Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(4,4′-bipyridinium) hexacyanoplatinate(IV) bis(4,4′-bipyridine)

John A. Schlueter,* Russell J. Funk and Urs Geiser

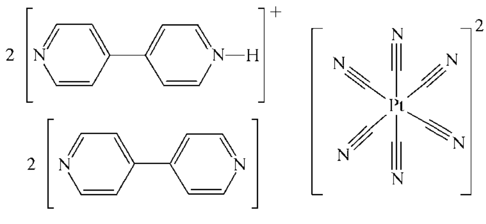
Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA
Correspondence e-mail: jaschlueter@anl.gov

Received 9 March 2005
Accepted 31 March 2005
Online 20 May 2005

In the title compound, $(C_{10}H_9N_2)_2[Pt(CN)_6]\cdot 2C_{10}H_8N_2$ or $[(Hbpy)^+]_2[Pt(CN)_6]^{2-}\cdot 2bpy$, where bpy is 4,4′-bipyridine, the $Hbpy^+$ cations and bpy molecules form a hydrogen-bonded two-dimensional cationic approximately square grid parallel to the (110) plane. The $[Pt(CN)_6]^{2-}$ dianions reside in the cavities within this grid, with the nitrile N atoms forming weak hydrogen bonds with the CH groups in the cationic lattice.

Comment

The 4,4′-bipyridine (bpy) ligand has commonly been used as a bidentate bridging ligand for the construction of both metal-organic frameworks (Noro *et al.*, 2000, 2002; Xu *et al.*, 2004) and hydrogen-bound networks (Sharma & Zaworotko, 1996). In the course of our efforts to prepare such frameworks, the title $(Hbpy)_2[Pt(CN)_6]\cdot 2bpy$ salt, (I), was obtained, and its crystal structure is described here.



(I)

Over 100 crystal structures containing bpy have been reported. The two amine positions allow for the formation of both the mono- ($Hbpy^+$) and the dication (H_2bpy^{2+}). Only nine crystal structures have been reported that contain both bpy and $Hbpy^+$. Four of these, with the formula $(Hbpy)[Ln(NO_3)_4(bpy)(H_2O)_2]$ (Ln = Nd, Pr, Ce and La), have a neutral bpy molecule coordinated to a lanthanide metal (Bukowska-Strzyzewska & Tosik, 1978; Al-Rasoul & Weakley, 1982; Sharma & Rogers, 1999). Similar to (I), four complexes have been reported to possess both uncoordinated neutral bpy and the $Hbpy^+$ monocation, *viz.* $(Hbpy)_2[Nd_2(NO_3)_8(bpy)(H_2O)_4]\cdot 3bpy$ (Weakley, 1984), $(Hbpy)_2(HQS)_2\cdot bpy\cdot 5H_2O$ (HQS is 8-hydroxyquinoline-5-sulfonate; Raj *et al.*, 2003), $[H_{0.72}(bpy)]^{0.72+}[(H_{0.5}O)_3PCH_2CH_2COOH_{0.78}]^{0.72-}$ (Bowes *et al.*, 2003) and $[Tm(pic)(H_2O)_6][Tm(pic)_2(H_2O)_4]_2(Hbpy)_2(pic)_6\cdot 5bpy$ (pic is picrate; Liang *et al.*, 2001). The remaining complex, $[Fe(SCN)_6][(Hbpy)(H_2bpy)(bpy)]$, reportedly contains all three of these species (Wei *et al.*, 2002).

The asymmetric unit of (I) contains two $Hbpy^+$ cations, one $[Pt(CN)_6]^{2-}$ dianion and two neutral bpy molecules. The atom-numbering scheme is shown in Fig. 1. The bond lengths (Table 1) in the bpy and $Hbpy^+$ species are essentially identical. The average ring-linking C—C bond length is 1.487 (4) Å, which is 0.11 Å longer than the average bond length observed for the ring C—C bonds, of 1.380 (6) Å. The average C—N bond length in bpy and $Hbpy^+$ is 1.325 (6) Å. For the non-protonated N atoms, the C—N—C angles range from 115.2 (3) to 117.7 (2)°, which is in good agreement with the average C═N—C angle observed in neutral bpy [115.6 (2)°; Boag *et al.*, 1999] and the average value reported in the Cambridge Structural Database (CSD; Version 5.24; Allen, 2002) for neutral bpy molecules (116.5°; Raj *et al.*, 2003). The protonated C═NH—C angles in (I) are both 120.2 (2)°, in agreement with the analogous angle in $(Hbpy)Br\cdot H_2O$ of 121.9 (2)° (Iyere *et al.*, 2002) and the average value of 121.5° reported for $Hbpy^+$ in the CSD (Raj *et al.*, 2003). The internal angles at the C atoms adjacent to N atoms are also affected by protonation of the amide. As the C—N—C angle is increased upon protonation, the average C—C—N angle is decreased from 123.9 (7) to 121.1 (2)° for C—C—NH. Similarly, but to a lesser extent, the angle about the C atom β to the N atom is increased upon protonation of the N atom, from 119.6 (3) to 120.3 (2)°. The C—C—C angle at the ring-connecting C atom is essentially identical in both

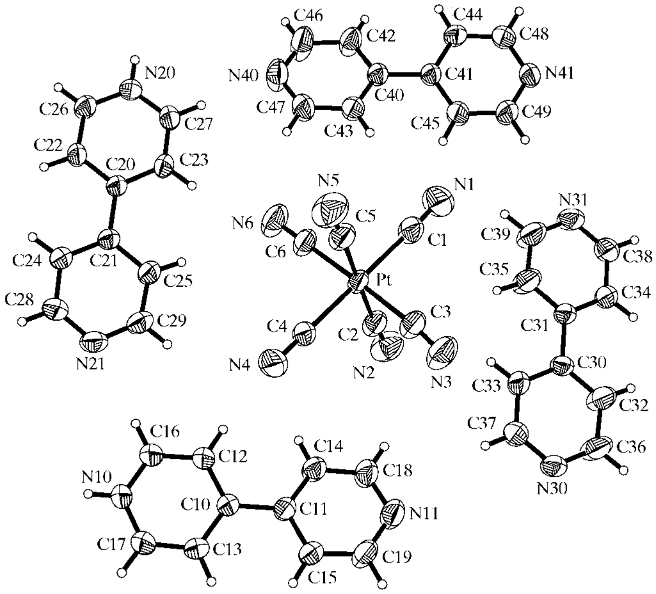


Figure 1
A view of the individual components of (I), showing the atom-numbering scheme; note that this is not a plot of the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

DOI: 10.1107/S0108270105010140

the protonated and the non-protonated rings, with an average value of 116.7 (3)°. All pyridyl rings are essentially planar, the greatest r.m.s. deviation from planarity (0.0076 Å) occurring for the ring associated with atom N30. The dihedral angles between the two pyridyl planes in (I) are 2.47 (13) and 15.22 (12)° for the bpy molecules, and 13.71 (10) and 9.82 (13)° for the Hbpy^+ cations. This dihedral angle is probably determined by crystal-packing forces. For example, in neutral bpy, the dihedral angles are 18.50 (12) and 34.85 (10)° (Boag *et al.*, 1999), and it is 29.6 (4)° in the monoprotonated $(\text{Hbpy})\text{Br}\cdot\text{H}_2\text{O}$ complex (Iyere *et al.*, 2002). Coplanar pyridyl rings have been observed for bpy in $[\text{Y(NO}_3)(\text{bpy})(\text{H}_2\text{O})_3]$ (Weakley, 1982) and for H_2bpy in $(\text{H}_2\text{bpy})(\text{ClO}_4)_2$ (Ng, 1999).

Only a handful of crystal structures containing the hexacyanoplatinate(IV) anion have been reported. The geometry of the $[\text{Pt(CN)}_6]^{2-}$ anion in (I) is essentially identical to the previously reported geometries in $[\text{Pt(CN)}_2(\text{dienH})][\text{Pt(CN)}_6]$ (dienH is 2,2′-diaminodiethylamine; Yanovskii *et al.*, 1984) and $[\text{Cd(tren)}][\text{Pt(CN)}_6]$ [tren is tris(2-aminoethyl)amine; Zhang *et al.*, 2002]. The Pt—C bond lengths, which range from 2.015 (3) to 2.026 (3) Å, and the C—N bond lengths, which average 1.133 (4) Å, are also nearly identical to those found in $[\text{Pt(CN)}_4]^{2-}$ (Ouahab *et al.*, 1989, 1993) and partially oxidized tetracyanoplatinates (Williams *et al.*, 1978; Johnson *et al.*, 1978).

As illustrated in Fig. 2, the crystal structure of (I) is characterized by two-dimensional grids of hydrogen-bound bpy and Hbpy^+ molecules that lie parallel to the (110) plane (Table 1). The bpy and Hbpy^+ molecules form a square network that is templated by the $[\text{Pt(CN)}_6]^{2-}$ anion. The strongest hydrogen bonding between the amine H atoms of the Hbpy^+ cations and the N atoms of the neutral bpy molecules leads to end-to-end dimers. Secondary hydrogen bonding occurs between the H atoms on the α-C atoms and the N atoms of bpy. Additional weak hydrogen bonding is present between the H atoms on the C atoms and the nitrile N atoms of the $[\text{Pt(CN)}_6]^{2-}$ anion. These weak hydrogen bonds organize orthogonal sets of dimers into a loose approximately square grid. The structure is also stabilized through many π–π interactions between adjacent pyridyl rings. The shortest of these have centroid–centroid distances in the range 3.56–3.86 Å.

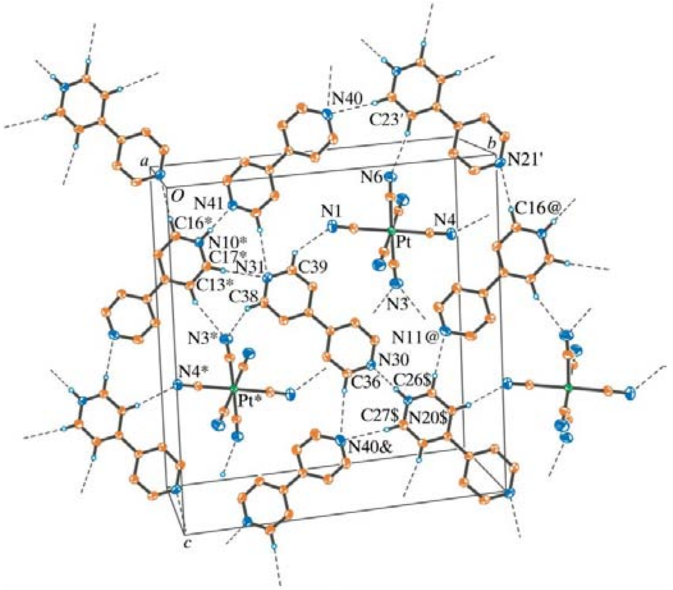


Figure 2
A packing diagram for (I), illustrating the two-dimensional approximately square network in the (110) plane. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are depicted as dashed lines. [Symmetry codes: (*) $1 + x, y, z$; (#) $2 - x, 1 - y, 1 - z$; ($) $1 - x, 1 - y, 1 - z$; (@) $x, 1 + y, z$; (′) $1 - x, 1 - y, -z$; (&) $x, y, 1 + z$.]

Experimental

Single crystals of (I) were prepared as a by-product of a solvothermal reaction designed to grow $\text{CuPt(CN)}_6(\text{bpy})_2$, which was expected to be analogous to $\text{CuSiF}_6(\text{bpy})$ (Noro *et al.*, 2000). Copper(II) tetrafluoroborate hydrate (1 mmol, 237 mg; Aldrich), potassium hexacyanoplatinate(IV) (1 mmol, 429 mg; Aldrich) and 4,4′-bipyridine (2 mmol, 312 mg; Aldrich) were placed in a 23 ml Teflon liner for a Parr acid digestion bomb along with ethanol (4 ml; Aaper) and water (6 ml). The bomb was sealed and heated at 413 K for 16 h. The temperature was then lowered at a rate of 10 K h^{-1}. Pale-pink crystals suitable for single-crystal X-ray diffraction were separated from a blue powder.

Crystal data

$(\text{C}_{10}\text{H}_9\text{N}_2)_2[\text{Pt(CN)}_6]\cdot 2\text{C}_{10}\text{H}_8\text{N}_2$
$M_r = 977.96$
Triclinic, $P\overline{1}$
$a = 7.4954\ (4)$ Å
$b = 16.3529\ (8)$ Å
$c = 16.9711\ (8)$ Å
$\alpha = 93.024\ (2)^\circ$
$\beta = 96.132\ (2)^\circ$
$\gamma = 90.623\ (2)^\circ$
$V = 2065.11\ (18)$ Å^3
$Z = 2$
$D_x = 1.573$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1792 reflections
$\theta = 2.4$–29.6°
$\mu = 3.45$ mm^{-1}
$T = 298\ (2)$ K
Rod, pink
0.44 × 0.18 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: integration (Sheldrick, 2001)
$T_{\min} = 0.287$, $T_{\max} = 0.636$
24 138 measured reflections
11 361 independent reflections
9009 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.025$
$\theta_{\max} = 29.6^\circ$
$h = -10 \rightarrow 10$
$k = -22 \rightarrow 22$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.065$
$S = 1.03$
11 361 reflections
550 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.1P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.070$
$\Delta\rho_{\max} = 0.84$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}

The acidic H atoms located on the amine N atoms of the Hbpy^+ cations were located in a Fourier difference map. The H atoms on the aromatic C atoms were positioned geometrically (C—H = 0.93 Å). All H atoms were refined with a riding model and with $U_{\text{iso}}(\text{H})$ values constrained to be 1.2 times U_{eq} of the carrier atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N20—H20···N30^{i}	0.86	1.80	2.665 (3)	178
N10—H10···N41^{ii}	0.86	1.82	2.683 (3)	178
C16—H16···N21^{iii}	0.93	2.42	3.347 (3)	175
C26—H26···N11^{iv}	0.93	2.44	3.372 (4)	176
C27—H27···N40^{v}	0.93	2.49	3.394 (4)	164
C17—H17···N31^{ii}	0.93	2.53	3.450 (4)	170
C49—H49···N31	0.93	2.54	3.458 (4)	168
C36—H36···N40^{vi}	0.93	2.62	3.538 (4)	171
C23—H23···N6^{v}	0.93	2.45	3.368 (4)	168
C22—H22···N4^{vii}	0.93	2.58	3.335 (4)	139
C13—H13···N3^{i}	0.93	2.61	3.483 (4)	157
C39—H39···N1	0.93	2.61	3.284 (5)	130
C38—H38···N3^{viii}	0.93	2.62	3.337 (4)	135

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y, -z$; (iv) $-x+1, -y, -z+1$; (v) $-x+1, -y+1, -z$; (vi) $x, y, z+1$; (vii) $x, y-1, z$; (viii) $-x+2, -y+1, -z+1$.

Work at Argonne National Laboratory is sponsored by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract No. W-31-109-ENG-38. RJF, an undergraduate student at the University of Chicago, is a participant in the US Department of Energy (DOE) Student Undergraduate Laboratory Research Internship (SULI) Program, sponsored by the Argonne Division of Educational Programs.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1000). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Al-Rasoul, K. & Weakley, T. J. R. (1982). *Inorg. Chim. Acta*, **60**, 191–196.
Boag, N. M., Coward, K. M., Jones, A. C., Pemble, M. E. & Thompson, J. R. (1999). *Acta Cryst.* C**55**, 672–674.
Bowes, K. F., Ferguson, G., Lough, A. J. & Glidewell, C. (2003). *Acta Cryst.* B**59**, 248–262.
Bruker (2001). *SAINT*. Version 6.28A. Bruker AXS Inc., Madison, Wisconsin, USA.
Bukowska-Strzyzewska, M. & Tosik, A. (1978). *Inorg. Chem. Acta*, **30**, 189–196.
Iyere, P. A., Boadi, W. Y., Brooks, R. S., Atwood, D. & Parkin, S. (2002). *Acta Cryst.* E**58**, o825–o827.
Johnson, P. J., Schultz, A. J., Underhill, A. E., Watkins, D. M., Wood, D. J. & Williams, J. M. (1978). *Inorg. Chem.* **17**, 839–844.
Liang, H., Liang, F.-P., Chen, Z.-L., Hu, R.-X. & Yu, K.-B. (2001). *J. Indian Chem. Soc.* **78**, 438.
Ng, S. W. (1999). *Acta Cryst.* C**55**, 2105–2107.
Noro, S.-I., Kitagawa, S., Kondo, M. & Seki, K. (2000). *Angew. Chem. Int. Ed.* **39**, 2082–2084.
Noro, S.-I., Kitaura, R., Kondo, M., Kitagawa, S., Ishii, T., Matsuzaka, H. & Yamashita, M. (2002). *J. Am. Chem. Soc.* **124**, 2568–2583.
Ouahab, L., Fettouhi, M., Halet, J. F., Yartsev, V. M., Garrigou, C., Delhaes, P. & Sourisseau, C. (1993). *New J. Chem.* **17**, 399–408.
Ouahab, L., Padiou, J., Grandjean, D., Garrigou-Lagrange, C., Delhaes, P. & Bencharif, M. (1989). *J. Chem. Soc. Chem. Commun.* pp. 1038–1041.
Raj, S. B., Muthiah, P., Bocelli, G. & Catoni, A. (2003). *Acta Cryst.* E**59**, o1980–o1983.
Sharma, C. V. K. & Rogers, R. D. (1999). *Chem. Commun.* pp. 83–84.
Sharma, C. V. K. & Zaworotko, M. J. (1996). *Chem. Commun.* pp. 2655–2656.
Sheldrick, G. M. (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1995). *SMART*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Weakley, T. J. R. (1982). *Inorg. Chim. Acta*, **63**, 161–168.
Weakley, T. J. R. (1984). *Inorg. Chim. Acta*, **95**, 317–322.
Wei, Y., Zhu, Y., Song, Y., Hou, H. & Fan, Y. (2002). *Inorg. Chem. Commun.* **5**, 166–170.
Williams, J. M., Johnson, P. L., Schultz, A. J. & Coffey, C. C. (1978). *Inorg. Chem.* **17**, 834–839.
Xu, L., Guo, G.-C., Liu, B., Wang, M.-S. & Huang, J.-S. (2004). *Inorg. Chem. Commun.* **7**, 1145–1149.
Yanovskii, A. I., Vaskes, Kh. Kh., Babkov, A. V., Antipin, M. Yu. & Struchkov, Yu. T. (1984). *Sov. J. Coord. Chem.* **10**, 954–957.
Zhang, H., Cai, J., Feng, X.-L., Sang, H.-Y., Liu, J.-Z., Li, X.-Y. & Ji, L.-N. (2002). *Polyhedron*, **21**, 721–728.