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# Red and yellow solvates of chloro(2,2′:6′,2″-terpyridine)-platinum(II) chloride and Pt···Pt interactions

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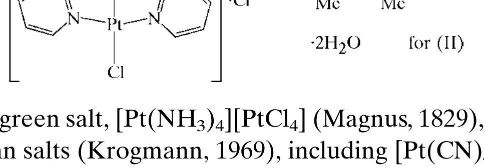
Crystallization of chloro(2,2′:6′,2″-terpyridine)platinum(II) chloride from dimethyl sulfoxide yields a red polymorph, $[\mathrm{PtCl(C_{15}H_{11}N_3)}]\mathrm{Cl}\cdot\mathrm{C_2H_6OS}$, (I), which exhibits stacking along the *a* axis through pairs of Pt···Pt($-x$, $-y$, $-z$) interactions of 3.3155 (8) Å. The cations are further associated through close Pt···Pt($1-x$, $-y$, $-z$) distances of 3.4360 (8) Å. Recrystallization from water gives a merohedrally twinned yellow–orange dihydrate form, $[\mathrm{PtCl(C_{15}H_{11}N_3)}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$, (II), with pairwise short Pt···Pt($1-x$, $2-y$, $-z$) contacts of 3.3903 (5) Å but no long-range stacking through the crystals. Interpair Pt···Pt($-x$, $2-y$, $-z$) distances between cation pairs in the hydrate are 4.3269 (5) Å.

## Comment

One-dimensional chains of metal atoms have been of interest to chemists and physicists for decades because of their potential as highly effective electronic conductors (Miller, 1982). Compounds containing such linear chains have been drawn naturally into the search for nanoscale electronic components, including wires (Wysodra *et al.*, 2004). The best studied are the columnar stacks of $d^8$ $\mathrm{Pt^{II}}$ compounds, such as Magnus' green salt, $[\mathrm{Pt(NH_3)_4}][\mathrm{PtCl_4}]$ (Magnus, 1829), and the Krogmann salts (Krogmann, 1969), including $[\mathrm{Pt(CN)_4}]^{2-}$ and $[\mathrm{Pt(oxalate)_2}]^{2-}$ (Mattes & Krogmann, 1964).



Other soluble platinum compounds with organic ligands also exhibit Pt···Pt stacking. The platinum diimine compound $[\mathrm{PtCl_2(bpy)}]$ (bpy is 2,2′-bipyridine) is well known to crystallize in two different polymorphs with distinct colors. The red polymorph (Osborn & Rogers, 1974) crystallizes in *Cmcm* and has infinite arrays of $[\mathrm{PtCl_2(bpy)}]$ molecules stacked on top of each other and rotated by 180°. The Pt atoms are 3.448 Å apart and form an infinite chain of Pt atoms in the lattice. The yellow polymorph (Textor & Oswald, 1974) crystallizes in *Pbca*, with the closest Pt···Pt distance being 4.524 Å.

We report here a similar phenomenon in structures of the related compound [PtCl(terpy)]Cl (terpy is 2,2′:6′,2″-terpyridine). A red form with a linear chain of Pt···Pt interactions through the crystal has been obtained *via* recrystallization from dimethyl sulfoxide (DMSO), [PtCl(terpy)]Cl·DMSO,

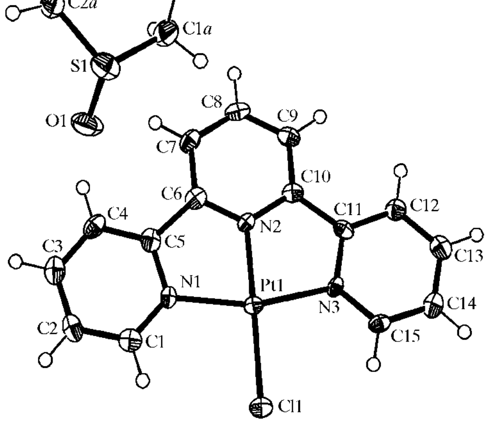


**Figure 1**
A view of the structure of a single molecule of (I), showing the dimethyl sulfoxide solvent molecule. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

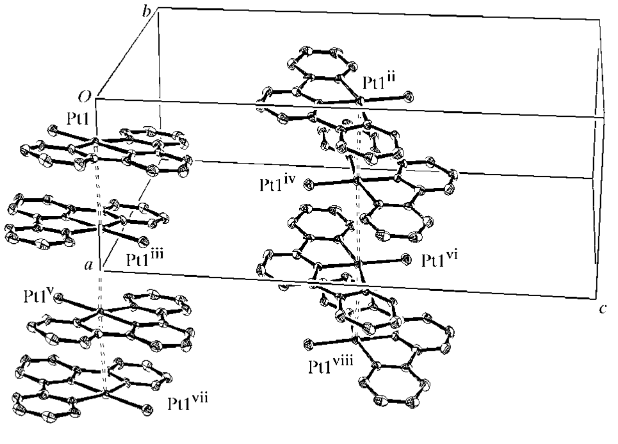


**Figure 2**
A view along the *c* axis of the unit cell of (I), showing the pairwise Pt···Pt interactions and the short Pt···Pt contacts between cation pairs along the *a* axis. Cl⁻ anions and dimethyl sulfoxide molecules have been omitted for clarity. [Symmetry codes: (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, -y, -z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $1+x, y, z$; (vi) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vii) $2-x, -y, -z$; (viii) $\frac{3}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.]

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(I). In contrast, a merohedrally twinned yellow crystalline form, [PtCl(terpy)]Cl·2$H_2O$, (II), has been obtained from water and shows pairwise Pt···Pt contacts, but no infinite chain.

The cation of compound (I), shown in Fig. 1, exhibits stacking along the *a* axis in line with the Pt···Pt vector, as can be seen in Fig. 2. There are two distinct Pt···Pt distances of 3.3155 (8) and 3.4360 (8) Å. The shorter Pt···Pt($-x$, $-y$, $-z$) distance is observed within pairs of $[PtCl(terpy)]^+$ cations and the slightly longer Pt···Pt($1 - x$, $-y$, $-z$) distance between adjacent pairs that lead to the infinite stacks. Adjacent cations in the chain are rotated by 180° with respect to each other. In contrast, the crystal structure of (II), shown in analogous views in Figs. 3 and 4, respectively, only exhibits one short Pt···Pt($1 - x$, $2 - y$, $-z$) contact of 3.3903 (5) Å, but no long-range stacking through the crystal.

Complexes with the $[PtCl(terpy)]^+$ cation have been characterized structurally previously, including with the perchlorate anion (Bailey *et al.*, 1995), with perchlorate cocrystallized with [Pt(thioquinolate)$_2$] (Tzeng *et al.*, 2003), with adenosine monophosphate (AMP) (Wong & Lippard, 1977), with $[PtCl_3(DMSO)]^-$ (Cini *et al.*, 2001), and with trifluoromethanesulfonate (Yip *et al.*, 1993). Selected data for these complexes and the two structures reported here are compared in Table 1. In several of the structures, close Pt···Pt contacts of less than 3.5 Å exist. In the structure cocrystallized with [Pt(thioquinolate)$_2$], however, the closest distance between the two chemically distinct Pt centers is 4.474 Å.

We note that the palladium hydrate derivative [PdCl(terpy)]Cl·2$H_2O$ has been reported and structurally characterized (Intille *et al.*, 1973*a*,*b*). The closest Pd···Pd distance is 3.863 Å. In the structure of [PdCl(terpy)]$_2$[PdCl$_4$] (Intille *et al.*, 1973*a*), there are pairs of cations with Pd···Pd contacts of 3.332 Å, but a long Pd···Pd distance of 6.592 Å between the cation and anion.

Two different packing arrangements in (I) and (II) have been achieved by varying only the solvent of recrystallization, and in which the solvent plays no obvious structure-directing role. These results suggest that the energy difference between the two structures is very small, which is consistent with previous studies of the [PtCl$_2$(bpy)] polymorphs. Notably, in neither (I) nor (II) does the $Cl^-$ anion act as a bridging ligand between the two cations, as is observed in the {[AuCl$_2$(bpy)]$_2$($\mu_2$-Cl)}Cl system (Micklitz *et al.*, 1989). Pt···Pt stacking interactions are common. However, such interactions have only recently been observed for isoelectronic Au$^{III}$ $d^8$ centers (Klapötke *et al.*, 2005). In both structures reported here, this affinity of the cationic Pt centers for each other is greater than their affinity for the $Cl^-$ ligand, which might have been expected on Coulombic grounds.

In summary, the compound [PtCl(terpy)]Cl forms red and yellow crystalline forms, depending on the solvent from which it is recrystallized. The red form exhibits close Pt···Pt contacts in a linear chain through the crystal, whereas the yellow form exhibits only pairwise contacts. These differences are similar to those observed in [PtCl$_2$(bpy)], except that in the latter no solvents are included in the crystals. In the case of [PtCl(terpy)]Cl, solvent inclusion is likely in the presence of the exogenous $Cl^-$ anion.

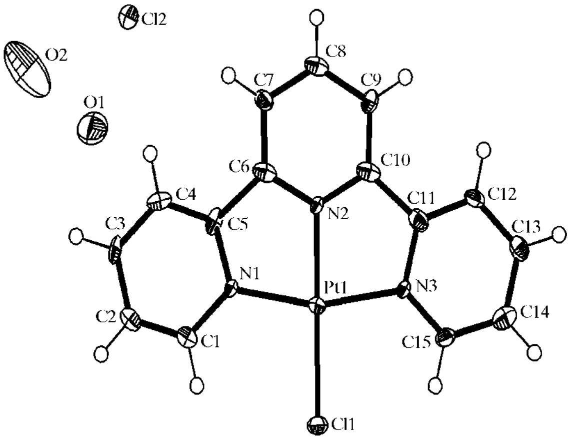

**Figure 3**
A view of the structure of a single molecule of (II), showing the two hydrate water molecules. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

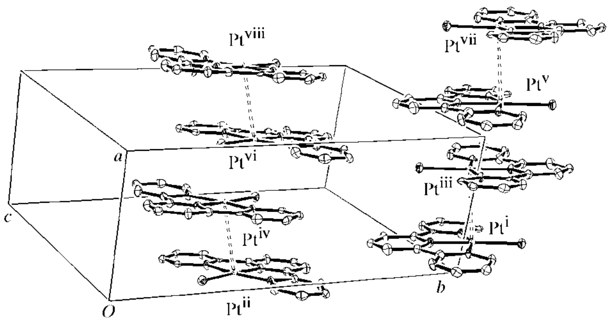

**Figure 4**
A view of the unit cell of (II), showing the short Pt···Pt distances between pairs of $[PtCl(terpy)]^+$ cations. $Cl^-$ anions and water molecules have been omitted for clarity. [Symmetry codes: (i) $x, y, z$; (ii) $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, 2 - y, z$; (iv) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 + x, y, z$; (vi) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (vii) $2 - x, 2 - y, -z$; (viii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

## Experimental

The platinum salt chloro(2,2′:6′,2″-terpyridine)platinum(II) chloride was prepared according to the method of Annibale *et al.* (2004). Crystals of (I) were grown by slow evaporation of a saturated dimethyl sulfoxide solution of [PtCl(terpy)]Cl, and crystals of (II) were grown by evaporation of an aqueous solution of the same compound.

### Compound (I)

*Crystal data*

[PtCl($C_{15}H_{11}N_3$)]Cl·$C_2H_6OS$
$M_r = 577.39$
Monoclinic, $P2_1/n$
$a = 6.7404$ (14) Å
$b = 13.298$ (3) Å
$c = 20.954$ (4) Å
$\beta = 90.331$ (3)°
$V = 1878.1$ (7) Å$^3$

$Z = 4$
$D_x = 2.042$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 7.88$ mm$^{-1}$
$T = 100$ (2) K
Rod, red
0.30 × 0.10 × 0.10 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.201$, $T_{\max} = 0.506$ (expected range = 0.180–0.455)

13395 measured reflections
4236 independent reflections
3215 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 27.6°$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.068$
$S = 1.15$
4236 reflections
226 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.029$
$\Delta\rho_{\max} = 1.42$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.60$ e Å$^{-3}$

## Compound (II)

*Crystal data*

$[PtCl(C_{15}H_{11}N_3)]Cl\cdot2H_2O$
$M_r = 535.29$
Monoclinic, $P2_1/n$
$a = 6.9085$ (6) Å
$b = 17.0822$ (15) Å
$c = 13.8402$ (12) Å
$\beta = 98.586$ (2)°
$V = 1615.0$ (2) Å$^3$

$Z = 4$
$D_x = 2.202$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 9.03$ mm$^{-1}$
$T = 100$ (2) K
Needle, orange–yellow
0.30 × 0.04 × 0.04 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.173$, $T_{\max} = 0.714$

10591 measured reflections
10591 independent reflections
8684 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.125$
$\theta_{\max} = 25.0°$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.133$
$S = 1.01$
10591 reflections
184 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.084P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.91$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.52$ e Å$^{-3}$

### Table 1

Comparison of Pt···Pt distances (Å) in [PtCl(terpy)]*X* structures.

Comparative data from the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002).

| CSD refcode | Anion | Neutral species | Pt···Pt | Reference |
|---|---|---|---|---|
| LAVWUA | $O_3SCF_3^-$ | | 3.329 (1)<br>3.575 | Yip *et al.* (1993) |
| QUGGOO | $[PtCl_3(DMSO)]^-$ | | 3.338<br>3.419 | Cini *et al.* (2001) |
| TPTAMP | Adenosine-5′-monophosphate | $2.25H_2O$ | 3.699 | Wong & Lippard (1977) |
| VASYAQ | $ClO_4^-$ | [Pt(thioquinolate)$_2$] | 3.353 | Tzeng *et al.* (2003) |
| ZEKTEO | $ClO_4^-$ | | 3.269<br>4.197 | Bailey *et al.* (1995) |
| (I) | $Cl^-$ | DMSO | 3.3155 (8)<br>3.4360 (8) | This work |
| (II) | $Cl^-$ | $2H_2O$ | 3.3903 (5)<br>4.3269 (5) | This work |

Compound (I) crystallizes as a dimethyl sulfoxide solvate, whereas compound (II) crystallizes with two equivalents of water. The H atoms of the water molecules could not be located or refined successfully. All other H atoms in the structures were placed using a riding model, with C—H = 0.95–0.98 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

For both compounds, data collection: *SMART* (Bruker, 2005); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Bruker, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; 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: FG3017). Services for accessing these data are described at the back of the journal.

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Annibale, G., Pitteri, B., Wilson, M. H. & McMillin, D. (2004). *Inorg. Synth.* **34**, 76–81.
Bailey, J. A., Hill, M. G., Marsh, R. E., Miskowski, V. M., Schaefer, W. P. & Gray, H. B. (1995). *Inorg. Chem.* **34**, 4591–4599.
Bruker (2005). *SMART* (Version 5.626), *SAINT* (Version 6.02) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Cini, R., Donati, A. & Giannettoni, R. (2001). *Inorg. Chim. Acta*, **315**, 73–80.
Intille, G. M., Pfluger, C. E. & Baker, W. A. Jr (1973*a*). *Cryst. Struct. Commun.* **2**, 217–220.
Intille, G. M., Pfluger, C. E. & Baker, W. A. Jr (1973*b*). *J. Cryst. Mol. Struct.* **3**, 47–54.
Klapötke, T. M., Krumm, B., Galvez-Ruiz, J. & Nöth, H. (2005). *Inorg. Chem.* **44**, 9625–9627.
Krogmann, K. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 35–42.
Magnus, G. (1829). *Ann. Chim. Phys. Ser. 2*, **40**, 110–137.
Mattes, R. & Krogmann, K. (1964). *Z. Anorg. Allg. Chem.* **332**, 247–256.
Micklitz, W., Lippert, B., Müller, G., Mikulcik, P. & Riede, J. (1989). *Inorg. Chim. Acta*, **165**, 57–64.
Miller, J. S. (1982). *Extended Linear Chain Compounds*, Vols. 1–3. New York: Plenum Press.
Osborn, R. S. & Rogers, D. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1002–1004.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Textor, M. & Oswald, H. R. (1974). *Z. Anorg. Allg. Chem.* **407**, 244–256.
Tzeng, B.-C., Lee, G.-H. & Peng, S.-M. (2003). *Inorg. Chem. Commun.* **6**, 1341–1343.
Wong, Y.-S. & Lippard, S. J. (1977). *J. Chem. Soc. Chem. Commun.* pp. 824–825.
Wysodra, M., Winkler, K., Sotrk, J. R. & Balch, A. L. (2004). *Chem. Mater.* **16**, 771–780.
Yip, H. K., Cheng, L. K., Cheung, K. K. & Che, C. M. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2933–2938.