

Linear Chain Metal Compounds: $[M(\text{mnt})(\text{CNMe})_2]$ [$M = \text{Ni, Pd, Pt}$; $\text{mnt} = 1,2\text{-S}_2\text{C}_2(\text{CN})_2$]

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Planar complexes $[M(\text{mnt})(\text{CNMe})_2]$ of the nickel triad metals show two different stacking motifs in the solid state, characterised by X-ray crystal structure analysis and EXAFS spectroscopy, in which inter-complex interactions lead to pseudo-one-dimensional molecular aggregates.

In the preceding communication we described the synthesis and structures of a number of salts containing square-planar coordinated metal complex anions and cations. The object of this work was the development of new routes to, and new structure types for, low-dimensional solids based on molecular transition metal complexes linked into chains by inter-complex interactions. Coulombic forces play a large part in the cohesion of salts. It was therefore of interest to us to explore the different features of structures based on neutral building blocks. Serendipitous preparation of such materials in the course of the reaction chemistry described in the preceding paper led us to undertake a more systematic study.

The reaction of the dication $[\text{Pd}(\text{CNMe})_4]^{2+}$ with the dianion $[\text{Ni}(\text{mnt})_2]^{2-}$ led not to the expected complex salt $[\text{Pd}(\text{CNMe})_4][\text{Ni}(\text{mnt})_2]$ (see preceding communication) but rather to brown needles of a compound **1** with lower symmetry, as evidenced by the IR spectrum in the isocyanide and cyano region $[\nu(\text{CN})/\text{cm}^{-1}$ (Nujol) at 2271s, 2257vs, 2245s, 2220m, 2209m and 2190w]. The identity of the product was deduced from an X-ray structure analysis using crystals obtained directly from the reaction by slow codiffusion of the reagents.

On the basis of the X-ray diffraction analysis compound **1** is best formulated as $[\text{Pd}_{0.42}\text{Ni}_{0.58}(\text{mnt})(\text{CNMe})_2]$, *i.e.* with a structure in which nickel and palladium occupy the same site within the crystallographic unit cell with refined occupancies of 0.58(1) and 0.42(1) respectively. The structure (Fig. 1) consists of eclipsed planar $[M(\text{mnt})(\text{CNMe})_2]$ units whose mean plane is inclined at 39.5° to the short crystallographic *b* axis [of 4.674(2) Å]. As a result the metal...metal contacts in this structure are the same length as the *b* axis but the inter-coordination-plane distances are 3.565 Å and the shortest interatomic distances involving the metals are $M\cdots S$ 3.712 Å. No evidence for local ordering or the existence of

superlattice reflections was observed in the diffraction pattern which was consistent with random occupancy of the two metals in the single site. The overall crystal structure contains a herring-bone type packing of the columns of neutral molecules [see Fig. 1(b)].

More detail on the local geometry was derived from EXAFS spectroscopic studies† on solid **1** conducted at the Ni and Pd-K edges. These gave metal–ligand distances‡ which are not averaged owing to the site disorder [*cf.* average M–S 2.201(2)

† Nickel and palladium K and platinum L_{III} absorption edge EXAFS data were collected at the Daresbury SRS on stations 7.1 and 9.2 in transmission mode using procedures as described previously.³ Model fitting was carried out with EXCURV90,⁴ using curved wave theory allowing for multiple scattering to third order for the nitrogen (and methyl carbon) atom shells of the cyanide (and isocyanide) ligands. Only shells significant at the 99% level⁵ were included in final models. Full details of the final models employed for compounds **1–4** are available from the authors on request. *Ab initio* phase shifts and back-scattering factors using spherical wave theory with 25 *l* values were used throughout. The use of these phase shifts and the values used for the proportion of absorption leading to EXAFS ('AFAC' = 0.8) and the magnitude of inelastic effects modelled by an imaginary potential ('VPI' = -4.0 eV), were checked using fits to data for compounds **2** and **3** in the solid state. Important intramolecular distances for compounds **1–3** in the solid state at 298 K and for **4** at 78 K include the following:

Compound	<i>d</i> (M–S)/Å	<i>d</i> (M–C)/Å
1 (M = Ni)	2.141(2)	1.859(4)
1 (M = Pd)	2.267(2)	1.979(4)
2 (M = Ni)	2.138(3)	1.844(6)
3 (M = Pd)	2.271(2)	1.984(5)
4 (M = Pt)	2.264(1)	1.946(3)

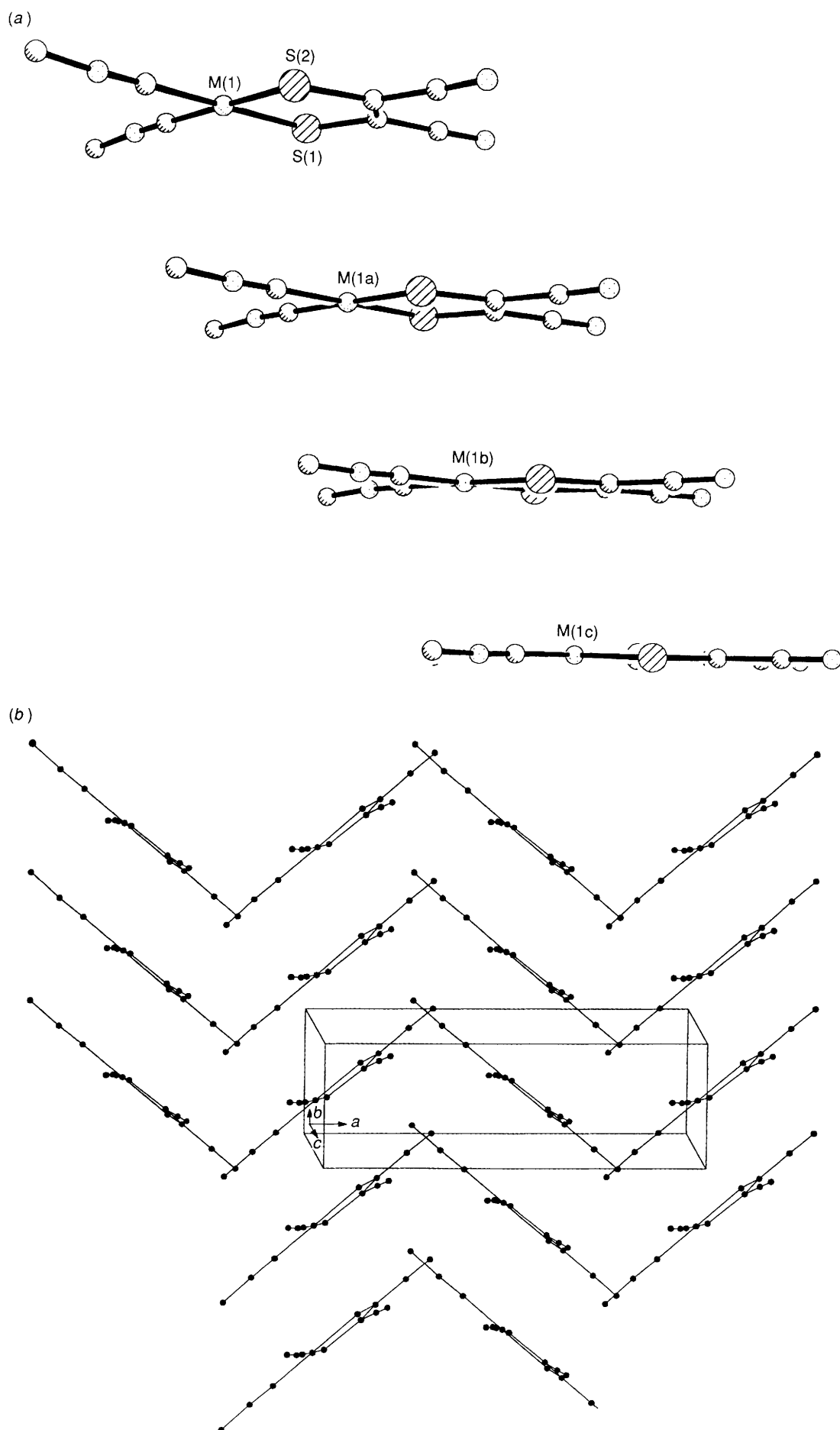


Fig. 1 (a) Geometry of portion of the linear chain formed by the molecules of $[\text{Ni}_{0.58}\text{Pd}_{0.42}(\text{mnt})(\text{CNMe})_2]$ **1** in its crystal structure. The structure of $[\text{Ni}(\text{mnt})(\text{CNMe})_2]$ **2** is essentially identical. The view is approximately perpendicular to the unit cell *b* axis. Hydrogen atoms have been omitted for clarity. (b) A slab (thickness 6 Å) of the crystal structure of **1** viewed perpendicular to the symmetry-related stacks present, showing the 'herring-bone' packing of molecules.

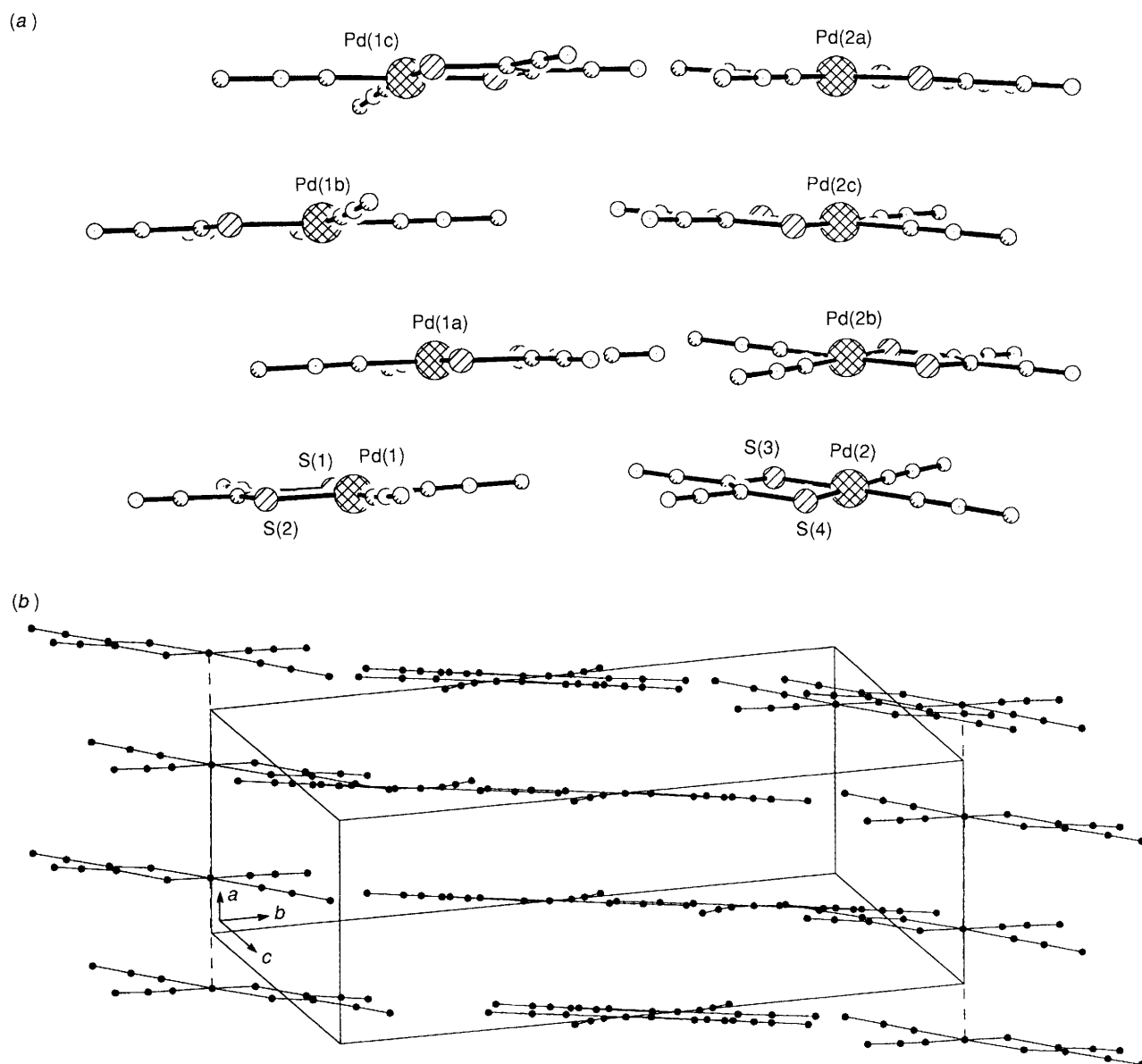


Fig. 2 (a) Geometry of portions of the two independent linear chains formed by the molecules of $[\text{Pd}(\text{mnt})(\text{CNMe})_2]$ **3** in its crystal structure. The view is approximately perpendicular to the unit cell a axis. Hydrogen atoms have been omitted for clarity. (b) Part of the crystal structure of **3** viewed edge-on to the layers of molecules formed by the two independent stacks.

and M–C 1.907(7) Å by X-ray diffraction \ddagger] and which are in good agreement with the average values found by X-ray

\ddagger *Crystal data for 1*: $\text{Ni}_{0.58}\text{Pd}_{0.42}\text{S}_2\text{C}_8\text{N}_4\text{H}_6$, $M = 301.02$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 19.238(8)$, $b = 4.674(2)$, $c = 13.904(6)$ Å, $V = 1250.2(9)$ Å³, $Z = 4$, $D_c = 1.599$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 1.832$ mm⁻¹, $F(000) = 598$, $T = 298$ K.

For **2**: $\text{NiS}_2\text{C}_8\text{N}_4\text{H}_6$, $M = 281.0$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 19.140(4)$, $b = 4.643(1)$, $c = 13.872(2)$ Å, $V = 1232.8(4)$ Å³, $Z = 4$, $D_c = 1.514$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 1.885$ mm⁻¹, $F(000) = 568$, $T = 298$ K.

For **3**: $\text{PdS}_2\text{C}_8\text{N}_4\text{H}_6$, $M = 328.68$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.427(1)$, $b = 8.174(2)$, $c = 20.772(4)$ Å, $\alpha = 82.450(15)$, $\beta = 88.051(15)$, $\gamma = 80.927(15)^\circ$, $V = 1234.5(4)$ Å³, $Z = 4$, $D_c = 1.769$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 1.814$ mm⁻¹, $F(000) = 640$, $T = 298$ 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 $R = 0.028$, 0.031 and 0.028 for **1**, **2** and **3** respectively for 1010, 950 and 3390 unique, absorption-corrected, observed [$I > 4\sigma(I)$] intensity data. The assignment of absolute structure for **1** and **2** was made by refinement of the Rogers parameter η . 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.

crystallography for the mono-metal compounds $[\text{M}(\text{mnt})(\text{CNMe})_2]$ **2**; $M = \text{Ni}$ and **3**; $M = \text{Pd}$ (see below).

The new complex $[\text{Ni}(\text{mnt})(\text{CNMe})_2]$ **2** was prepared by a method similar to that used² for the synthesis of $[\text{Pd}(\text{mnt})(\text{CNMe})_2]$ **3** and $[\text{Pt}(\text{mnt})(\text{CNMe})_2]$ **4**, namely by the addition of MeNC and then $\text{Na}_2[\text{mnt}]$ to an aqueous solution of NiCl_2 . Crystals of $[\text{Ni}(\text{mnt})(\text{CNMe})_2]$ **2** are strictly isostructural with those of **1** with only minor differences in the lattice dimensions [notably b and hence the shortest Ni...Ni = 4.643(1) Å and the Ni...NiS₂C₂ plane distance = 3.554 Å; average Ni–S 2.145(2) and Ni–C 1.848(7) Å]. In contrast the palladium complex $[\text{Pd}(\text{mnt})(\text{CNMe})_2]$ **3** has a completely different crystal structure although of course a very similar molecular structure [average Pd–S 2.277(2) and Pd–C 1.996(5) Å]. In **3** there are two different types of stacks of molecules, the metal coordination planes in each stack being approximately perpendicular to the crystallographic a axis of the triclinic cell (Fig. 2). In each case the stack consists of pairs of molecules related by inversion centres translated along the unit cell a axis. In one column [Pd(2), Pd(2a), Pd(2b), Pd(2c) in Fig. 2] the molecules lie with the palladium atoms almost directly above one another [Pd...Pd 3.699(1) and 3.729(1) Å], with the Pd coordination planes separated by 3.58 and 3.63 Å.

In contrast, in the second column the molecules are substantially slipped relative to one another leading to longer Pd...Pd distances [4.105(2) and 4.846(2) Å] although the Pd coordination planes are mutually parallel and separated by only 3.41 and 3.55 Å. These latter coordination planes are near coplanar with those of the palladium atoms of the first column (being inclined at an angle of 8.7°) leading to a structure in which there are sheets of molecules of **3** in planes approximately perpendicular to the *a* axis [see Fig. 2(b)].

All attempts to obtain crystals of the platinum analogue of **2** and **3**, [Pt(mnt)(CNMe)₂] **4**, have thus far proved fruitless. EXAFS studies† of compounds **1–4** gave dimensions about the metal atoms in good agreement with the available diffraction data but did not provide unambiguous evidence as to the nature of the intermolecular interactions. The anisotropic nature of these structures and the variation of structure type with metal prompt us to explore both the relationship of crystal and molecular structure and the properties of the solids. The outcome of these studies will form the basis of future publications.

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