

Preliminary Communication

The co-stacking of a planar metal complex and a novel 1,3-dithiole:
the synthesis and crystal structure
of $[\text{Pt}(\text{mnt})(\text{CNMe})_2] \cdot (\text{NC})_2\text{C}_2\text{S}_2\text{CNMe}$

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Abstract

The reaction of $[\text{NBu}_4]_2\text{Cu}(\text{mnt})_2$ with $[\text{Pt}(\text{CNMe})_4][\text{PF}_6]_2$ gives $[\text{Pt}(\text{mnt})(\text{CNMe})_2] \cdot (\text{NC})_2\text{C}_2\text{S}_2\text{CNMe}$, an X-ray study of which reveals co-stacking of neutral planar metal and organic molecules.

Key words: Platinum; Co-stacking; Crystal structure; Dithiole; Isocyanide

Introduction

We have recently described reactions in which square planar metal dithiolene anions $[\text{M}(\text{mnt})_2]^z$ ($\text{mnt} = [\text{S}_2\text{C}_2(\text{CN})_2]^{2-}$, $\text{M} = \text{Ni}, \text{Pd}$, and Pt , $z = -2$; $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$, and Au , $z = -1$) and cationic isocyanide complexes $[\text{M}'(\text{CNMe})_4]^{2+}$ ($\text{M}' = \text{Pd}$ and Pt) give novel linear chain metal complexes such as $[\text{Pt}(\text{CNMe})_4][\text{Pd}(\text{mnt})_2]$, $[\text{Pt}(\text{CNMe})_4][\text{M}(\text{mnt})_2]$ ($\text{M} = \text{Pd}$ and Au) [1], and $[\text{M}(\text{mnt})(\text{CNMe})_2]$ ($\text{M} = \text{Ni}$ and Pd) [2]. These species, both charged and neutral, display a range of stacked and/or layered structures in the solid state. We now show that a similar reaction, between $[\text{Pt}(\text{CNMe})_4]^{2+}$ and $[\text{Cu}(\text{mnt})_2]^{2-}$, results in rearrangement and interligand coupling to give $[\text{Pt}(\text{mnt})(\text{CNMe})_2] \cdot (\text{NC})_2\text{C}_2\text{S}_2\text{CNMe}$ (**1**) in which the neutral square planar metal complex co-stacks with a novel organic heterocycle.

Results and Discussion

When a mixture of $[\text{Pt}(\text{CNMe})_4][\text{PF}_6]_2$ (150 mg, 0.23 mmol) and $[\text{NBu}_4]_2[\text{Cu}(\text{mnt})_2]$ (142 mg, 0.17 mmol) was kept in MeCN (13 cm³) at 0°C for 15 h, pale yellow

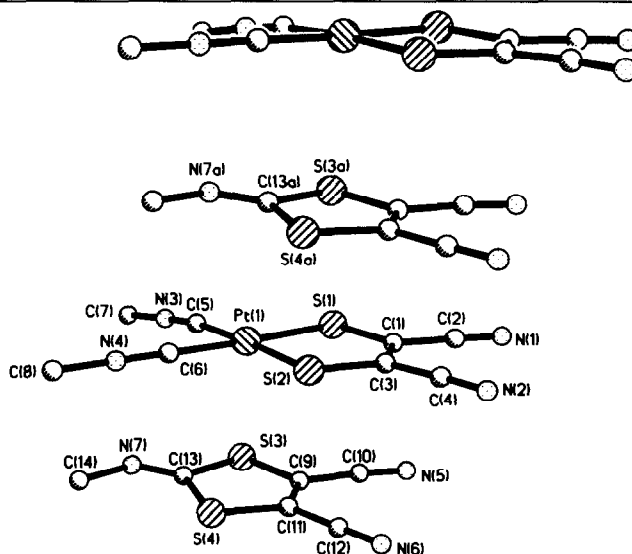


Fig. 1. Part of one of the columns of **1a** and **1b** which make up the crystal structure of **1**. Important molecular geometry parameters include: bond lengths (Å), Pt(1)–S(1) 2.278(4), Pt(1)–S(2) 2.279(4), Pt(1)–C(5) 1.940(16), Pt(1)–C(6) 1.959(15), S(1)–C(1) 1.737(15), S(2)–C(3) 1.748(14), S(3)–C(9) 1.704(15), S(3)–C(13) 1.822(17), S(4)–C(11) 1.724(13), S(4)–C(13) 1.791(18), N(7)–C(13) 1.22(2), N(7)–C(14) 1.48(2), C(9)–C(11) 1.32(2).

crystals were formed which were washed with dichyl ether and air dried (yield 13.4 mg, 13%). The colour of the crystalline product, the absence of the expected $\nu(\text{CN})$ band for the dianion, and the elemental analysis data (C, H, and N) clearly showed that the expected salt $[\text{Pt}(\text{CNMe})_4][\text{Cu}(\text{mnt})_2]$ had not been formed. In the absence of further useful spectroscopic information, an X-ray crystallographic study [3*] was carried out on (**1**).

The crystal structure analysis revealed that (**1**) consists of two near-planar molecular species, $[\text{Pt}(\text{mnt})(\text{CNMe})_2]$ (**1a**) and $(\text{NC})_2\text{C}_2\text{S}_2\text{CNMe}$ (**1b**). The Pt–S and Pt–C distances are in reasonable accord with those determined by EXAFS spectroscopy for a solid sample of pure **1a** [2]. Molecules of **1a** and **1b** are arranged in columns with their molecular planes approximately parallel to one another and tilted relative to the crystallographic *b* axis (which is parallel to the column). The mean planes of **1a** and **1b** are inclined at 29.9° and

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* Reference number with asterisk indicates a note in the list of references.

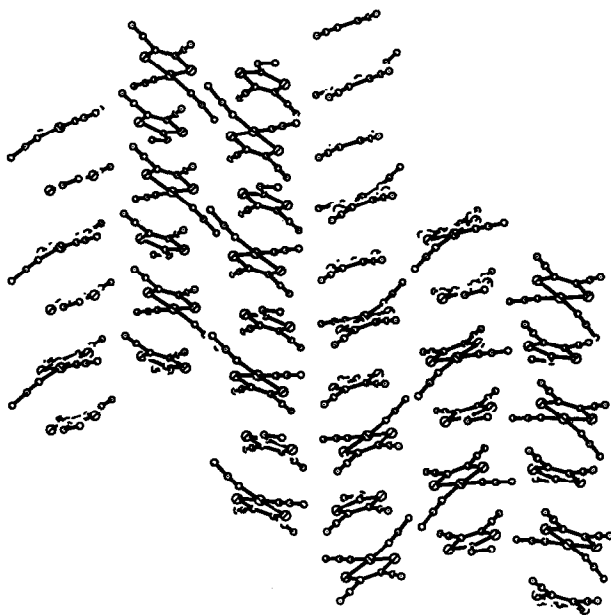


Fig. 2. Part of the crystal structure of **1** showing the layer formed by aligned dimers of columns. Of the six columns shown, columns 2 and 3, and 4 and 5 (numbering from left to right across the diagram) are linked by weak S...S, and S...CN interactions (see text).

22.8° to the crystallographic *b* axis and at 7.1° to one another. The platinum atom of **1a** lies 3.58 Å away from the **1b** mean plane and C(13) lies 3.36 Å away from the **1a** mean plane. The column formed by alternating molecules of **1a** and **1b** is shown in Fig. 1 and a larger portion of the crystal structure in Fig. 2. The columns are associated in pairs by weak edge-to-edge intermolecular contacts in the molecular planes. The shortest inter-column S...S and S...CN distances (of between 3.75 and 3.90 Å) are between S(1) in one column and S(3), C(10) and N(5) of **1b** in a symmetry-related neighbouring column. It is notable that these interactions involve the sulphur atom (S(3)) on the edge of **1b** away from the methyl group C(14). Similar edge-to-edge interactions involving mnt ligands are present in crystals of [Pd(mnt)(CNMe)₂] [2] and [Pt(CNMe)₄][Au(mnt)₂]₂ [1]. The pairs of columns in **1** are aligned in rows to form layers (see Fig. 2), and the entire crystal structure is assembled by superposition of these layers.

The preparation of the novel heterocycle (NC)₂-C₂S₂CNMe [**1b**], 2-(methylimino)-4,5-dicyano-1,3-dithiole] from [Pt(CNMe)₄]²⁺ and [Cu(mnt)₂]²⁻ differs from previous synthetic routes [4] and involves a mechanism which must include electron-transfer; the 1,3-dithiole contains the elements of the isocyanide MeNC and the neutral species S₂C₂(CN)₂ that is related formally to the dianionic mnt ligand of [Cu(mnt)₂]²⁻ by two-electron oxidation. As yet we have been unable to prepare **1b** or analogues in the absence of [Pt(mnt)(CNMe)₂]; there was no reaction between Na₂mnt and Cn^tBu in refluxing MeCN during 3 h nor between [NBu₄]ⁿ[Cu(mnt)₂] and CN^tBu under the same conditions during 8 h. However, its planarity, its stacking with the planar metal complex [Pt(mnt)(CNMe)₂], and its delocalised structure suggest **1b** to be a potential precursor for novel organic charge-transfer complexes.

Acknowledgements

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References and notes

- 1 N.G. Connelly, J.G. Crossley, A.G. Orpen and H. Salter, *J. Chem. Soc., Chem. Commun.*, (1992) 1564.
- 2 N.G. Connelly, J.G. Crossley and A.G. Orpen, *J. Chem. Soc., Chem. Commun.*, (1992) 1568.
- 3 Crystal Data for (1): C₁₄H₉N₇Pt, *M* = 598.6, monoclinic, space group *P*2₁/*n* (non-standard No. 14), *a* = 14.252(5), *b* = 7.926(3), *c* = 18.062(7) Å, β = 100.75(3)°, *V* = 2004.5(13) Å³, *Z* = 4, *D_x* = 1.98 gcm⁻³, λ = 0.71073 Å, μ = 74.3 cm⁻¹, *F*(000) = 1136, *T* = 295 K, crystal dimensions 0.15 × 0.4 × 0.7 mm, final difference map features in range 1.6 to -1.8 eÅ⁻³. Data were collected on a Nicolet P3m diffractometer for a unique portion of reciprocal space for 4 < 2θ < 40°. The structure was solved by heavy atom methods and refined by full-matrix least-squares (SHELXTL-PLUS, 166 variables) against *F* data corrected for absorption (transmission coefficients 0.95–0.12) and extinction, to *R* = 0.049 and *S* = 1.68 for the 1604 observed [*I* > 2σ(*I*)] unique data. Tables of atomic coordinates, bond lengths, bond angles and displacement parameters for **1** have been deposited with the Cambridge Crystallographic Data Centre.
- 4 H. Gotthardt, in A.R. Katritzky and C.W. Rees (eds.), *Comprehensive Heterocyclic Chemistry*, Vol-6, Chapter 4.32, Pergamon, Oxford, 1984.