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The one-dimensional chain structure of [Cu(en)$_2$Pt(CN)$_4$] (en is ethylenediamine)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
R factor = 0.022
wR factor = 0.055
Data-to-parameter ratio = 18.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, *catena*-poly[di-μ-cyano-1:2$\kappa^2 C$:N;-1:2'$\kappa^2 C$:N-dicyano-1-$\kappa^2 C$-bis(ethylenediamine-2$\kappa^2 N,N'$)platinum(II)copper(II)], [CuPt(CN)$_4$(C$_2$H$_8$N$_2$)$_2$]$_n$, (I), consists of one-dimensional chains running along the [111] direction. Both Cu and Pt atoms are located on centres of symmetry in an alternating array of [Cu(en)$_2$]$^{2+}$ (en is ethylenediamine) and [Pt(CN)$_4$]$^{2-}$ units. The Pt—C coordination bond distances of 1.985 (4) and 1.995 (4) Å are longer than those of an analogous Ni^{II} complex. Moreover, due to Jahn–Teller distortion, the axial Cu—N bond distance of 2.562 (5) Å is longer than the equatorial ones of 2.014 (4) and 2.017 (4) Å.

Comment

Cyanide-bridged coordination polymers have received much attention because of their wide application in the fields of molecule-based magnets (Ohba & Okawa, 2000; Okawa & Ohba 2002), photo-functional compounds (Sato, 2003; Sato *et al.*, 2003) and other advanced functional materials. Escax *et al.* (2005) have focused on the importance that (three-dimensional) structural strain of the lattice weakens the ligand field strength of cyanide ligands in the photo-induced magnetization of Fe–Co Prussian blue analogues. Therefore, so-called Jahn–Teller switching (Falvello, 1997) may be a promising new strategy for the switching of electronic states in cyanide-bridged coordination polymers. Indeed, we have observed a photo-induced and thermally accessible structural change in [Cu(en)$_2$](ClO$_4$)$_2$ (en is ethylenediamine; Akitsu & Einaga, 2003). We have also recently reported the first chiral trinuclear Mn^{III}–Ni^{II}–Mn^{III} cyano-bridged complex exhibiting a thermally accessible structural change (Akitsu *et al.*, 2005). Moreover, numerous coordination polymers, such as one-dimensional Cu^{II}–Ni(CN)$_4$ (Kuchár *et al.*, 2003), Cd^{II}–Ni(CN)$_4$ (Petříček *et al.*, 2005), Cu^{II}–Pd(CN)$_4$ (Kuchár *et al.*, 2004) and Cu^{II}–Ag$_2$(CN)$_3$ (Černák, Chomič, Gravereau *et al.*, 1998), and two-dimensional Cu^{I}/Cu^{II}–Ni(CN)$_4$ (Černák & Abboud, 2002), have been designed in recent years. Interestingly, among these it has been reported that Ni(en)$_2$M(CN)$_4$ compounds afford slightly elongated or compressed octahedral coordination geometries for M = Ni^{II} or Pd^{II}, respectively (Černák *et al.*, 1988). In order to compare the isostructural complexes [Cu(en)$_2$][Ni(CN)$_4$] (Lokaj *et al.*, 1991) and [Cu(en)$_2$][Pd(CN)$_4$] (Černák *et al.*, 2001) by element substitution, we report here the crystal structure of the title compound, (I), [Cu(en)$_2$][Pt(CN)$_4$].

Compound (I) consists of one-dimensional chains running along the [111] direction. The unit-cell volume of (I) [353.9 (4) Å^3] is larger than that of the corresponding Pd^{II} [347.63 (6) Å^3; Černák *et al.*, 2001] and Ni^{II} [333.9 (9) Å^3;

Lokaj *et al.*, 1991] complexes, mainly due to the larger ionic radius of the Pt[II] ion. Both Cu and Pt atoms are located on centres of symmetry in an alternating array of $[Cu(en)_2]^{2+}$ and $[Pt(CN)_4]^{2-}$ units (Fig. 1). In the latter units, the bridging cyano groups are in *trans* positions. The Pt—C bond distances (Table 1) are longer than those of the analogous Pd[II] or Ni[II] complexes but comparable with those for non-bridging cyano groups in the dinuclear heterometallic complex $[(CN)_3Pt(\mu\text{-}CN)Cu(NH_3)_4]$ (Escorihuela *et al.*, 2001). The C≡N bond distances of the cyano groups of 1.149 (6) (bridging) and 1.143 (6) Å (non-bridging) are similar to normal values in $[Pt(CN)_4]^{2-}$ units (Knoeppel & Shore, 1996). The significantly bent Cu1—N2—C2 bond angle of 121.6 (4)° suggests ionic character for the Cu—N bond.

(I)
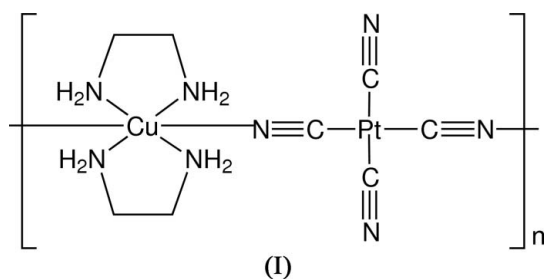
Jahn–Teller distortion results in the axial Cu—N bond distance being longer than the equatorial ones (Table 1). The axial Cu1–N2 bond length of 2.562 (5) Å in (I) is longer than those in the analogous Pd[II] [2.544 (2) Å; Černák *et al.*, 2001] and Ni[II] complexes [2.533 (4) Å; Lokaj *et al.*, 1991]. The degree of tetragonal Jahn–Teller distortion of the Cu[II] sites in (I) is $T = 0.787$ (T is the ratio of in-plane Cu—N bond lengths to axial Cu—N bond lengths; Hathaway & Billing, 1970). The T values for the mononuclear complex $[Cu(en)_2](ClO_4)_2$ are 0.780, 0.785 and 0.791 at 297, 274 and 120 K, respectively (Akitsu & Einaga, 2003).
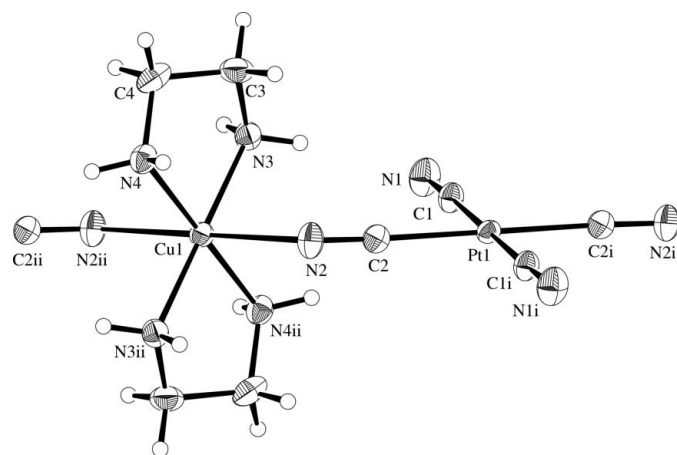
Figure 1
A segment of the polymeric structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) −x, −y, −z; (ii) 1 − x, 1 − y, 1 − z.]

In the crystal structure of (I), there are N—H⋯N hydrogen bonds (Table 2), although some H⋯N distances are longer than normal values.

Experimental

The precursor complex, $[Cu(en)_2](ClO_4)_2$, was obtained from a methanol solution (10 ml) of a mixture of $Cu(ClO_4)_2\cdot6H_2O$ (0.375 g, 1.00 mmol) and ethylenediamine (0.120 g, 2.00 mmol) as a blue precipitate which formed immediately at 293 K (yield 0.205 g, 53.5%). Compound (I) was obtained by slow diffusion of a methanol solution (10 ml) of $[Cu(en)_2](ClO_4)_2$ (24.4 mg, 0.0640 mmol) into an aqueous solution (5 ml) of $K_2[Pt(CN)_4]$ (27.5 mg, 0.0640 mmol) at 293 K. After several days, blue single crystals of (I) were obtained from the surface (yield: 3.90 mg, 9.7%). Analysis calculated for $C_8H_{16}CuN_8Pt$: C 19.90, H 3.34, N 23.20%; found: C 20.14, H 3.25, N 23.44%. Electronic spectrum (diffuse reflectance): 18200 cm^{-1} [$F(R_d)$ 2.56] (*d–d* transition of Cu[II] ion). Weiss constant = −2.73 K (antiferromagnetic interaction). IR (KBr) 2122 cm^{-1} (cyanide).

Crystal data

$[CuPt(CN)_4(C_2H_8N_2)_2]$	$Z = 1$
$M_r = 482.92$	$D_x = 2.266$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.560$ (4) Å	Cell parameters from 25
$b = 7.350$ (5) Å	reflections
$c = 8.068$ (3) Å	$\theta = 10.0–13.9°$
$\alpha = 107.27$ (4)°	$\mu = 11.37$ mm^{-1}
$\beta = 90.92$ (4)°	$T = 298$ (2) K
$\gamma = 106.54$ (6)°	Prism, blue
$V = 353.9$ (4) Å^3	$0.30 \times 0.20 \times 0.20$ mm

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.044$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = −8 \rightarrow 8$
(North *et al.*, 1968)	$k = −9 \rightarrow 3$
$T_{min} = 0.060$, $T_{max} = 0.103$	$l = −10 \rightarrow 10$
1844 measured reflections	3 standard reflections
1630 independent reflections	every 150 reflections
1628 reflections with $I > 2\sigma(I)$	intensity decay: 1.4%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.022$	$+ 0.0221P]$
$wR(F^2) = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
1628 reflections	$\Delta\rho_{max} = 1.05$ e Å^{-3}
86 parameters	$\Delta\rho_{min} = -2.32$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	(Sheldrick, 1997)
	Extinction coefficient: 0.241 (8)

Table 1
Selected geometric parameters (Å, °).

Pt1—C2	1.985 (4)	Cu1—N2	2.562 (5)
Pt1—C1	1.995 (4)	N1—C1	1.143 (6)
Cu1—N3	2.014 (4)	N2—C2	1.149 (6)
Cu1—N4	2.017 (4)		
C2—Pt1—C1	88.08 (17)	Cu1—N2—C2	121.6 (4)
N3—Cu1—N4	84.40 (17)	N1—C1—Pt1	175.6 (4)
N2—Cu1—N3	91.69 (16)	N2—C2—Pt1	177.1 (4)
N2—Cu1—N4	87.69 (17)		

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N3—H3$C\cdots$N1	0.90	2.37	3.247 (5)	166
N3—H3$D\cdots$N1^{iii}	0.90	2.33	3.145 (7)	150
N3—H3$D\cdots$N2^{ii}	0.90	2.84	3.212 (5)	107
N4—H4$D\cdots$N2	0.90	2.84	3.196 (5)	105

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

H atoms were placed in calculated positions, with C—H = 0.97 Å and N—H = 0.90 Å, and included in the final cycles of refinement using riding constraints, with U_{iso}(H) = 1.2U_{eq}(C,N). The highest peak and deepest hole are located 0.90 and 0.83 Å, respectively, from atom Pt1.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

References

Akitsu, T. & Einaga, Y. (2003). *Bull. Chem. Soc. Jpn*, **77**, 763–764.
Akitsu, T., Takeuchi, Y. & Einaga, Y. (2005). *Acta Cryst.* E**61**, m502–m505.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Černák, J. & Abboud, K. A. (2002). *Acta Cryst.* C**58**, m167–m170.
Černák, J., Chomič, J., Baloghová, D. & Dunaj-Jurčo, M. (1988). *Acta Cryst.* C**44**, 1902–1905.
Černák, J., Chomič, J., Gravereau, P., Orendáčová, A., Orendáč, M., Kováč, J., Feher, A. & Kappenstein, C. (1998). *Inorg. Chim. Acta*, **281**, 134–140.
Černák, J., Skoršepa, J., Abboud, K. A., Meisel, M. W., Orendáč, M., Orendáčová, A. & Feher, A. (2001). *Inorg. Chim. Acta*, **326**, 3–8.
Escax, V., Champion, G., Arrio, M.-A., Zacchigna, M., Cartier dit Moulin, C. & Bleuzen, A. (2005). *Angew. Chem. Int. Ed.* **44**, 4798–4801.
Escorihuela, I., Falvello, L. R. & Tomas, M. (2001). *Inorg. Chem.* **40**, 636–640.
Falvello, L. R. (1997). *J. Chem. Soc. Dalton Trans.* pp. 4463–4475.
Hathaway, B. J. & Billing, D. E. (1970). *Coord. Chem. Rev.* **5**, 143–207.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Knoeppel, D. W. & Shore, S. G. (1996). *Inorg. Chem.* **35**, 5328–5334.
Kuchár, J., Černák, J. & Abboud, K. A. (2004). *Acta Cryst.* C**60**, m492–m494.
Kuchár, J., Černák, J., Mayersová, Z., Kubáček, P. & Žák, Z. (2003). *Solid State Phenomena*, Vol. 90–91, *Solid State Chemistry V*, edited by P. Sajgalík, M. Drábik & S. Varga, pp. 323–328. Uetikon-Zurich: Trans Tech Publications Inc.
Lokaj, J., Gyerová, K., Sopková, A., Sivý, J., Kettmann, V. & Vrábel, V. (1991). *Acta Cryst.* C**47**, 2447–2448.
Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ohba, M. & Okawa, H. (2000). *Coord. Chem. Rev.* **198**, 313–328.
Okawa, H. & Ohba, M. (2002). *Bull. Chem. Soc. Jpn*, **75**, 1191–1203.
Petříček, V., Dušek, M. & Černák, J. (2005). *Acta Cryst.* B**61**, 280–286.
Rigaku (1999). *WinAFC Diffractometer Control Software*. Rigaku Corporation, Tokyo, Japan.
Sato, O. (2003). *Acc. Chem. Res.* **36**, 692–700.
Sato, O., Hayami, S., Einaga, Y. & Gu, Z.-Z. (2003). *Bull. Chem. Soc. Jpn*, **76**, 443–470.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.