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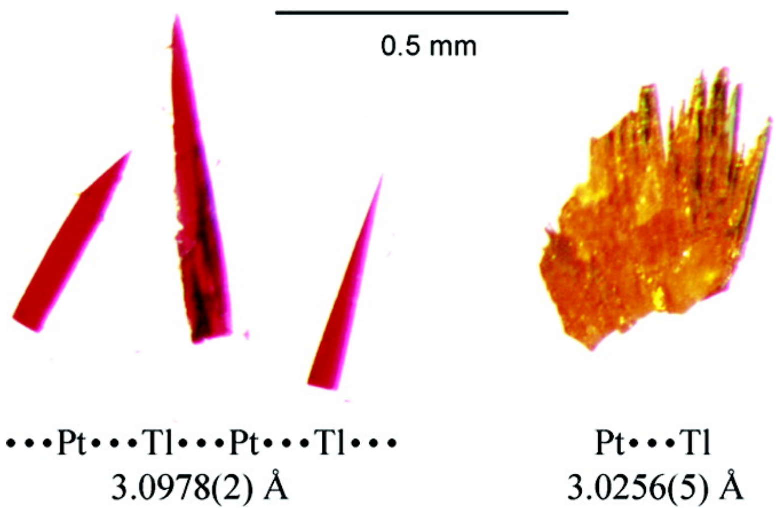

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Polymorphs with Varying Platinum(II)−Thallium(I) Interactions

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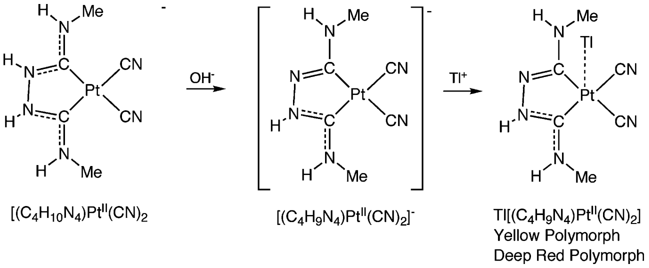
Polymorphs of molecular substances usually involve differences in molecular conformation, molecular orientation, or crystal packing.[1] Rarely do polymorphs have variations in the bonding interactions of their components; however, when such changes occur, especially if the changes involve the interruption of extended metal−metal interactions, they can have profound effects on the materials' spectroscopic and physical properties.

Metal ions with the closed shell and pseudo-closed shell d^8, d^{10}, and s^2 electronic structures, such as Pt(II), Au(I), and Tl(I), are known to interact with one another to form weak metal−metal bonds.[2] These metallophilic interactions are sufficiently weak so that they can readily be perturbed by a variety of environmental factors, including crystal packing effects. However, at present, only a limited number of polymorphs are known in which such metallophilic interactions differ within them. A relevant example involves $Pt^{II}(2,2'\text{-bipyridine})Cl_2$, which forms red and yellow polymorphs.[3] In the red form, the molecules pack so that extended chains of platinum ions are formed with a Pt···Pt distance of 3.45 Å,[3b] while in the yellow form, the molecules are widely separated with the platinum ions isolated from one another.[3c] Crystallization of $[Au^I(CNC_6H_{11})_2](PF_6)$ produces a colorless and a yellow polymorph.[4] Each form contains chains of cations with a Au···Au separation of 3.1822(3) Å in the colorless polymorph and much shorter distances in the 2.9643(6)−2.9803(6) Å range in the yellow one. Linear, two-coordinate $Au^I(PPh_2Me)Cl$ crystallizes as two polymorphs: one containing a dimer joined by a single Au···Au interaction and the other containing a trimer, again, connected by Au···Au interactions.[5a] Each of the colorless polymorphs has a distinct emission spectrum.[5b] Colorless $Au^I(P(p\text{-tol})_3)Cl$ crystallizes as two polymorphs: one with no Au···Au interaction and the other with a dimeric structure and one close Au···Au interaction.[6]

As shown in Scheme 1, treatment of an aqueous solution of yellow $(C_4H_{10}N_4)Pt^{II}(CN)_2{\cdot}H_2O$[7] in 0.10 M potassium hydroxide with an equimolar amount of thallium(I) nitrate produces the red polymorph of $Tl^I[(C_4H_9N_4)Pt^{II}(CN)_2]$ as thin red blades with a green reflectance in 80% yield. After removal of these red crystals by decantation, ethanol was added to the solution. Gradual evaporation produced the yellow polymorph in 5% yield. Figure 1 shows a photograph of samples of the two polymorphs. Crystallographic characterization of $(Ph_4As)[(C_4H_9N_4)Pt^{II}(CN)_2]$[7] has shown that this salt consists of isolated planar anions with no close Pt···Pt contacts (see Supporting Information).

Scheme 1



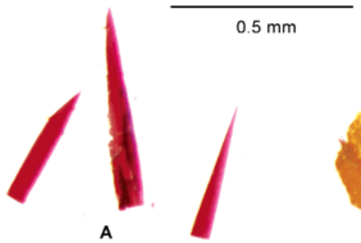


Figure 1. A photograph of the polymorphs of $Tl[(C_4H_9N_4)Pt(CN)_2]$.

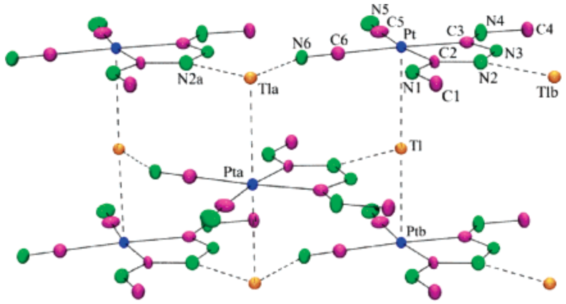


Figure 2. A view of the red polymorph of $\{Tl^I[(C_4H_9N_4)Pt^{II}(CN)_2]\}_n$ with 50% thermal contours for all non-hydrogen atoms. (Atom colors: carbon, purple; nitrogen, green; platinum, blue; thallium, orange.) Selected bond distances (Å): Pt−Tl, 3.0978(2); Pt−C2, 2.030(8); Pt−C3, 2.03(1); Pt−C5, 2.03(1); Pt−C6, 2.01(1); Tl−N2, 2.626(8); Tla−N6, 2.691(9). Selected bond angles (deg): Pt−Tl−Pta, 171.37(2); Tl−Pt−Tlb, 171.37(2); C2−Pt1−C3, 78.2(4); C2−Pt1−C6, 95.0(4); C3−Pt1−C5, 93.0(4); C5−Pt−C6, 93.8(4); N2a−Tl−N6, 78.7(2); Pta−Tla−N2a, 92.97(1); Pta−Tla−N6, 93.65(1).

Diffraction quality crystals of the red polymorph were removed from the reaction mixture and characterized by single-crystal X-ray crystallography.[8] A portion of its structure is shown in Figure 2. This polymorph involves an extended ···Pt···Tl···Pt···Tl··· chain. The Pt···Tl distance is 3.0978(2) Å, and the Pt−Tl−Pt and Tl−Pt−Tl angles are equivalent (171.37(2)°). For comparison, in centrosymmetric $Tl^I_2[Pt^{II}(CN)_4]$, which has a planar $[Pt^{II}(CN)_4]^{2-}$ unit with two thallium ions directly above and below the Pt ion, the Pt···Tl distance is 3.140(1) Å and the Tl−Pt−Tl angle is 180°.[8] In other complexes containing Pt−Tl interactions, the Pt−Tl distances range from 3.5 to 2.6 Å.[10] In this red polymorph, the anion has the expected planar structure that is found in a number of related platinum complexes with the same chelating dicarbene ligand.[11] The thallium ions are four-coordinate. In addition to the two Pt···Tl interactions, each thallium ion is connected to another anion and the nitrogen atom of a cyano group in a different anion. These interactions produce layers of anions connected by Tl−N bonds, as seen in Figure 2. These layers are, in turn, joined vertically through the Pt···Tl interactions.

A portion of the structure of the yellow polymorph is shown in Figure 3. This form lacks the extended ···Pt···Tl···Pt···Tl··· chain

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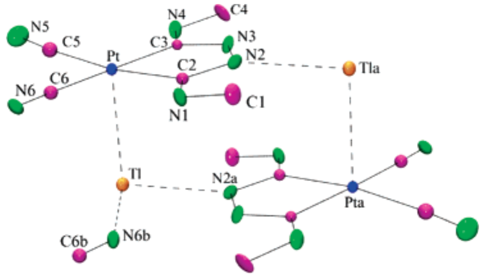

Figure 3. A view of the dimeric unit in the yellow polymorph of Tl[($C_4H_9N_4$)]Pt(CN)$_2$] with 50% thermal contours for all non-hydrogen atoms. The fragment, C6b and N6b, is part of another anion (atom colors as in Figure 1). Selected bond distances (Å): Pt−Tl, 3.0256(5); Pt−C2, 2.027(7); Pt−C3, 2.007(7); Pt−C5, 2.040(8); Pt−C6, 1.988(7); Tl−N2a, 2.596(6); Tl−N6b, 2.687(7). Selected bond angles (deg): C2−Pt−C3, 78.2(3); C2−Pt−C6, 93.6(3); C3−Pt−C5, 95.8(3); C5−Pt−C6, 93.8(4); N2a−Tl−N6b, 79.5(2); Pt−Tl−N2a, 91.4(1); Pt−Tl−N6b, 89.0(1).

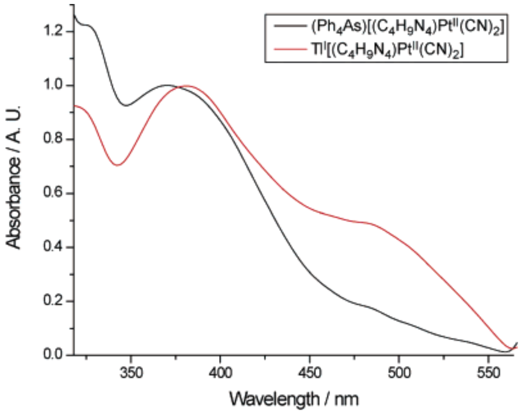

Figure 4. Electronic spectra of the red polymorph of Tl[($C_4H_9N_4$)Pt^{II}(CN)$_2$] and (Ph$_4$As)[($C_4H_9N_4$)Pt^{II}(CN)$_2$] in KBr pellets. Absorbance is given in arbitrary units.

seen in the red polymorph. Rather, dimers connected by pairs of Pt⋯Tl interactions are present. In these, the Pt⋯Tl distance (3.0256(5) Å) is slightly shorter than the comparable distance in the red form. The platinum ion has the expected planar geometry with the Pt atom only 0.080(4) Å from the plane of the four ligating carbon atoms toward the thallium ion. The thallium ion in the yellow polymorph has three-coordinate, pyramidal geometry with bonding to one platinum ion, to the deprotonated nitrogen atom of a chelating ligand of the adjacent anion, and to a cyano group in another anion.

Figure 4 shows a comparison of the electronic spectra of the red polymorph of Tl^{I}[($C_4H_9N_4$)Pt^{II}(CN)$_2$] with that of the parent anion in (Ph$_4$As)[($C_4H_9N_4$)Pt^{II}(CN)$_2$], with the samples dispersed in potassium bromide. Both compounds have peaks at ca. 380 nm that likely arise from the platinum^{II}(biscarbene) portion and are similar to transitions seen in the spectra of the related compounds (e.g., [($C_4H_9N_4$)Pt^{II}(CNCH$_3$)$_2$]Cl).[11] However, the red polymorph of Tl^{I}[($C_4H_9N_4$)Pt^{II}(CN)$_2$] has a low-energy feature at 480 nm that is absent in the spectrum of (Ph$_4$As)[($C_4H_9N_4$)Pt^{II}(CN)$_2$]. The low-energy peak in the red form of Tl^{I}[($C_4H_9N_4$)Pt^{II}(CN)$_2$] results from the extended thallium(I)−platinum(II) interactions. The solid-state electronic spectrum of the yellow polymorph of Tl^{I}[($C_4H_9N_4$)Pt^{II}(CN)$_2$] (λ_{max}, 363 nm) is similar to that of (Ph$_4$As)[($C_4H_9N_4$)Pt^{II}(CN)$_2$] and gives no evidence of the low-energy transition seen for the red polymorph.

The red and yellow forms of Tl^{I}[($C_4H_9N_4$)Pt^{II}(CN)$_2$] represent a unique case where polymorphs that differ in the nature of metallophilic interactions are produced in a heterodimetallic complex. The formation of the extended ⋯Pt⋯Tl⋯Pt⋯Tl⋯ chain in the red polymorph is a feature not present in the other known examples of Pt−Tl compounds but is related to the ⋯Au⋯Tl⋯Au⋯Tl⋯ chains prepared by Fackler, Laguna, and co-workers.[12] The divergent optical properties of the two forms provide insight into the nature of platinum(II)−thallium(I) interactions and could potentially lead to the development of chemical sensors.

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Supporting Information Available: Synthetic procedures, a drawing of (Ph$_4$As)[($C_4H_9N_4$)Pt^{II}(CN)$_2$], X-ray crystallographic data for (Ph$_4$As)[($C_4H_9N_4$)Pt^{II}(CN)$_2$], and the red and yellow polymorphs of Tl^{I}[($C_4H_9N_4$)Pt^{II}(CN)$_2$] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Bernstein, J. *Polymorphism in Molecular Crystals*; Clarendon Press: Oxford, 2002. (b) Braga, D.; Grepioni, F. *Chem. Soc. Rev.* **2000**, *29*, 229. (c) Dunitz, J. D.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193.

(2) (a) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597. (b) Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55.

(3) (a) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1934**, 965. (b) Osborn, R. S.; Rogers, D. *J. Chem. Soc., Dalton Trans.* **1974**, 1002. (c) Herber, R. H.; Croft, M.; Coyer, M. J.; Bilash, B.; Sahiner, A. *Inorg. Chem.* **1994**, *33*, 2422. (d) Achar, S.; Catalano, V. J. *Polyhedron* **1997**, *16*, 1555.

(4) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1033.

(5) (a) Toronto, D. V.; Weissbart, B.; Tinti, D. S.; Balch, A. L. *Inorg. Chem.* **1996**, *35*, 2484. (b) Weissbart, B.; Toronto, D. V.; Balch, A. L.; Tinti, D. S. *Inorg. Chem.* **1996**, *35*, 2490.

(6) Bott, R. C.; Healy, P. C.; Smith, G. *Aust. J. Chem.* **2004**, *57*, 213.

(7) Rouschias, G.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 2097.

(8) Crystal data for Tl[($C_4H_9N_4$)Pt(CN)$_2$] red polymorph: red, platelike needle with a green, metallic reflection, orthorhombic, space group *Pnma*, $a = 19.504(1)$ Å, $b = 6.1780(4)$ Å, $c = 8.7946(6)$ Å, $V = 1021.7(1)$ Å^3, $Z = 4$, $D_c = 3.671$ Mg/m^3, $T = 90(2)$ K; $R1 = 0.0364$, $wR2 = 0.0784$ for all data; conventional $R1 = 0.0283$ computed for 1135 observed data ($I > 2\sigma(I)$) with 0 restraints and 83 parameters. Yellow polymorph: yellow block, monoclinic, space group $P2_1/c$, $a = 9.137(1)$ Å, $b = 7.122(1)$ Å, $c = 16.715(2)$ Å, $\beta = 104.815(2)°$, $V = 1051.5(2)$ Å^3, $Z = 4$, $D_c = 3.567$ Mg/m^3, $T = 90(2)$ K; $R1 = 0.0438$, $wR2 = 0.0583$ for all data; conventional $R1 = 0.0280$ computed for 2613 observed data ($I > 2\sigma(I)$) with 0 restraints and 109 parameters.

(9) Nagle, J. K.; Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 319.

(10) (a) Pyykkö, P.; Patzschke, M. *Faraday Discuss.* **2003**, *124*, 41. (b) Ma, G.; Kritikos, M.; Glaser, J. *Eur. J. Inorg. Chem.* **2001**, 1311.

(11) Stork, J. R.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **2004**, *43*, 7508.

(12) (a) Fernandez, E. J.; Lopez de Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Perez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 2022. (b) Fernandez, E. J.; Lopez de Luzuriaga, J. M.; Monge, M.; Montiel, M.; Olmos, M. E.; Perez, J.; Laguna, A.; Mendizabal, F.; Mohamed, A. A.; Fackler, J. P., Jr. *Inorg. Chem.* **2004**, *43*, 3573.

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