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Preparation and characterization of metal complexes with an extended TTF dithiolato ligand, bis(propylenedithiotetrathiafulvalenedithiolato)-nickelate and -cuprate†

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Novel monoanionic nickel and dianionic copper complexes with the extended TTF dithiolato ligand, propylenedithiotetrathiafulvalenedithiolate [$\text{ptdt}^{2-} = (S_8C_9H_6)^{2-}$], have been synthesized. Characterization of monoanionic tetraphenylphosphonium and tetramethylammonium salts of $\text{Ni(ptdt)}_2{}^-$ and the dianionic tetraphenylphosphonium salt of $\text{Cu(ptdt)}_2{}^{2-}$ have been performed, using cyclic voltammetry, electrical resistivity measurements, magnetic susceptibility measurements and X-ray crystal structure determination. The geometries around the Ni atoms are almost square planar. In both Ni complexes, one of the extended ligands of $\text{Ni(ptdt)}_2{}^-$ is overlapping with that of the adjacent anion separated by about half of the unit of the molecule, forming a one-dimensional chain. The adjacent chains are connected by transverse short S···S contacts. $\text{Cu(ptdt)}_2{}^{2-}$ has a distorted tetrahedral geometry around the Cu atom and the dihedral angle between the planes of the dithiolato ligand is 54.2°. The crystal structures of $\text{Ni(ptdt)}_2{}^-$ and $\text{Cu(ptdt)}_2{}^{2-}$ complexes show the possibility of novel 2D or 3D intermolecular contacts through ptdt ligands. The complex $[\text{Me}_4\text{N}][\text{Ni(ptdt)}_2]\cdot\text{Me}_2\text{CO}$ is a semiconductor with a room temperature conductivity of 1.4×10^{-3} S cm^{-1} and activation energy of 9.9×10^{-2} eV.

In recent investigations of molecular conductors and superconductors, there is increasing interest in molecules with extended π-conjugation frameworks.[1] This is because such molecules can stabilize multi-cation states and increase intermolecular interactions. Furthermore metal complexes with extended π ligands are expected to open a new field of molecular conductors owing to the variety of central metal atoms and possible modifications of the extended π-conjugation ligands. However, only a few conducting metal complexes with elongated dithiolene-type ligands have been prepared.

Recently, Narvor *et al.* have reported the synthesis, structure and conductive properties of nickel complexes of tetrathiafulvalenedithiolate, which exhibited a fairly high conductivity in the neutral state.[2] However bulky terminal SR (R = alkyl) groups sticking out from the molecular plane might prevent close intermolecular S···S contacts. Nakano *et al.* have prepared metal complexes of ethylenedithiotetrathiafulvalenedithiolate ($C_8H_4S_8{}^{2-}$, etdt^{2-}).[3] The etdt metal complexes, however, have poor solubility as is often the case for molecules with extended π-conjugation, which is unfavorable for obtaining good single crystals. Thus a crystal structure of an M(etdt)_2 compound has not been reported. Therefore, an improvement of the solubility seems to be necessary for further development.

In order to increase solubility, we prepared a new ligand which incorporates an additional methylene group into etdt^{2-}. One of the important requirements for constituent molecules of the molecular conductors is good planarity of the molecules. However in metal complexes with tetrathiafulvalenedithiolate, the planarity of the whole molecule may be not so important. The long ligand will be preferably favorable for increasing overlapping between the molecules. Each of the two tetrathiafulvalene moieties joined to the central transition metal atom will be able to produce S···S networks even if the metal complex molecule has a twisted conformation. Thus transition metal complexes with elongated π-ligands will provide new types of molecular conducting systems. Here, we report the preparation of a new ligand, propylenedithiotetrathiafulvalenedithiolate ($C_9H_6S_8{}^{2-}$, ptdt^{2-}) and the crystal structures of a precursor of the ligand $\text{ptdt(CH}_2\text{CH}_2\text{CN)}_2$, the tetraphenylphosphonium salt of a square-planar Ni complex, $(\text{Ph}_4\text{P})[\text{Ni(ptdt)}_2]\cdot1.4\text{Me}_2\text{CO}$ **1**, the tetramethylammonium salt of the Ni complex, $(\text{Me}_4\text{N})[\text{Ni(ptdt)}_2]\text{Me}_2\text{CO}$ **2** and a tetrahedral Cu complex, $(\text{Ph}_4\text{P})_2[\text{Cu(ptdt)}_2]\cdot1.2\text{Me}_2\text{CO}$ **3**.

Experimental

Synthesis and crystal growth

Reagent-grade tetrahydrofuran was purified and distilled over sodium–benzophenone prior to use. Methanol was refluxed over Mg and distilled; other solvents and chemicals were used as received. Schlenk techniques were used in carrying out manipulations under argon atmosphere. NMR spectra were measured on a JEOL JNM-EX 270 Model spectrometer. Cyclic voltammetry data were recorded by BAS CV-60W. The ptdt^{2-} ligand was synthesized as shown in Scheme 1.

Initially, we used *p*-acetoxybenzyl as the protecting group in cross-coupling to synthesize the unsymmetrical precursor of ptdt^{2-}. Gemmell *et al.*[4] and Misaki *et al.*[5] reported that their unsymmetrical TTF derivatives were obtained in high yields using this protecting group. In our case, however, the cross-coupling method gave more than five products and our target molecule was obtained in only 4.6% yield. We then used cyanoethyl as the protecting group, and succeeded in obtaining **7** in high yield.

Preparation of 4,5-propylenedithio-1,3-dithiole-2-thione 4. $(\text{Et}_4\text{N})_2[\text{Zn(dmit)}_2]$ (43 g) was dissolved in 200ml of acetonitrile and 26 g of 1,3-dibromopropane was added and the solution stirred for 2 d at room temperature. The resulting orange precipitate was filtered off and to the residue dichloromethane was added and the solution was filtered. Activated charcoal (0.2 g) was added to the filtrate and the solution was

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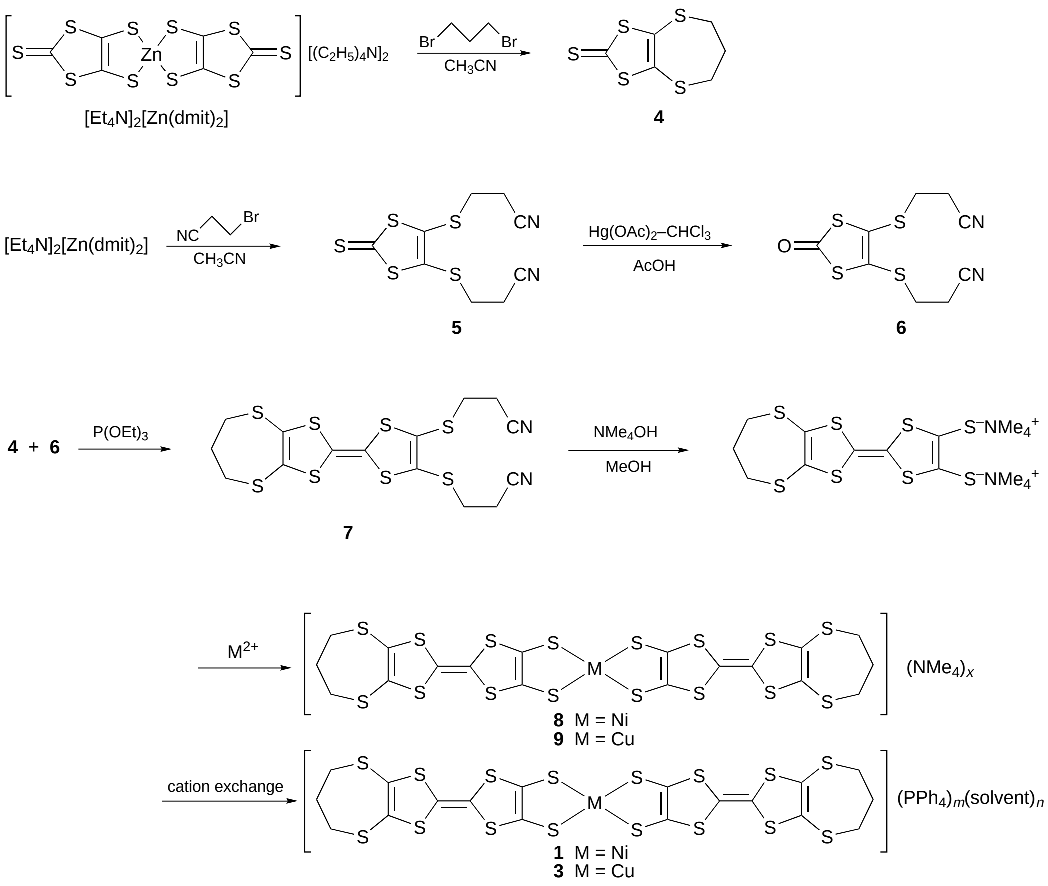

Scheme 1

refluxed for 30 min. The solution was filtered and ethanol was added. Yellow crystals were obtained from this solution at −20 °C. Yield 19.6g. {68.7% based on $(Et_4N)_2[Zn(dmit)_2]$}.

Preparation of 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione 5. $(Et_4N)_2[Zn(dmit)_2]$ (10 g) was dissolved in 80 ml of acetonitrile and 7 g of 3-bromopropionitrile was added to the solution and was refluxed for 1 h. The solution was filtered off and then concentrated. After adding 125 ml of dichloromethane, the solution was washed three times with water. Then the solution was dried with magnesium sulfate. After removing the drying agent, ethanol was added at −20 °C. Brown yellow needle crystals were obtained. Yield 5.6 g. {66.1% based on $(Et_4N)_2[Zn(dmit)_2]$}.

4,5-Bis(2-cyanoethylthio)-1,3-dithiole-2-one 6. To 4.8 g of **5** and 12.1 g of $Hg(CH_3COO)_2$ in a 300 ml flask were added 160 ml of chroloform–acetic acid (3:1). The solution was stirred at room temperature overnight. A white precipitate was obtained and filtered off using Celite. The filtered solution was washed with water, saturated $NaHCO_3$ aqueous solution, water and dried with Na_2SO_4. After removing the drying agent, the filtrate was concentrated and ethanol was added at −20 °C. Milky white crystals were obtained. Yield 3.7 g. (83.7% based on **5**).

2,3-Bis(2-cyanoethylthio)-6,7-propylenedithiotetrathiafulvalene 7. To 4.4 g of **4** and 3.0 g of **6** in a 200 ml flask under an argon atmosphere was added freshly distilled $P(OC_2H_5)_3$ (130 ml) under flushing argon. The reaction mixture was then raised to 110 °C. After reaction for 1 h, the red solution was cooled to room temperature and a precipitate was obtained at −20 °C. The precipitate was dissolved into dichloromethane and **7** was isolated by dichloromethane silica gel column chromatography. The solution was concentrated, ethanol added and cooled to −20 °C. Orange yellow needle crystals were obtained. Yield 3.1 g. (60.5% based on **6**) (Found: C, 37.48; H, 2.95; N, 5.84; S, 53.30. $C_{15}H_{14}N_2S_8$ requires C, 37.63; H, 2.95; N, 5.85; S, 53.58%). ^1H NMR(270 MHz, $CDCl_3$, ref. TMS) δ_H: 3.08 (4H, t, $J=$ 7.1 Hz), 2.76–2.69 (8H, m), 2.41 (2H, m).

Preparation of 8. The following procedures were performed under an argon atmosphere. To 101 mg of **7** in a 300 ml flask was added 22 ml of THF and the solution was cooled to −78 °C using a dry-ice bath. The tetramethylammonium salts were obtained by deprotection with 0.2 ml of Me_4NOH followed by addition of 20 ml of a methanol solution containing 5 mg of $NiCl_2 \cdot 6H_2O$. This solution was stirred overnight and then gradually warmed to room temperature. The obtained precipitate was filtered off and dried *in vacuo* (1 mmHg) and obtained as a brown powder.

Preparation of 9. The following procedures were performed under an argon atmosphere. To 101 mg of **7** in a 300 ml flask was added 22 ml of THF. The solution was then cooled to −78 °C using a dry-ice bath. The tetramethylammonium salts was prepared by deprotection with 0.2 ml of Me_4NOH followed by addition of a 20 ml methanol solution of 5 mg of $CuCl_2 \cdot 2H_2O$ at −78 °C. This solution was stirred overnight and the reaction mixture was warmed gradually to room temperature. The obtained green precipitate was filtered off and dried at 1 mmHg pressure.

Preparation of 1 and 2. Compound **8** and tetraphenylphosphonium bromide were placed in separate compartments of an H-cell under argon. Acetone was poured into the H-cell which was left to stand undisturbed. After 10 days, red plate crystals of **1** were obtained. Crystals of **2** were obtained unexpectedly in the procedure of the electrocrystallization using a current of 0.1 μA in an H-shaped cell with platinum electrodes under an argon atmosphere. The crystals were obtained using 10 mg of **8** and tetramethylammonium bromide and then adding 20 ml of acetone. Black block crystals were collected from the bottom of the H-cell after 3 weeks.

Preparation of 3. Compound **9** and tetraphenylphosphonium bromide were placed in separate compartments of an H-cell under argon. Acetone was poured into the H-cell which was left to stand undisturbed. After 10 days green plate crystals were obtained.

Cyclic voltammetry

Cyclic voltammetry (CV) of $(Me_4N)_2[Cu(ptdt)_2]$ **9** and $(Me_4N)[Ni(ptdt)_2]$ **8** were carried out in acetonitrile using $(Bu_4N)ClO_4$ as supporting electrolyte at 100 mV s^{-1} over the potential range -1.8 to $+2.0$ V. The working and counter electrode were platinum and the reference electrode was Ag/Ag$^+$. $(Me_4N)_2[Cu(ptdt)_2]$ and $(Me_4N)[Ni(ptdt)_2]$ showed qualitatively similar features, but the latter's peak intensities decreased on repeated scanning due to the formation of an insoluble film of the neutral 1 : 1 salt on the electrode. $(Me_4N)_2[Cu(ptdt)_2]$ showed one reduction process at -0.73 V *vs.* SCE and two oxidation process at -0.08 and $+1.15$ V *vs.* SCE, while $(Me_4N)[Ni(ptdt)_2]$ showed peaks at -0.45, -0.15, and $+1.20$ V. The CV data of these compounds indicate that the peak at -0.08 V of the Cu complex appears to correspond to the process $Cu(ptdt)_2{}^{2-} \rightarrow Cu(ptdt)_2{}^{-}$ and the peak at -0.45 V of the Ni complex corresponds to the process $Ni(ptdt)_2{}^{2-} \rightarrow Ni(ptdt)_2{}^{-}$; $Ni(ptdt)_2{}^{2-}$ is readily oxidized to $Ni(ptdt)_2{}^{-}$.

Crystal structure determination

Intensity data were measured on Rigaku AFC-7R, AFC-5R or AFC-6S automated four-circle diffractometers using graphite monochromated Mo-Kα radiation at 23 °C. Empirical absorption corrections were performed. The experimental details and crystal data are listed in Table 1. The structure were solved by direct methods. Anisotropic temperature factors were used for the non-hydrogen atoms and refinement was by full-matrix least-squares methods. The calculated positions of hydrogen atoms [d(C–H) = 0.95 Å] were included in the final calculation except for the solvent molecules. The populations of the solvent molecules are refined initially and fixed in the final calculation. Atomic scattering factors were taken from ref. 6. The absolute configuration of the crystal structure of **7** could not be determined owing to an insufficient number of Friedel pair reflections. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.[7] Full crystallographic details excluding structure factors have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue I. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/54.

Magnetic susceptibility

The magnetic susceptibility was measured at a field of 2 T from 300 to 2 K using a Quantum Design MPMS SQUID magnetometer.

Electrical resistivity

Resistivities were measured by a conventional four-probe method using gold wire (0.02 mm) with gold paint as a contact in the temperature range 300–77 K.

Results and Discussion

Crystal structures

2,3-Bis(2-cyanoethylthio)-6,7-propylenedithiotetrathiafulvalene : ptdt(CH_2CH_2CN)$_2$ 7. The ptdt(CH_2CH_2CN)$_2$ molecule is shown in Fig. 1(*a*) and selected bond lengths are listed in Table 2. Atoms S(1), S(2), S(3), S(4), C(1) and C(2) lie in a good plane A while atoms S(3), S(4), S(5), S(6), S(7), S(8), C(3), C(4), C(5) and C(6) including a tetrathiafulvalene group form a fairly good plane B. Atoms S(7), S(8), C(5), C(6), C(7), C(8) and

Table 1 Crystal and experimental data

	$(Me_4N)[Ni(ptdt)_2]\cdot Me_2CO$	$(Ph_4P)[Ni(ptdt)_2]\cdot 1.4Me_2CO$	$(Ph_4P)_2[Cu(ptdt)_2]\cdot 1.2Me_2CO$	ptdt$(CH_2CH_2CN)_2$
formula	$C_{25}H_{30}S_{16}NNiO$	$C_{47.40}H_{44.60}S_{16}PNiO_{1.40}$	$C_{69.60}H_{59.20}S_{16}CuP_2O_{1.20}$	$C_{15}H_{14}N_2S_8$
crystal color, habit	black, block	red, plate	green, block	orange, needle
crystal system	triclinic	monoclinic	monoclinic	monoclinic
formula mass	932.18	1190.53	1553.29	478.77
a/Å	12.799(1)	28.567(3)	21.420(6)	9.96(3)
b/Å	13.306(1)	8.289(6)	11.826(4)	6.707(9)
c/Å	12.539(2)	25.295(6)	29.18(1)	15.08(5)
α/degrees	91.172(9)			
β/degrees	108.421(7)	108.08(1)	91.20(3)	101.0(2)
γ/degrees	109.482(6)			
V/Å^3	1890.9(4)	5694(3)	7390(3)	988(3)
space group	$P\bar{1}$	$C2/c$	$P2/c$	$P2_1$
Z	2	4	4	2
D_x/g cm^{-3}	1.637	1.389	1.396	1.608
dimensions/mm	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.20 × 0.30 × 0.10	0.30 × 0.10 × 0.60
radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
diffractometer	AFC 5R	AFC 7R	AFC 5R	AFC 6S
μ/cm^{-1}	14.21	9.93	8.34	9.05
$2\theta_{max}$/degrees	55.0	55.0	55.0	55.3
total reflections	9230	7155	18 277	2619
reflections used	8693	7007	17 814	2483
parameters refined	397	288	790	226
scan technique	ω–2θ	ω	ω	ω–2θ
scan width	$1.57 + 0.30\tan\theta$	$0.73 + 0.30\tan\theta$	$0.73 + 0.30\tan\theta$	$1.10 + 0.30\tan\theta$
ω scan speed (degrees min^{-1})	12	16	16	8.0
R, R_w	0.039, 0.034	0.060, 0.058	0.065, 0.055	0.035, 0.036
final shift/error	0.67	0.59	0.06	0.06
residual d/e Å^{-3}	0.34	0.77	0.38	0.24

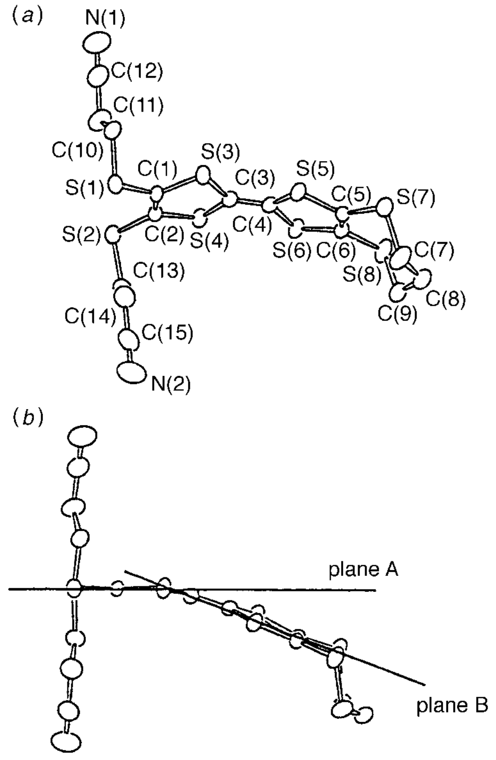

Fig. 1 (*a*) ORTEP drawing[8] of $\mathrm{ptdt(CH_2CH_2CN)_2}$ showing the atom labelling at the 50% probability level. (*b*) Side view of $\mathrm{ptdt(CH_2CH_2CN)_2}$.

Table 2 Selected bond lengths (Å) for $\mathrm{ptdt(CH_2CH_2CN)_2}$

S(1)—C(1)	1.752(6)	S(7)—C(5)	1.738(6)
S(2)—C(2)	1.761(6)	S(7)—C(7)	1.821(8)
S(3)—C(1)	1.751(6)	S(8)—C(6)	1.754(6)
S(3)—C(3)	1.744(6)	S(8)—C(9)	1.847(9)
S(4)—C(2)	1.753(6)	C(1)—C(2)	1.328(8)
S(4)—C(3)	1.771(6)	C(3)—C(4)	1.342(7)
S(5)—C(4)	1.743(6)	C(5)—C(6)	1.310(8)
S(5)—C(5)	1.752(6)	C(7)—C(8)	1.46(1)
S(6)—C(4)	1.752(6)	C(8)—C(9)	1.50(1)
S(6)—C(6)	1.766(6)		

C(9) form a seven-membered heteroring. This seven-membered ring adopts a chair conformation and is tilted from plane B. The central C(3)—C(4) bond length is 1.342(7) Å, which is similar to that of the C=C bond length in neutral bis(propylenedithio)-tetrathiafulvalene [1.341(4) Å].[9] The C(1)—C(2) and C(5)—C(6) distances are 1.328(8) and 1.310(8) Å, respectively, which are shorter than the central C(3)—C(4). Fig. 1(*b*) shows that C(7), C(8) and C(9) show the largest deviation from plane A, of 4.06, 4.27 and 3.91 Å, respectively. The dihedral angle of planes A and B is 21.25 °.

$\mathbf{(Ph_4P)[Ni(ptdt)_2]\cdot 1.4Me_2CO}$ 1. The $\mathrm{Ni(ptdt)_2^-}$ anion is shown in Fig. 2(*a*) and selected bond lengths and angles are shown in Table 3. The $\mathrm{Ni(ptdt)_2^-}$ anion is located on an inversion center. Atoms Ni(1), C(1), C(2), S(1), S(2), S(3) and S(4) lie on a common plane A while the terminal propylenic group is bent. The mean deviation of the atoms from the least-squares plane is *ca.* 0.03 Å. Atoms S(7) and S(8) show the largest deviation from the plane at 2.062 and 1.998 Å. The planarity of the molecule is better than the neutral $\mathrm{ptdt(CH_2CH_2CN)_2}$ molecule [Fig. 2(*b*)]. Atoms S(5), S(6), S(7), S(8), C(5) and C(6) form a plane B with the dihedral angle between planes A and B being 30.13 °. The square-planar Ni complex shows Ni—S distances of 2.154(2) and 2.167(2) Å and S—Ni—S angles of 92.93(7) and 87.07(7) °. The distances and angles of $\mathrm{Ni(ptdt)_2^-}$ are similar to those of the analogous compound in which propylene groups are substituted for the two methyl groups [2.172(5), 2.160(7) Å and 93.3(2), 86.7(2) °, respectively].[2] The central C(3)—C(4) bond length is 1.323(8) Å, which is shorter than that in **7**. The seven-membered heteroring is flexible and those in $\mathrm{ptdt(CH_2CH_2CN)_2}$ **1** and $\mathrm{Ni(ptdt)_2^-}$ **2** bend at S(7) and S(8) in the opposite direction. The crystal structure of **1** [Fig. 3(*a*)] showed that one of the ligands of $\mathrm{Ni(ptdt)_2^-}$ is overlapping with that of the adjacent anion separated by the translation $1/2\boldsymbol{a}-1/2\boldsymbol{b}$, forming a one-dimensional chain along [110]. The overlapping mode of $\mathrm{Ni(ptdt)_2^-}$ is shown in Fig. 3(*b*), which shows that

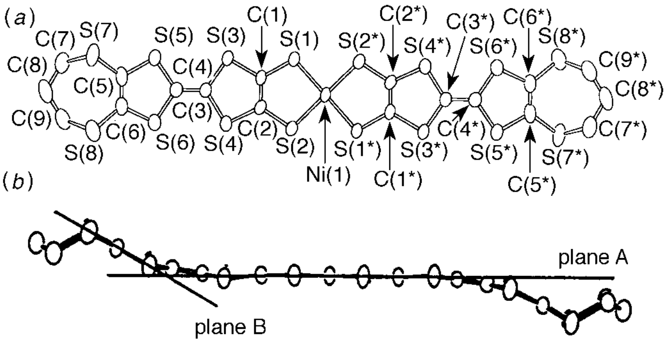

Fig. 2 (*a*) ORTEP drawing of the monoanion $\mathrm{Ni(ptdt)_2^-}$ showing the atom labelling at the 50% probability level. (*b*) Side view of $\mathrm{Ni(ptdt)_2^-}$ in $\mathrm{(Ph_4P)[Ni(ptdt)_2]\cdot 1.4Me_2CO}$.

Table 3 Selected bond lengths (Å) and angles (degrees) for $\mathrm{(Ph_4P)[Ni(ptdt)_2]\cdot 1.4Me_2CO}$

Ni(1)—S(1)	2.154(1)	S(6)—C(6)	1.752(7)
Ni(1)—S(2)	2.167(2)	S(7)—C(5)	1.736(7)
S(1)—C(1)	1.735(7)	S(7)—C(7)	1.809(8)
S(2)—C(2)	1.707(6)	S(8)—C(6)	1.739(8)
S(3)—C(1)	1.765(6)	S(8)—C(9)	1.783(8)
S(3)—C(3)	1.757(7)	C(1)—C(2)	1.345(9)
S(4)—C(2)	1.762(7)	C(3)—C(4)	1.323(8)
S(4)—C(3)	1.773(7)	C(5)—C(6)	1.36(1)
S(5)—C(4)	1.755(7)	C(7)—C(8)	1.49(1)
S(5)—C(5)	1.757(7)	C(8)—C(9)	1.54(1)
S(6)—C(4)	1.765(7)		
S(1)—Ni(1)—S(1)	180.00	S(1)—Ni(1)—S(2)	87.07(7)
S(1)—Ni(1)—S(2)	92.93(7)	S(1)—Ni(1)—S(2)	92.93(7)
S(1)—Ni(1)—S(2)	87.07(7)	S(2)—Ni(1)—S(2)	180.00

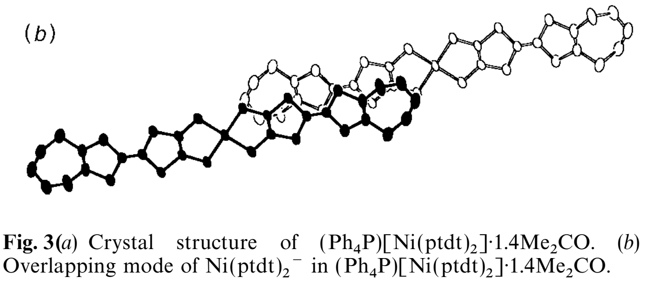

Fig. 3(*a*) Crystal structure of $\mathrm{(Ph_4P)[Ni(ptdt)_2]\cdot 1.4Me_2CO}$. (*b*) Overlapping mode of $\mathrm{Ni(ptdt)_2^-}$ in $\mathrm{(Ph_4P)[Ni(ptdt)_2]\cdot 1.4Me_2CO}$.

the $Ni(ptdt)_2^-$ anion is deviated along the short axis of the molecule. The interplanar distance is *ca.* 3.25 Å on average. The shortest Ni···Ni distance is 14.87 Å while the shortest intermolecular S···S contact is 3.320(3) Å [S(1)···S(7)], corresponding to the transverse S···S short contact with the neighbouring chain. Along the *c*-axis, however, no interaction is expected because the large tetraphenylphosphonium cations prevent the overlap of anions in this direction. The acetone of crystallization shows slight evidence of disorder with one of the C—C bond lengths being a little shorter than the other [C—C = 1.28(2), C=O 1.17(1), C—C 1.57(2) Å] and the angles deviate from 120° [134(1), 112(1), 104(1)°]. The population of the acetone molecule was determined by least-squares refinement as 0.7. The stereoview of anion arrangement of $(Ph_4P)[Ni(ptdt)_2]\cdot 1.4Me_2CO$ is shown in Fig. 4.

$(Me_4N)[Ni(ptdt)_2]\cdot Me_2CO$ 2. The $Ni(ptdt)_2^-$ anion is shown in Fig. 5 and selected bond lengths and angles are listed in Table 4. Atoms Ni(1), C(1), C(2), S(1), S(2), S(3), S(4), C(10), C(11), S(9), S(10), S(11) and S(12) are in a common plane and the terminal propylenic group is bent. The mean deviation of atoms from the least-squares plane is *ca.* 0.07 Å. Atoms S(7), S(8) S(15) and S(16) show the largest deviation from the plane at 1.309, 1.390, 1.202 and 1.512 Å, respectively. Thus the planarity of the molecule is fairly high. The almost square-planar Ni complex shows Ni—S distance of 2.163(1), 2.172(1), 2.174(1) and 2.164(1) Å while the S—Ni—S angles within the five-membered ring are 93.11(4) and 92.86(4)° the remainder are 85.52(4) and 88.72(4)°, respectively. The dihedral angle between the planes S(1)NiS(2) and S(3)NiS(4) is 4.86°. The central C=C bond lengths, C(3)—C(4) and C(12)—C(13) are 1.352(5) and 1.332(5) Å, respectively. The crystal structure of **2** is shown in Fig. 6(*a*). Fig. 6(*b*) shows that one of the ligands of $Ni(ptdt)_2^-$ is overlapping with that of an adjacent anion separated by about half of the unit of the molecule, forming a one-dimensional chain along [101]. The overlapping mode of $Ni(ptdt)_2^-$ is ring-over-bond type and the interplanar distance is 3.30 Å. The overlap in the anion chain of **2** is larger than that in **1**. The shortest intermolecular S···S distance is 3.525(2) Å [S(7)···S(15)], shown in Fig. 6(*a*) as dotted lines. Along the [011] direction, the shortest transverse S···S and Ni···Ni distances are 3.559(2) Å [S(8)···S(13)] and 6.562(1) Å, respectively. The characteristic feature of stacking is short S···S contacts between the neighbouring chains along the [201] direction, which was not observed for **1** owing to the large tetraphenylphosphonium cation. The interaction is expected because the small tetramethylammonium cation does not prevent contacts of the anions in this direction. The acetone of crystallization is not disordered.

Table 4 Selected bond lengths (Å) and angles (degrees) for $(Me_4N)[Ni(ptdt)_2]\cdot Me_2CO$

Ni(1)—S(1)	2.163(1)	S(11)—C(12)	1.763(4)
Ni(1)—S(2)	2.172(1)	S(12)—C(11)	1.748(4)
Ni(1)—S(9)	2.174(1)	S(12)—C(12)	1.767(4)
Ni(1)—S(10)	2.164(1)	S(13)—C(13)	1.758(4)
S(1)—C(1)	1.712(4)	S(13)—C(14)	1.756(4)
S(2)—C(2)	1.717(4)	S(14)—C(13)	1.745(4)
S(3)—C(1)	1.763(4)	S(14)—C(15)	1.748(4)
S(3)—C(3)	1.761(4)	S(15)—C(14)	1.753(4)
S(4)—C(2)	1.767(4)	S(15)—C(16)	1.815(5)
S(4)—C(3)	1.755(4)	S(16)—C(15)	1.747(4)
S(5)—C(4)	1.760(4)	S(16)—C(18)	1.808(5)
S(5)—C(5)	1.765(4)	C(1)—C(2)	1.358(5)
S(6)—C(4)	1.753(4)	C(3)—C(4)	1.352(5)
S(6)—C(6)	1.765(4)	C(5)—C(6)	1.341(5)
S(7)—C(5)	1.739(4)	C(7)—C(8)	1.511(6)
S(7)—C(7)	1.816(5)	C(8)—C(9)	1.519(6)
S(8)—C(6)	1.740(4)	C(10)—C(11)	1.361(5)
S(8)—C(9)	1.806(4)	C(12)—C(13)	1.332(5)
S(9)—C(10)	1.715(4)	C(14)—C(15)	1.343(5)
S(10)—C(11)	1.711(4)	C(16)—C(17)	1.515(6)
S(11)—C(10)	1.759(4)	C(17)—C(18)	1.519(7)
S(1)—Ni(1)—S(2)	93.11(4)	S(2)—Ni(1)—S(9)	88.72(4)
S(1)—Ni(1)—S(9)	175.84(6)	S(2)—Ni(1)—S(10)	176.43(6)
S(1)—Ni(1)—S(10)	85.52(4)	S(9)—Ni(1)—S(10)	92.86(4)

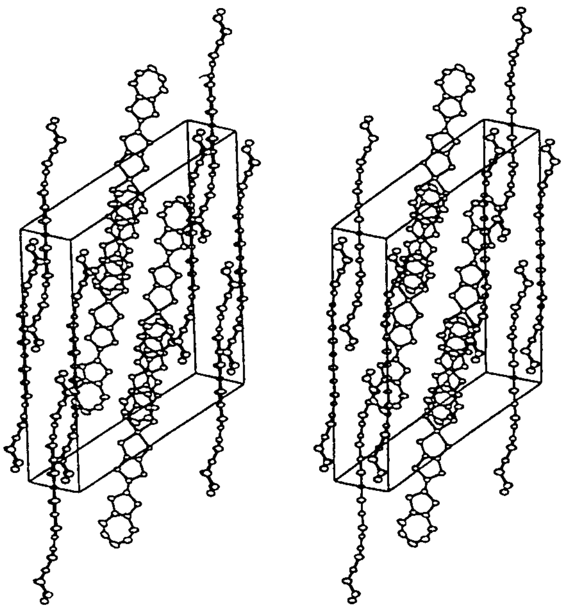

Fig. 4 Stereoview of the crystal structure of $(Ph_4P)[Ni(ptdt)_2]\cdot 1.4Me_2CO$.

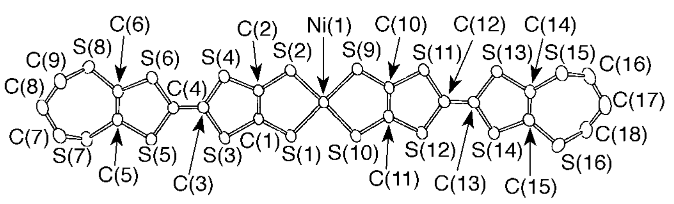

Fig. 5 ORTEP drawing of the monoanion $Ni(ptdt)_2^-$ showing the atom labelling at the 50% probability level

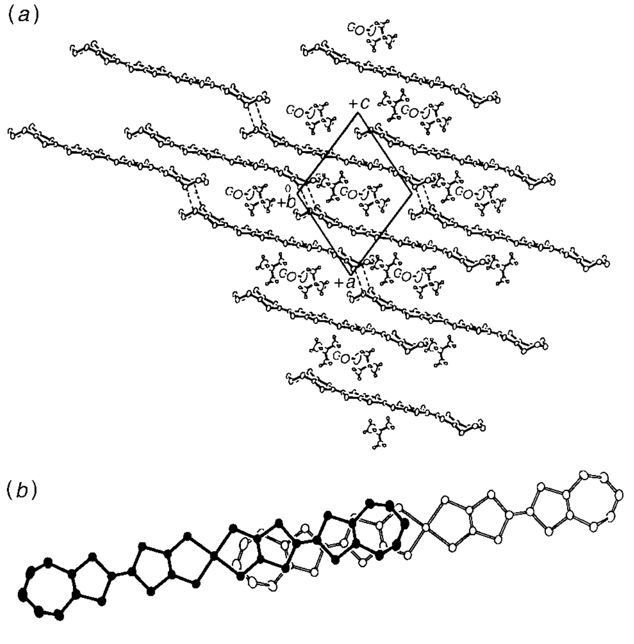

Fig. 6 (*a*) Crystal structure of $(Me_4N)[Ni(ptdt)_2]\cdot Me_2CO$. (*b*) Overlapping mode of $Ni(ptdt)_2^-$ in $(Me_4N)[Ni(ptdt)_2]\cdot Me_2CO$.

$(Ph_4P)_2[Cu(ptdt)_2]\cdot 1.2Me_2CO$ 3. The $Cu(ptdt)_2{}^{2-}$ anion is shown in Fig. 7 and selected bond lengths and angles are listed in Table 5. The terminal propylenic group of $Cu(ptdt)_2{}^{2-}$ is bent as found for the Ni complex. A distorted tetrahedral geometry is observed around the Cu atom with Cu—S distances of 2.279(4), 2.273(4), 2.282(4) and 2.265(4) Å and S—Cu—S angles of 93.6(1), 93.2(1), 140.3(2) and 142.0(2)°. The dihedral angle between the planes S(1)CuS(2) and S(9)CuS(10) is 54.2°. The central C=C bond lengths C(3)—C(4) and C(12)—C(13) are 1.35(1) and 1.35(2) Å, respectively. The geometry around the Cu atom is almost the same as in $[epy]_2[Cu(dmit)_2]$ (epy = *N*-ethylpyridinium; dmit = 4,5-dimercapto-1,3-dithiole-2-thione).[10] In this case the dihedral angle is 57.3°. The crystal structure is shown in Fig. 8 and the schematic stacking pattern of **3** is shown in Fig. 9. The anions form a one-dimensional chain along the *c*-direction with both ligands, which overlap in ring-over-bond type with those of adjacent anions. The interplanar distance is *ca.* 3.39 Å and the Cu···Cu distance is 14.78 Å. The shortest intermolecular S···S distance is 3.582(7) Å [S(16)···S(16)], which correspond to short transverse contacts between adjacent chains. The large tetraphenylphosphonium cations prevent overlapping along the *b* direction. The π-conjugated systems of the ptdt ligand are large enough to form conduction pathways in the crystal. In the case of $[epy]_2[Cu(dmit)_2]$, owing to the small size of the ligand, the stacking of $Cu(dmit)_2$ is only *via* one side of the ligand, which prevents formation of a good conduction pathway. The next step for the development of new types of molecular conductors may be oxidation of the complexes.

Magnetic susceptibilities

The temperature dependence of the magnetic susceptibility of $(Me_4N)_2[Cu(ptdt)_2]$ within the temperature range 2–300 K obeys Curie behavior, indicating non-interacting spins for $(Me_4N)_2[Cu(ptdt)_2]$. The diamagnetic component of the magnetic susceptibility was estimated by use of Pascal law to be -4.9×10^{-4} emu mol^{-1}.[11] The room temperature magnetic susceptibility of 9.8×10^{-4} emu mol^{-1} suggests 0.8 spins per molecule, which is consistent with the presence of Cu^{2+}.

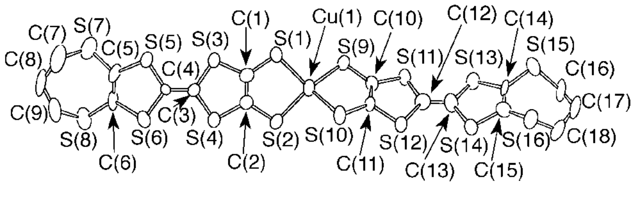

Fig. 7 ORTEP drawing of the dianion $Cu(ptdt)_2{}^{2-}$ showing the atom labelling at the 50% probability level

Table 5 Selected bond lengths (Å) and angles (degrees) for $(Ph_4P)_2[Cu(ptdt)_2]\cdot 1.2Me_2CO$

Cu(1)—S(1)	2.279(4)	S(11)—C(12)	1.74(1)
Cu(1)—S(2)	2.273(4)	S(12)—C(11)	1.78(1)
Cu(1)—S(9)	2.282(4)	S(12)—C(12)	1.74(1)
Cu(1)—S(10)	2.265(4)	S(13)—C(13)	1.77(1)
S(1)—C(1)	1.73(1)	S(13)—C(14)	1.79(1)
S(2)—C(2)	1.74(1)	S(14)—C(13)	1.76(1)
S(3)—C(1)	1.77(1)	S(14)—C(15)	1.74(1)
S(3)—C(3)	1.76(1)	S(15)—C(14)	1.75(1)
S(4)—C(2)	1.75(1)	S(15)—C(16)	1.81(1)
S(4)—C(3)	1.75(1)	S(16)—C(15)	1.72(1)
S(5)—C(4)	1.73(1)	S(16)—C(18)	1.78(1)
S(5)—C(5)	1.75(1)	C(1)—C(2)	1.34(2)
S(6)—C(4)	1.76(1)	C(3)—C(4)	1.35(1)
S(6)—C(6)	1.76(1)	C(5)—C(6)	1.35(2)
S(7)—C(5)	1.76(1)	C(7)—C(8)	1.50(2)
S(7)—C(7)	1.81(2)	C(8)—C(9)	1.48(2)
S(8)—C(6)	1.72(1)	C(10)—C(11)	1.34(2)
S(8)—C(9)	1.84(1)	C(12)—C(13)	1.35(2)
S(9)—C(10)	1.74(1)	C(14)—C(15)	1.35(2)
S(10)—C(11)	1.72(1)	C(17)—C(18)	1.53(2)
S(11)—C(10)	1.76(1)	C(16)—C(17)	1.51(2)
S(1)—Cu(1)—S(2)	93.6(1)	S(2)—Cu(1)—S(9)	142.0(2)
S(1)—Cu(1)—S(9)	101.6(1)	S(2)—Cu(1)—S(10)	96.9(1)
S(1)—Cu(1)—S(10)	140.3(2)	S(9)—Cu(1)—S(10)	93.2(1)

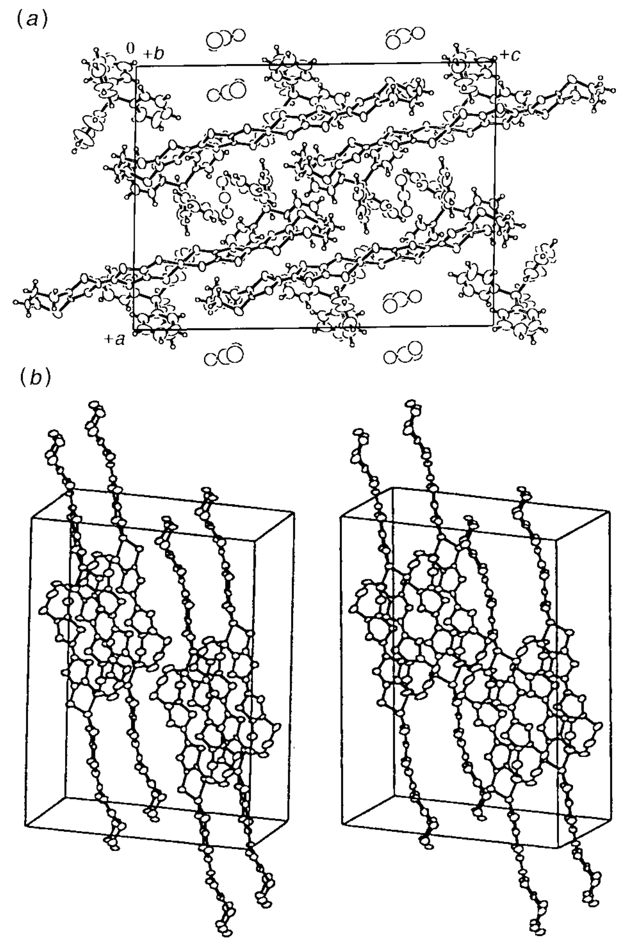

Fig. 8 (*a*) Crystal structure of $(Ph_4P)_2[Cu(ptdt)_2]\cdot 1.2Me_2CO$. (*b*) Stereoview of $(Ph_4P)_2[Cu(ptdt)_2]\cdot 1.2Me_2CO$.

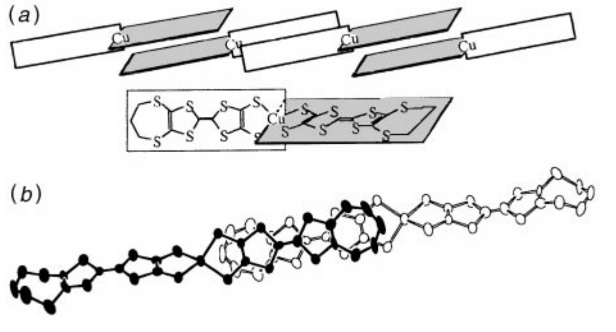

Fig. 9 Schematic molecular arrangement and overlapping mode of $(Ph_4P)_2[Cu(ptdt)_2]\cdot 1.2Me_2CO$

Electrical resistivities

The temperature dependence of the resistivity of $(Me_4N)[Ni(ptdt)_2]\cdot Me_2CO$ was measured by usual four-probe method and was semiconducting (Fig. 10). The room temperature conductivity is 1.4×10^{-3} S cm^{-1} and the activation energy is 9.9×10^{-2} eV.

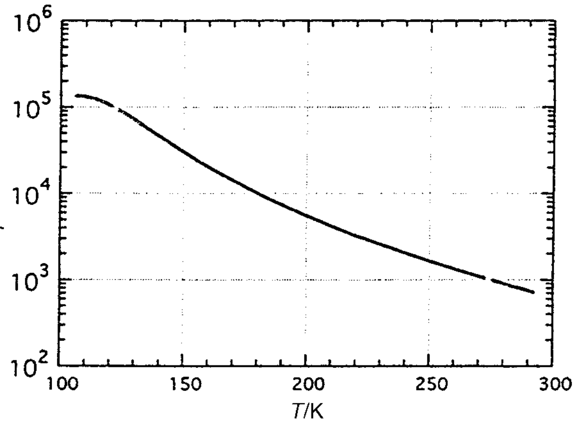

Fig. 10 Temperature dependence of the electrical resistivity of $(Me_4N)[Ni(ptdt)_2]\cdot Me_2CO$

Conclusion

Two inevitable requirements for the design of the good conductors are: (1) the formation of conduction pathway and (2) the formation of charge carriers. As for requirement (1), the crystal structures of **1**, **2** and **3** show possibility of novel 2D or 3D intermolecular contacts through ptdt ligands in place of 'spanning overlapping' of the $Ni(dmit)_2$ complexes, which is the only unique example of a 2D molecular arrangement of conducting transition metal complexes.[12–15] Moreover, a new molecular conductor with π–d interactions will be expected if a magnetic transition metal atom is incorporated.[16] In order to meet requirement (2), further experiments are required. Very recently black crystals of fairly conducting neutral $Ni(ptdt)_2$ have been obtained by electrocrystallization with a room temperature conductivity of 2.1 S cm^{-1} and an activation energy of 0.11 eV. The conductivity is significantly higher than values normally observed for other neutral complexes such as dithiolenes ($<10^{-3}$ S cm^{-1}) or TTF dithiolenes ($<10^{-1}$ S cm^{-1}).[2]

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