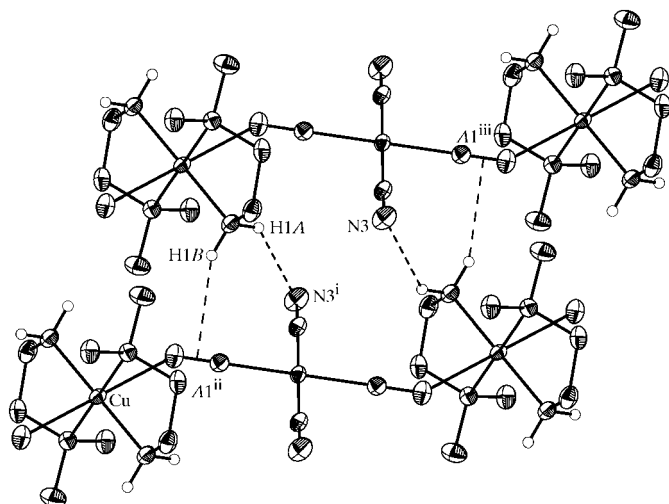

Figure 1
A view of the 2,2-*TT*-type chain of CDPC, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (iii) $-x$, $1-y$, $-z$; (iv) $1-x$, $1-y$, $1-z$.]

Figure 2
A view of the structure of CDPC, showing the hydrogen-bonding system. [Symmetry codes: (i) $1 - x$, $1 - y$, $-z$; (ii) $1 + x$, y, z; (iii) $-x$, $1 - y$, $-z$.]

The title compound differs from CENC in that two H atoms in CENC are replaced by methyl groups in CDPC, and therefore only two H atoms can be involved in hydrogen bonds (Table 2). In CDPC, atom H1A forms a weak hydrogen bond to atom N3 of the terminal cyano group of a neighboring chain (Fig. 2). The observed (N—)H⋯N distance (2.60 Å) is longer than the analogous distance in CENC (2.32 Å) and comparable to that in CDNC (2.57 Å), suggesting weaker hydrogen-bonding interactions in CDPC and CDNC than in CENC. The second H atom (H1B) is oriented almost perpendicular (the N—H⋯A1 angle, where A1 is the mid-point of the C6≡N4 cyano group, is 156°) with respect to the bridging cyano group of the same neighboring chain at ($1 - x$, y, z), suggesting a weak interaction with the π molecular orbital of the cyano group. This distance (2.67 Å) is at the limit of such interactions (Saenger & Jeffrey, 1991). The distance between the H atom and atom N4 at ($1 - x$, y, z) is 2.75 Å, but the N atom coordinates weakly to the Cu atom, and thus the C6≡N4 cyano group can be considered to be a bridging ligand. The next shortest distance is that between atom C5 and atom C3 at ($1 + x$, $1 - y$, $1 + z$) from a neighboring chain [3.572 (2) Å]; this contact may correspond only to a van der Waals interaction.

Experimental

A solution formed by mixing a 0.1 *M* warm aqueous solution of CuSO$_4$ (10 ml, 1 mmol) and dmen (0.22 ml, 2 mmol) in methanol (10 ml) and water (10 ml) was mixed with a 0.1 *M* warm aqueous solution of K$_2$[Pd(CN)$_4$] (10 ml, 1 mmol). The resulting precipitate was dissolved by addition of a concentrated aqueous solution of ammonia (25%). Finally, the solution was filtered and left to stand at room temperature (291 K). The first single crystals appeared as blue plates after a day. IR, ν(NH): 3337 (*s*), 3272 (*vs*); ν(CH): 2988, 2903 (*w*), 2851 (*w*); ν(CN): 2128 (*vs*); δ(NH$_2$): 1584 (*s*); δ(Pd–CN): 379 (*s*). Analysis found: C 32.42, H 5.43, N 25.08%; calculated: C 32.01, H 5.37, N 24.88%.

Crystal data

[CuPd(CN)$_4$(C$_4$H$_{12}$N$_2$)$_2$]
$M_r = 450.33$
Monoclinic, $P2_1/n$
$a = 6.6940$ (3) Å
$b = 13.8197$ (7) Å
$c = 9.1759$ (5) Å
$\beta = 97.609$ (1)°
$V = 841.38$ (7) Å^3
$Z = 2$
$D_x = 1.778$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 53 reflections
$\theta = 2.0$–28.0°
$\mu = 2.34$ mm^{-1}
$T = 173$ (2) K
Plates, blue
$0.32 \times 0.24 \times 0.02$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: by integration based on measured indexed crystal faces (*SHELXTL*; Bruker, 1998)
$T_{min} = 0.515$, $T_{max} = 0.954$

7247 measured reflections
1926 independent reflections
1624 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 27.5°$
$h = -8 \rightarrow 8$
$k = -17 \rightarrow 17$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.041$
$S = 1.10$
1916 reflections
105 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 0.2936P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—C6	1.9905 (15)	N2—C4	1.4809 (19)
Pd—C5	2.0008 (15)	N2—C2	1.4888 (18)
Cu—N1	1.9926 (11)	N1—C1	1.4755 (19)
Cu—N2	2.1149 (12)	N4—C6	1.1465 (19)
Cu—N4	2.5528 (13)	C5—N3	1.1459 (19)
N2—C3	1.4805 (18)	C1—C2	1.508 (2)
C6—Pd—C5	90.03 (6)	C6—N4—Cu	138.03 (12)
N1—Cu—N2	85.33 (5)	N4—C6—Pd	178.74 (13)
N1—Cu—N4	90.55 (5)	N3—C5—Pd	178.83 (14)
N2—Cu—N4	87.02 (4)		

Table 2
Hydrogen-bonding geometry (Å, °).

*A*1 is the mid-point of the bridging C6≡N4 cyano group of a neighboring chain.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯N3^i	0.92	2.60	3.3482 (18)	139
N1—H1B⋯A1^{ii}	0.92	2.67	3.533 (2)	156

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 + x, y, z$.

H atoms were placed in idealized positions and treated as riding on their parent atoms, with C—H distances of 0.98–0.99 Å and N—H distances of 0.92 Å. The U_{iso}(H) values were set at $1.2U_{eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 2001); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1492). Services for accessing these data are described at the back of the journal.

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