A novel eight-membered Cu_4I_4 ring supported by sulfur atoms of an $M(mnt)_2$ moiety: syntheses and crystal structures of $(NBu^n{}_4)_2[M(mnt)_2Cu_4I_4]$ (M = Ni, Pd, Pt; mnt = 1,2-dicyano-1,2-ethylenedithiolato) with doubly-bridged one-dimensional chain structures

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Crystal structure analyses of the title compounds revealed that they have almost the same structure with a novel eight-membered Cu_4I_4 ring supported by an $M(mnt)_2$ moiety, two cyano groups out of the four of which coordinate to two copper(I) ions in neighboring molecules, resulting in the formation of a unique doubly-bridged one-dimensional chain structure.

There is considerable growing interest in copper(I) coordination polymer chemistry due to a variety of fascinating multi-dimensional structures and the possibility for developing new functional materials.[1] Molecules having cyano groups sometimes can be good bridging ligands since their moderate coordination abilities to copper(I) ions make it possible to obtain single crystals suitable for X-ray analyses.[2] In order to add functionality to copper(I) polymers, we chose $[M(mnt)_2]^{n-}$ (M = Ni, Pd, Pt; mnt = 1,2-dicyano-1,2-ethylenedithiolato; n = 1, 2) as bridging ligands for copper(I) ions. Conducting and magnetic properties of compounds containing $[M(mnt)_2]^{n-}$ moieties have been extensively studied.[3] However, mixed metal coordination compounds containing a $M(mnt)_2$ moiety are rare. A series of compounds with μ-bridging silver(I) ions, $[Ag(PR_3)_2]_2M(mnt)_2$,[4] is the only known example so far to our knowledge.[5] Here, we report the syntheses and structures of new mixed metal coordination polymer compounds, $(NBu^n{}_4)_2[M(mnt)_2Cu_4I_4]$ (M = Ni **1**, Pd **2**, Pt **3**), which represent the first examples of $M(mnt)_2$ functioning as a bridging ligand. They have novel eight-membered Cu_4I_4 rings supported by sulfur atoms of $M(mnt)_2$.

Reddish black crystals of **1**–**3** were prepared by reaction of CuI and $(NBu^n{}_4)_2[M(mnt)_2]$[6] in THF at room temperature followed by diffusion with diethyl ether.† Single crystal X-ray structure analyses of **1**–**3**‡ showed that all three compounds have essentially the same structure. Fig. 1 displays an ORTEP drawing of the molecular structure of **1** with the atom numbering scheme. The $Ni(mnt)_2$ moiety retains its original planar structure and there is no significant change in Ni–S bond lengths compared to those of the parent compound. One side of the $Ni(mnt)_2$ moiety is covered by an eight-membered ring of Cu_4I_4 with copper atoms being close to the mnt sulfur atoms (Cu–S 2.35 Å av.). Each copper atom is located almost directly above the corresponding sulfur atom, and not between two sulfur atoms like for the bridging mode observed in $[Ag(PR_3)_2]_2M(mnt)_2$ compounds.[4] Within the eight-membered ring, copper and iodine atoms are connected alternately with Cu–I distances ranging from 2.517(3) to 2.643(1) Å. This eight-membered ring is considered to be a new isomeric form of the Cu_4X_4 arrangement with cubane- and step-like conformations having been reported previously for $[Cu_4X_4L_n]$ complexes.[7] The molecule has a C_2 symmetry axis lying normal to the $Ni(mnt)_2$ plane through the Ni atom. There are two independent copper atoms, Cu(1) and Cu(2): the former has a distorted tetrahedral coordination with two I, one S and one N atom while the latter§ shows a distorted trigonal planar coordination with two I and one S atom. It should be noted that the Ni(1)···Cu(2) distance of 2.887(4) Å is shorter than the sum of the van der Waals radii, indicating a weak interaction.

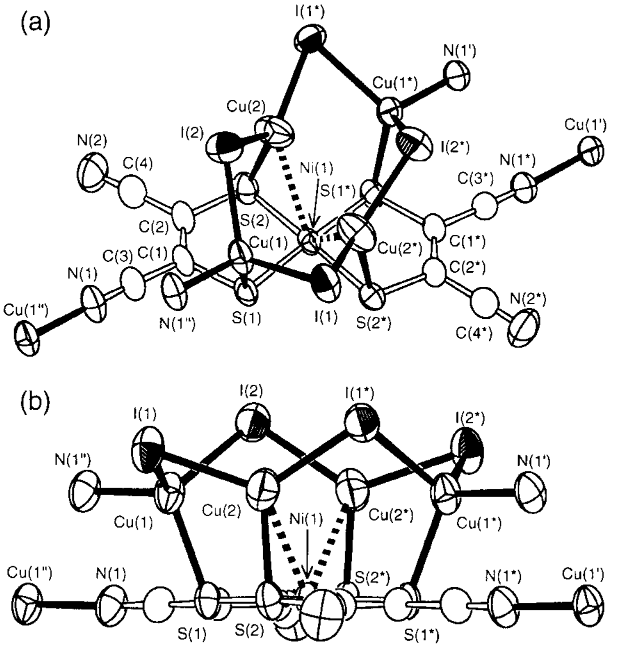

Fig. 1 (a) Top and (b) side views of ORTEP drawings of the $[Ni(mnt)_2Cu_4I_4]^{2-}$ dianion in **1**.

The nitrogen atom coordinating to the Cu(1) atom is from the cyano group in the neighboring molecule. This means that two cyano groups out of four in a molecular unit of **1** coordinate to two Cu(1) atoms in neighboring molecules, resulting in the formation of a doubly-bridged one-dimensional chain structure as shown in Fig. 2. This is the first example in which a $Ni(mnt)_2$ moiety acts as a bridging ligand in a coordination polymer. The chains run parallel along the c-axis direction, being separated from each other by bulky $NBu^n{}_4{}^+$ cations as shown in Fig. 3. A pressed pellet of **1** after exposure to iodine vapor for seven days gave an electrical conductivity of 1.6×10^{-3} S cm^{-1} at room

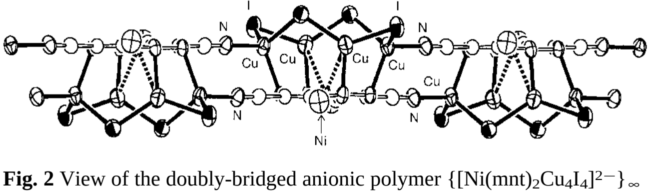

Fig. 2 View of the doubly-bridged anionic polymer $\{[Ni(mnt)_2Cu_4I_4]^{2-}\}_\infty$ in **1**.

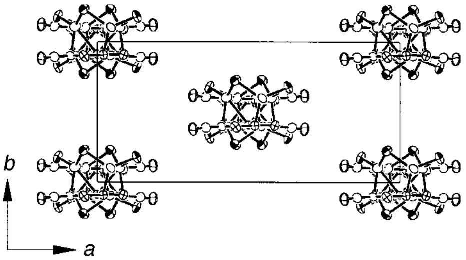

Fig. 3 Molecular packing of **1** viewed from the *c*-axis direction. The $\mathrm{NBu^n{}_4}^+$ cations are omitted for clarity.

temperature, while the undoped material is an insulator. In spite of the polymeric structure in the solid state, **1** is soluble in THF. A ^{13}C NMR spectrum measured in d_8-THF shows two peaks at δ 115.4 and 126.0 which are shifted from those observed for $\mathrm{Ni(mnt)_2}^{2-}$ (δ 118.1 and 125.4). These shifts indicate the presence of a slightly modified $\mathrm{Ni(mnt)_2}^{2-}$ framework, probably $[\mathrm{Ni(mnt)_2Cu_4I_4}]^{2-}$, in solution. The Cu–S bonds in **1** are expected to be strong enough to be maintained in THF solution whereas Cu–N(cyano) bonds are expected to dissociate. The weakness of the Cu–N(cyano) bond is exemplified by the observation of uncoordinated cyano groups in the crystal structure.

The structures of **2** and **3** are almost the same as that of **1**. The main differences are the M···Cu(2) distances which are 2.947(2) and 2.856(4) Å for Pd(1)···Cu(2) and Pt(1)···Cu(2), respectively. These distances are also shorter than the sum of the van der Waals radii, indicating weak interactions between these metal atoms. The consistency of the framework in changing the center metal atom indicates that the Cu–S interaction is dominant in determining the framework of their molecular units. Effects of changing cations as well as changing halogens on the molecular framework and the conductivity are under investigation.

In summary, we have characterized novel mixed metal compounds **1**–**3**, which have an eight-membered $\mathrm{Cu_4I_4}$ ring supported by an $\mathrm{M(mnt)_2}$ moiety. Two cyano groups out of four in the $\mathrm{M(mnt)_2}$ moiety coordinate to two Cu(I) ions in neighboring molecules, resulting in the formation of a unique doubly-bridged one-dimensional chain structure. This is the first example showing that the $\mathrm{M(mnt)_2}$ moiety acts as a bridging ligand for metal ions.

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Notes and references

† *Procedure* for **1**: a suspension of $\mathrm{(NBu^n{}_4)_2[Ni(mnt)_2]}$ (41.2 mg, 0.05 mmol) and CuI (38 mg, 0.2 mmol) in THF (15 ml) was stirred for 24 h at room temp. The resultant solution was filtered and the filtrate was poured into a glass tube. The same amount of ether was added slowly and the tube was sealed. After standing for one week at room temp. reddish black crystals of $\mathrm{(NBu^n{}_4)_2[Ni(mnt)_2Cu_4I_4]}$ **1** were obtained (14.7 mg, 18.5%). Similar methods were used for the preparation of **2** and **3**. Reddish black crystals of $\mathrm{(NBu^n{}_4)_2[Pd(mnt)_2Cu_4I_4]}$ **2**, (20.1 mg, 24.6%) and $\mathrm{(NBu^n{}_4)_2[Pt(mnt)_2Cu_4I_4]}$ **3**, (21.7 mg, 25.2%) were obtained.

‡ *Crystal data*: for **1**: $\mathrm{I_4NiCu_4S_4N_6C_{40}H_{72}}$; M = 1585.79, monoclinic, space group $C2/c$ (no. 15), a = 29.22(2), b = 11.457(3), c = 20.430(5) Å, β = 121.87(2)°, U = 5808(4) Å^3, Z = 4, μ(Mo-Kα) = 4.062 mm^{-1}, 6665 unique reflections (R_{int} = 0.033), of which 4529 were observed [$I > 2\sigma(I)$]. At final convergence $R1$ [$I > 2\sigma(I)$] = 0.0402, $wR2$ (all data) = 0.1339 for 273 variables, S = 1.262; For **2**: $\mathrm{I_4PdCu_4S_4N_6C_{40}H_{72}}$; M = 1633.49, monoclinic, space group $C2/c$ (no. 15), a = 29.260(5), b = 11.458(7), c = 20.714(4) Å, β = 122.57(1)°, U = 5852(3) Å^3, Z = 4, μ(Mo-Kα) = 4.017 mm^{-1}, 6727 unique reflections (R_{int} = 0.035), of which 3933 were observed [$I > 2\sigma(I)$]. At final convergence $R1$ [$I > 2\sigma(I)$] = 0.0447, $wR2$ (all data) = 0.1391 for 273 variables, S = 1.074. For **3**: $\mathrm{PtI_4Cu_4S_4N_6C_{40}H_{72}}$; M = 1633.49, monoclinic, space group $C2/c$ (no. 15), a = 29.179(3), b = 11.462(4), c = 20.735(2) Å, β = 122.602(6)°, U = 5841(1) Å^3, Z = 4, μ(Mo-Kα) = 6.028 mm^{-1}, 6706 unique reflections (R_{int} = 0.058), of which 4201 were observed [$I > 2\sigma(I)$]. At final convergence $R1$ [$I > 2\sigma(I)$] = 0.0435, $wR2$ (all data) = 0.1040 for 273 variables, S = 0.982. All data collections were performed on a Rigaku AFC5R or AFC7R diffractometer using the ω–2θ scan technique ($2\theta_{\mathrm{max}}$ = 55.0°). The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of a least-squares refinement converged including the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. CCDC 182/1155. See http://www.rsc.org/suppdata/cc/1999/455/ for crystallographic files in .cif format.

§ The second copper atom was found to be disordered. 92% at Cu(2) and 8% at Cu(3) which is dislocated 0.91 Å from Cu(2) atom towards [I(2*)].

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