

New Linear Chain Mixed Metal Compounds: Complex Salts of $[\text{Pt}(\text{CNMe})_4]^{2+}$

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The X-ray crystal structures of the salts $[\text{Pt}(\text{CNMe})_4][\text{Pd}(\text{mnt})_2]$, $[\text{Pt}(\text{CNMe})_4][\text{Pd}(\text{mnt})_2]_2 \cdot 2\text{MeCN}$ and $[\text{Pt}(\text{CNMe})_4][\text{Au}(\text{mnt})_2]_2 \cdot \text{MeCN}$ [$\text{mnt} = 1,2\text{-S}_2\text{C}_2(\text{CN})_2$] show a variety of stacking and layer motifs in the solid state; inter-complex interactions lead to low-dimensional molecular aggregates.

Unusual, highly anisotropic, solid-state properties arise when metal complexes of general formula ML_4 ($\text{M} = \text{Pt}^{\text{II}}, \text{Ir}^{\text{I}}$ etc., $\text{L} = \text{CN}, \text{CO}$ etc.) interact strongly with one another through linear chain contacts.¹ It is clearly of interest to explore the factors controlling the aggregation of these monomeric complexes to form chain polymer species. One limitation on such studies is the degree of functionalisation which is possible at the ligands, notably for carbonyl and cyano complexes. As a result, exploration of the materials chemistry of polymeric species of this sort has focussed on the variation of solid-state structure with counterion and solvent of crystallisation. We have therefore sought to develop chemistry based on more readily functionalised ligands (in this work isocyanides) and to allow for systematic variation of the metals around which the complexes are centred. In this and an accompanying paper we report synthetic and structural studies on planar complexes of the nickel triad which show a variety of modes of linear or near-linear inter-complex association in the solid state.

Our simple synthetic strategy involves the reaction in solution of a dicationic metal(II) tetrakis(isocyanide) $[\text{M}(\text{CNR})_4]^{2+}$ ($\text{M} = \text{Pd}, \text{Pt}$) with an anionic bis(dithiomaleonitrile) $[1,2\text{-S}_2\text{C}_2(\text{CN})_2, \text{mnt}]$ complex $[\text{M}'(\text{mnt})_2]^{n-}$ ($\text{M}' = \text{Ni}, \text{Pd}, \text{Pt}, \text{Au}$; $n = 1, 2$) to form a complex salt. Typically, rather insoluble solid material precipitates from solution in yields of 20–50%; crystals suitable for X-ray structure

analysis, which have IR spectra (Nujol mull) identical to the precipitated product, may be obtained directly from the reaction by slow codiffusion of the reagents. For certain combinations of ions, notably when $\text{M} = \text{Pd}$, other modes of reaction may be seen; ligand exchange reactions result in the formation of neutral species of the type $[\text{M}(\text{mnt})(\text{CNMe})_2]$. These reactions and the structures of the products, which also contain linear polymeric complex aggregates, are discussed in the following paper.

The reaction of $[\text{Pt}(\text{CNMe})_4][\text{PF}_6]_2$ with stoichiometric amounts of $[\text{NBu}^n]_n[\text{M}'(\text{mnt})_2]$ ($\text{M}' = \text{Ni}$ or Pd , $n = 1$ or 2 ; $\text{M}' = \text{Pt}$, $n = 2$; $\text{M}' = \text{Au}$, $n = 1$) in CH_2Cl_2 or MeCN gave precipitates with elemental analyses consistent with the presence of products with the general formula $[\text{Pt}(\text{CNMe})_4][\text{M}'(\text{mnt})_2]_n$. The IR spectra of the products (as Nujol mulls) confirm the absence of the $[\text{PF}_6]^-$ anion; no absorptions were observed at *ca.* 835 cm^{-1} . However, the absorptions in the cyanide stretching region do not correspond simply to the superposition of bands due to the individual ions present. Compare, for example, the spectrum of $[\text{Pt}(\text{CNMe})_4][\text{Pd}(\text{mnt})_2]$ **1** [$\nu(\text{CN})/\text{cm}^{-1}$ 2295s, 2283vs, broad, 2213w and 2195s] with those of $[\text{Pt}(\text{CNMe})_4][\text{PF}_6]_2$ [$\nu(\text{CN})/\text{cm}^{-1}$ 2308vs] and $[\text{NBu}^n]_n[\text{Pd}(\text{mnt})_2]$ [$\nu(\text{CN})/\text{cm}^{-1}$ 2214m, 2195s and 2187vs]. We have therefore determined the crystal structures of three new salts, namely $[\text{Pt}(\text{CNMe})_4][\text{Pd}(\text{mnt})_2]$

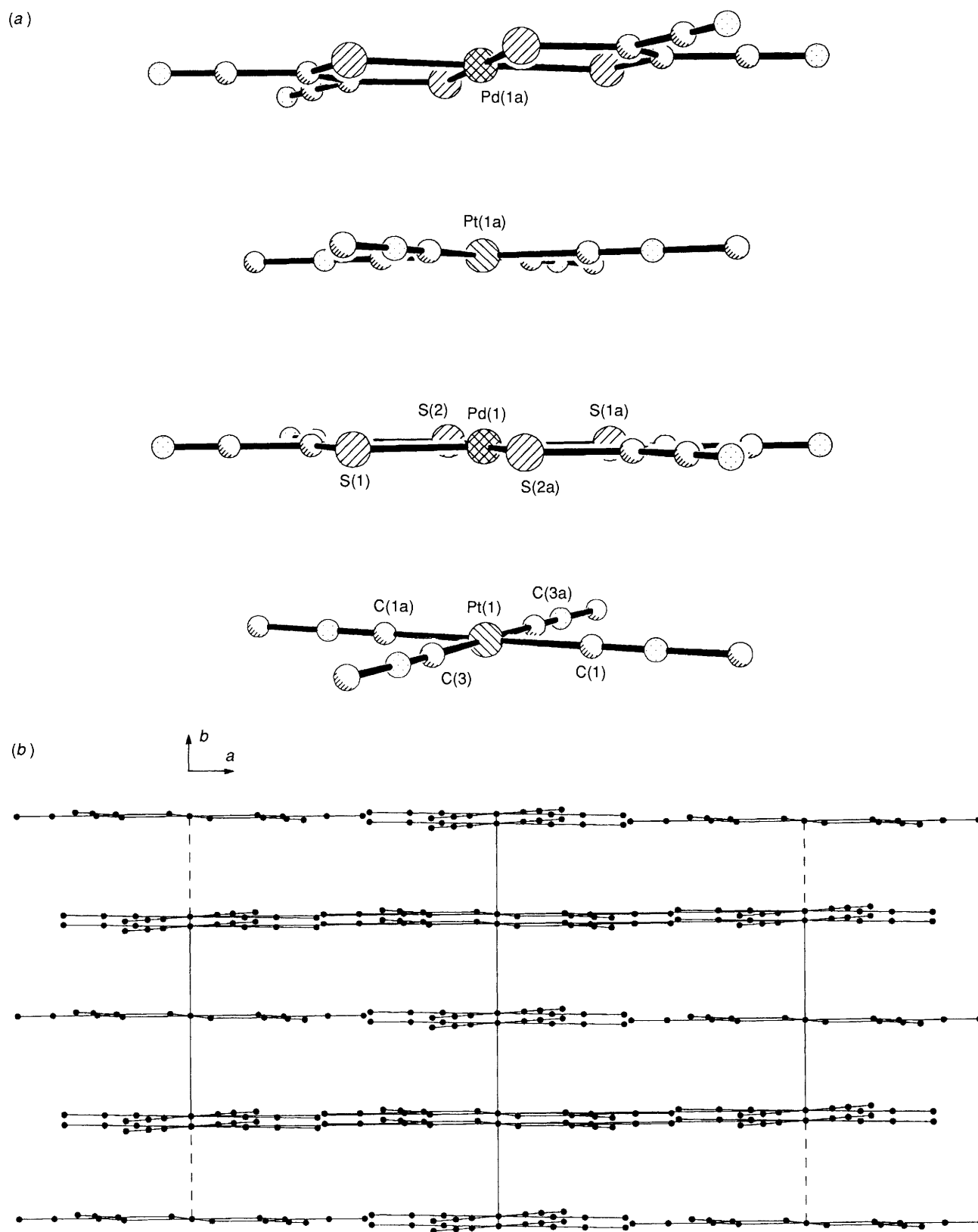


Fig. 1 (a) Geometry of a portion of the linear chain formed by dications and dianions in the crystal structure of **1**. Hydrogen atoms have been omitted for clarity. (b) Part of the crystal structure of **1** viewed nearly perpendicular to the unit cell *b* axis.

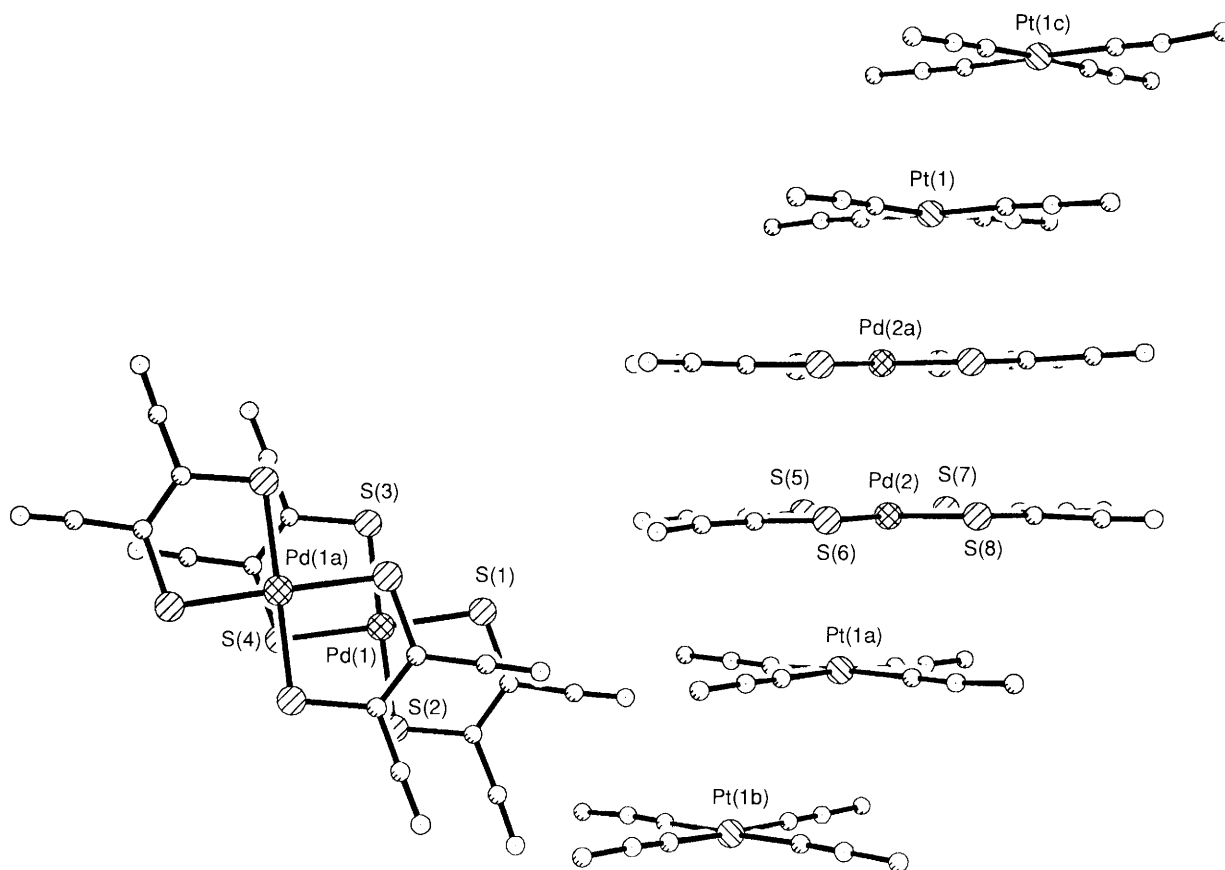


Fig. 2 Geometry of a portion of the linear chain formed by dications and dimers of monoanions, and the loose extra-stack dimer of mono-anions present in the crystal structure of $[\text{Pt}(\text{CNMe})_4][\text{Pd}(\text{mnt})_2]_2 \cdot 2 \cdot \text{MeCN} \cdot \text{H}_2\text{O}$. The view is approximately perpendicular to the unit cell b axis. Hydrogen atoms and solvent molecules have been omitted for clarity.

1, $[\text{Pt}(\text{CNMe})_4][\text{Pd}(\text{mnt})_2]_2$ **2** and $[\text{Pt}(\text{CNMe})_4][\text{Au}(\text{mnt})_2]_2$, the latter two as solvates.[†] These compounds exemplify the two principal stoichiometries which can be envisaged from the use of mono- or di-anionic bis(mnt) complexes {in these cases $[\text{Pd}(\text{mnt})_2]^{2-}$ or $[\text{Pd}(\text{mnt})_2]^-$ and $[\text{Au}(\text{mnt})_2]^-$ } and two different electron counts in the anion (formally d^8 in the Pd^{II} and Au^{III} compounds **1** and **3**, and d^9 in the Pd^{I} species **2**).

Portions of the unit cell of each of **1**, **2**·MeCN and **3**·MeCN are shown in Figs. 1, 2 and 3. The structure of **1** contains a

[†] Crystal data for **1**: $\text{PdPtS}_4\text{C}_{16}\text{H}_{12}\text{N}_8$, $M = 746.1$, monoclinic, space group $C2/m$ (No. 12), $a = 19.933(4)$, $b = 6.614(1)$, $c = 9.152(3)$ Å, $\beta = 94.09(2)^\circ$, $V = 1203.5(5)$ Å³, $Z = 2$, $D_c = 2.059$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 6.92$ mm⁻¹, $F(000) = 704$, $T = 298$ K.

2·MeCN: $\text{Pd}_2\text{PtS}_8\text{C}_{24}\text{H}_{16}\text{N}_{12} \cdot 4\text{H}_6\text{N}_2$, $M = 1232.93$, monoclinic, space group $P2_1/n$ (No. 14), $a = 14.063(6)$, $b = 14.385(6)$, $c = 20.668(9)$ Å, $\beta = 91.28(3)^\circ$, $V = 4180.0(31)$ Å³, $Z = 4$, $D_c = 1.93$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 4.63$ mm⁻¹, $F(000) = 2368$, $T = 298$ K.

3·MeCN: $\text{Au}_2\text{PtS}_8\text{C}_{24}\text{H}_{16}\text{N}_{12} \cdot 2\text{C}_2\text{H}_3\text{N}$, $M = 1355.0$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.524(5)$, $b = 25.176(11)$, $c = 13.958(6)$ Å, $\beta = 114.98(3)^\circ$, $V = 3989.3(28)$ Å³, $Z = 4$, $D_c = 2.26$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 11.29$ mm⁻¹, $F(000) = 2504$, $T = 298$ K.

In each case data were collected on a Nicolet P3m diffractometer for a unique quadrant of reciprocal space with $4 < 2\theta < 50^\circ$. The structures were solved by heavy-atom methods and refined by least-squares to $R = 0.033, 0.046$ and 0.063 respectively for 1368, 3383 and 1622 unique, absorption-corrected, observed [$I > 4\sigma(I)$] intensity data. For **2**·MeCN unidentified electron density close to the dimerised $[\text{Pd}(\text{mnt})_2]^{2-}$ anions in the columnar stacks making four short atom...S contacts could be modelled as an oxygen atom or, more satisfactorily, as a low occupancy disordered [0.103(3)] orientation of the Pd(2) atom in the dimer. For **3**·MeCN the solvate molecules are at least partly disordered along the channels through the structure. Atomic coordinates, bond lengths, bond angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

linear column of $[\text{Pd}(\text{mnt})_2]^{2-}$ dianions and $[\text{Pt}(\text{CNMe})_4]^{2+}$ dications along the monoclinic b axis with strictly planar coordination at both Pd and Pt. These planes are exactly perpendicular to the b axis and separated by $b/2$ [*i.e.* Pt(1)···Pd(1) 3.307(1) Å]. This type of linear association of doubly charged metal complex ions occurs in one of the earliest prepared linear metal chain species, namely Magnus' green salt $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$.² As shown in Fig. 1(b) the stacks are arranged so as to lead to the formation of neutral layers of cations and anions parallel to the ac plane of the unit cell at $y = 0.0, 0.5, 1.0$ etc. In contrast to this simple pattern, the forms of association seen in **2**·MeCN and **3**·MeCN are more complex.

In **2**·MeCN·H₂O slightly slipped stacks are observed, in which the metal coordination planes are near parallel and are inclined at *ca.* 18° to the crystallographic b axis along which the stack extends. Surprisingly these columns do not consist of alternating anions and cations but of near perfectly eclipsed pairs of mono-anions, weakly dimerised to form $[\{\text{Pd}(\text{mnt})_2\}_2]^{2-}$ units in which the shortest metal...metal contacts are observed [Pd(2)···Pd(2a) 3.426(2) Å, Pd(2)···PdS₄ plane 3.405 Å], which interleave [Pd(2)···Pt(1a) 3.530(2) Å, Pd(2)···PtC₄ plane 3.38 Å] strongly slipped pairs of dications [Pt(1)···Pt(1c) 4.284(1) Å, Pt···PtC₄ plane 3.52 Å]. These stacks are charged carrying a net positive charge per $[\text{Pt}(\text{CNMe})_4][\text{Pd}(\text{mnt})_2]$ unit. In addition the cationic columns are linked by weak [Pd(1)···S(8) 3.84 Å] interactions to a second, looser, dimer of mono-anions [Pd(1)···Pd(1a) 4.240(2) Å, Pd(1)···PdS₄ 3.75 Å]. MeCN solvate molecules fill voids in the structure but with no close contacts to neighbouring ions.

Crystals of compound **3** as its acetonitrile solvate, which has identical stoichiometry to that of **2** as far as the metal-containing ions are concerned, have a very different structure.

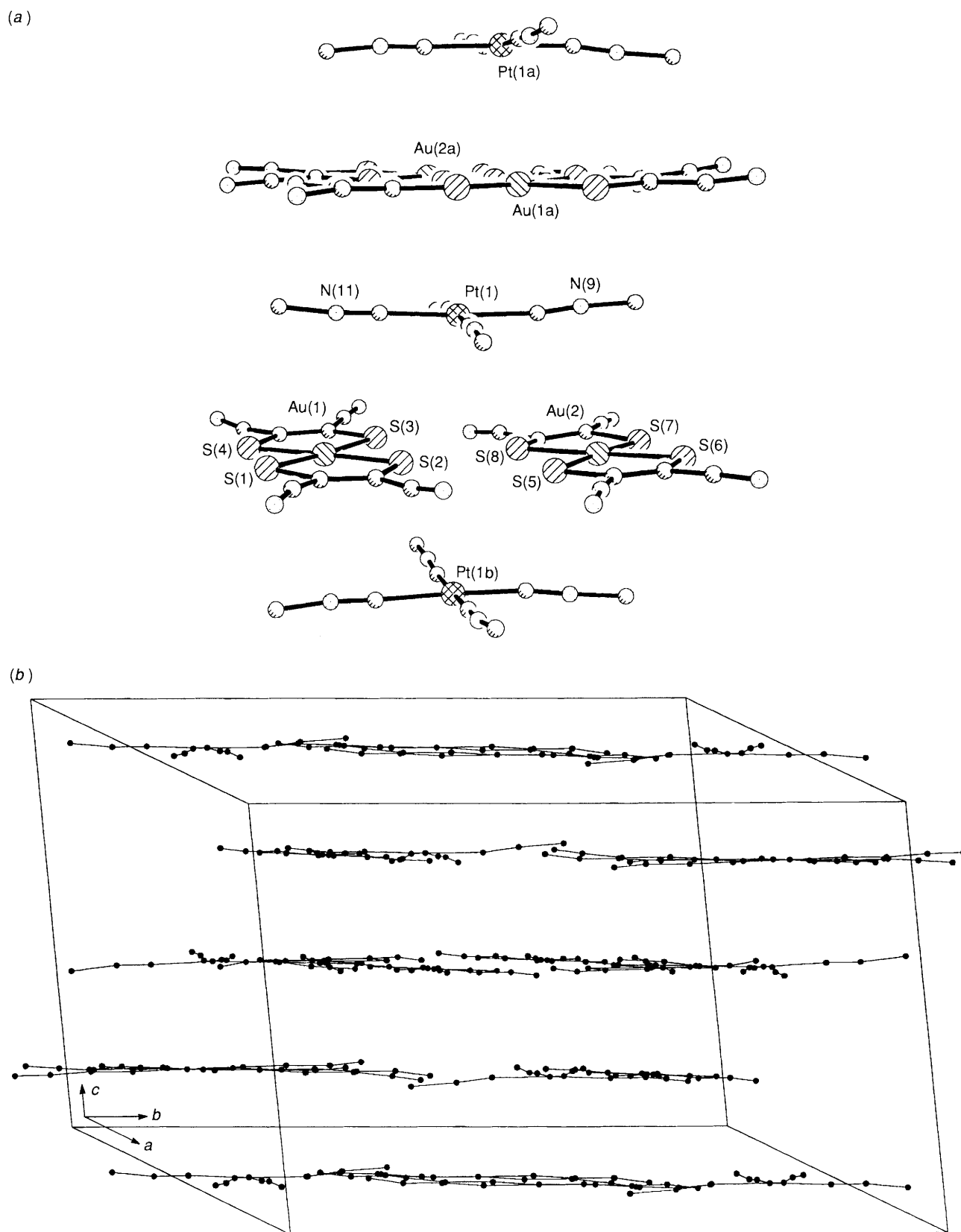


Fig. 3 (a) Geometry of a portion of the linear chain formed by dications and pairs of monoanions in the crystal structure of $[\text{Pt}(\text{CNMe})_4][\text{Au}(\text{mnt})_2]_2 \cdot 3\text{-MeCN}$. Hydrogen atoms and solvent molecules have been omitted for clarity. (b) Part of the crystal structure of 3-MeCN viewed edge-on to the layers formed perpendicular to the columns of ions.

In solid **3**·MeCN, there are *neutral* columns of planar complex ions in which $[\text{Pt}(\text{CNMe})_4]^{2+}$ dications are separated by pairs of $[\text{Au}(\text{mnt})_2]^-$ monoanions, the pairs being formed by edge-to-edge interactions ($\text{S}\cdots\text{S}$ *ca.* 3.75–3.80 Å) rather than the face-to-face interactions seen in **2**. Within the columns the inter-coordination plane distances are close to 3.45 Å [$\text{Pt}(\mathbf{1})\cdots\text{Au}_2\text{S}_8$ 3.424 and 3.463 Å] and the crystallographic *c* axis is roughly perpendicular to these planes (at 82°). The shortest interatomic distances involving the metals between complexes are $\text{Au}\cdots\text{N}$ 3.57 Å and $\text{Pt}\cdots\text{S}$ 3.76 Å. Furthermore the dications lie in almost exactly the same plane as the pairs of anions of neighbouring neutral columns, thereby generating neutral sheets essentially perpendicular to the columns. The solvate molecules lie in channels which run through the structure parallel to the stacks. As in the structure of **1** within the layers perpendicular to the stacks the cyano groups of the mnt ligands interdigitate with the CNMe ligands.

The properties of these solid-state compounds and their derivatives, and the effects on crystal structure of the geometry of the complex ions, remain to be explored. What is clear however is that our synthetic strategy allows systematic

control of stoichiometry, promises access to functionalised derivatives (*e.g.* with other dithiolate ligands or isocyanides) and has already allowed preparation of new highly anisotropic solids. Moreover, the use of square-planar dithiolene anions as one unit of the salts introduces potential redox activity (and hence conductivity) and, as in $[\text{Pd}(\text{mnt})_2]^-$, paramagnetic centres (and unusual magnetic behaviour).

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References

- 1 For example see *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum Press, New York, 1982, and references therein.
- 2 N. Atoji, J. W. Richardson and R. E. Rundle, *J. Am. Chem. Soc.*, 1957, **79**, 3017.