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Synthesis, structure and properties of new dithiolene complexes containing a 1,3,5-trithiepin ring

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Mono-tetrabutylammonium salts of nickel, copper, and gold 1,3,5-trithiepin-6,7-dithiolato (ttdt) complexes **1a–c** have been prepared and the structures of **1b** and **1c** determined by X-ray crystallography. Cyclic voltammograms of these complexes showed oxidation peaks in the range 0.23–0.46 V (*vs.* SCE). Partially oxidised salts of these complexes were obtained either as amorphous or polycrystalline solids. The electrical conduction properties are reported. The crystal structure of (TTF)[Au(ttdt)$_2$] obtained from the reaction of **1c** and TTF$_3$(BF$_4$)$_2$ was determined by X-ray crystallography.

Bis(dithiolene) transition metal complexes have been investigated extensively during the last two decades, because of their potential for the preparation of molecular conductors or superconductors.[1] Recently, large third order non-linear optical properties have been found in some of these complexes, and some of these complexes are also of interest because of their unique magnetic behaviour. The crystal structures of these complexes which contain columnar stacks of anions and their associated cations play an important role in determining their solid state properties.

One area of current interest in the field of molecular conductors is to construct molecular systems in which either donors and acceptors (or ions) or donors and donors are interlinked. This can be achieved for example, by introducing a hydrogen bonding network.[2] From this point of view, the study of compounds which include non-conjugated group 16 elements at the periphery of donors (or acceptors) are important. Studies of TTF derivatives which have peripheral seven-membered rings including SCH$_2$OCH$_2$S and SCH$_2$SCH$_2$S group have been reported recently.[3] The radical cation salts of these donors showed relatively high room temperature conductivities (10^{-1}–10^{2} S cm^{-1}) and also exhibited metal-like electrical conduction properties down to 4.2 K.

In contrast to these cationic salts, metal dithiolene complexes containing these moieties will give rise to anionic partially oxidised salts and therefore the lone pairs of electrons on the peripheral heteroatoms could interact favourably with counter-cations in charge transfer salts. Kato *et al.* reported the preparation and the structure of the nickel bis(dithiolate) **1a**.[4] Although the platinum and palladium complexes of this ligand were prepared by Faulmann *et al.*, the preparation of partially oxidised salts of these complexes was unsuccessful.[5] Therefore, we have studied the preparation and the properties of bis(dithiolene) complexes **1a–c** (Scheme 1) in which the metals (nickel, copper and gold) are coordinated by the 1,3,5-trithiepin-6,7-dithiolato ligand (ttdt) having the 1,3,5-trithiodimethyl group in the periphery of the molecule [M(ttdt)$_2$]$^{x-}$.

Preparation of (R$_4$N)[M(ttdt)$_2$] (R = Bu^n, Me; M = Ni, Cu, Au)

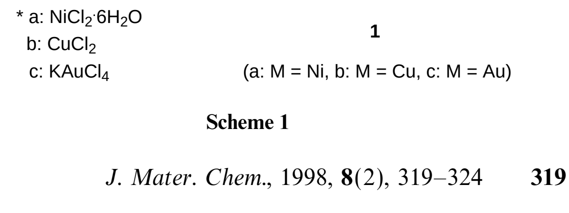
(Bu$^n_4$N)[Ni(ttdt)$_2$] was prepared starting from 1,3-dithiolo[4,5-*f*][1,3,5]trithiepin-2-thione **2** by the reported method.[4] K$_2$(ttdt) **3** was prepared by the hydrolysis of thione **2** with an excess of potassium hydroxide in ethanol and isolated by filtration under nitrogen. K$_2$(ttdt) was allowed to react with NiCl$_2$·6H$_2$O in methanol. Addition of tetrabutylammonium bromide to the reaction mixture followed by filtration and recrystallisation yielded the green–black solid product (Scheme 1).

(Bu$^n_4$N)[M(ttdt)$_2$] (M = Cu **1b**, Au **1c**) were prepared similarly by using copper(II) chloride or potassium tetrachloroaurate. The corresponding tetramethylammonium salts of **1a–c** were prepared using a similar procedure with tetramethylammonium bromide. All these complexes gave satisfactory analytical data.

The IR spectra contain absorption bands corresponding to the weakened C=C bond at around 1380 cm^{-1} for all the complexes and the absorption band corresponding to the C—S bond appeared around 850 cm^{-1}. Complexes **1b** and **1c** exhibited a singlet in ^{1}H NMR spectra due to the SCH$_2$ group at *δ ca.* 4.0.

Crystal structure of (Bu$^n_4$N)[M(ttdt)$_2$] (M = Au, Cu)

The crystal structures of the copper and gold complexes (**1b**, **1c**) were determined by X-ray crystallography. The crystal



Scheme 1

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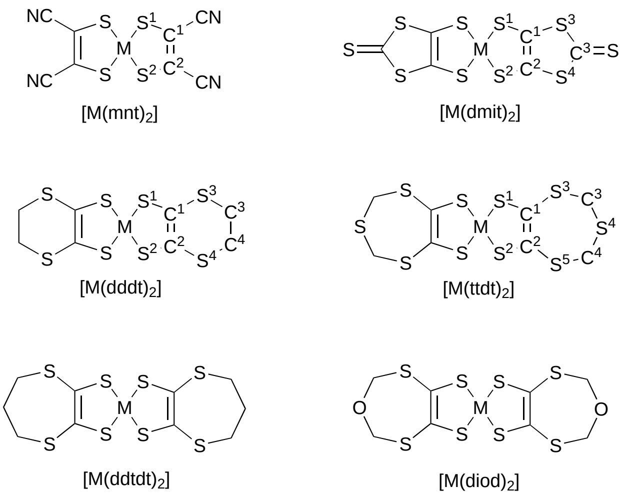

Fig. 1 Compounds under study

structures of these complexes are shown in Fig. 2 and 3. The bond lengths and S—M—S angles found in **1a–c** and related complexes are summarized in Table 1.

The crystal structures of **1a–c** are similar and the structural parameters of outer trithiepin rings are nearly the same. The differences observed between the structures of these complexes are associated with the structural parameters of the inner metallocycles because of the different central metal atoms. The structures of these complexes are nearly planar about the metal atom and the outer trithiepin rings take up a chair-like conformation.

The copper complex **1b** has basically a planar metallocycle with a slight twist associated with the two dithiolene planes (four sulfur atoms around the copper atom are deviated from their mean plane by 0.09–0.17 Å). This basically planar structure is also observed for $[Cu(mnt)_2]^-$ (the deviations of sulfur atoms from the mean plane were 0.05–0.11 Å)[6a] but is in sharp contrast with the fact that the dithiolene planes in the crystal of $[Cu(dddt)_2]^-$ (Bu^n_4 salt) and $[Cu(dmit)_2]^{2-}$ are twisted to 29°[6b] and 57°,[6c] respectively. The C=C bond length of the metallocycle, 1.325 Å, is a little longer than that of a usual C=C bond and similar to the value in $[Cu(mnt)_2]^-$ (1.32 Å) but slightly shorter than that found for $[Cu(dddt)_2]^-$ (1.39 Å) or $[Cu(dmit)_2]^{2-}$ (1.36 Å). The exo-C—S bond lengths of the ligand at 1.753–1.764 Å, are close to the C—S bond lengths of the metallocycle (1.743–1.764 Å) and similar to the corresponding distances in related copper complexes (1.75–1.76 Å). These values are in between the usual C=S bond length (1.71 Å) and C—S bond length (1.81 Å), suggesting that the C—S bonds on the dithiolene planes are delocalized. The Cu—S bond lengths of between 2.181 and 2.190 Å, resemble those in $[Cu(mnt)_2]^-$ (2.170 Å) and $[Cu(dddt)_2]^-$ (2.181 Å). The C—S bond length present in the peripheral trithiepin ring is *ca.* 1.80 Å, slightly longer than the C—S bonds of $[Cu(dddt)_2]^-$ (1.75 and 1.77 Å).

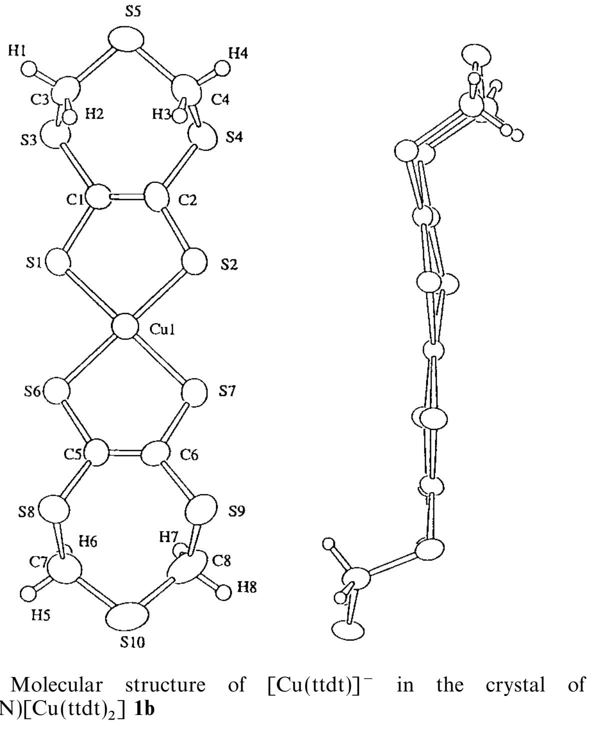

Fig. 2 Molecular structure of $[Cu(ttdt)]^-$ in the crystal of $(Bu^n_4N)[Cu(ttdt)_2]$ **1b**

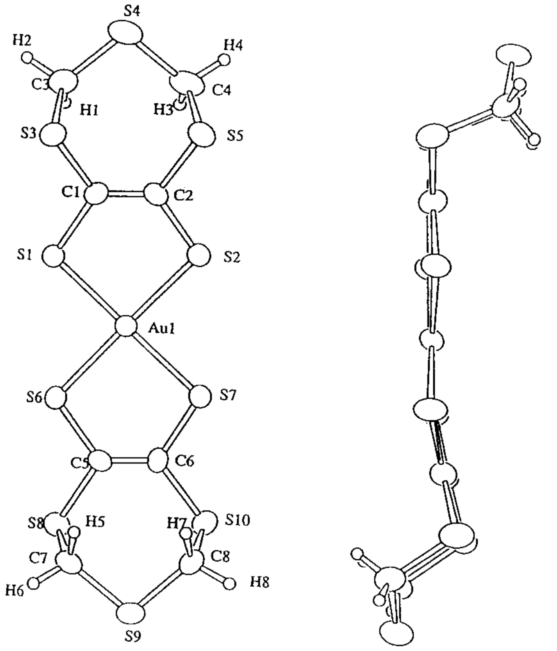

Fig. 3 Molecular structure of $[Au(ttdt)]^-$ in the crystal of $(Bu^n_4N)[Au(ttdt)_2]$ **1c**

The structure of the gold complex **1c** is similar to those of the nickel and copper complexes (**1a**, **1b**), having basically a planar structure around the gold atom with a chair-like bent peripheral trithiepin rings. The bond lengths and S—Au—S angle are close to the corresponding values of other gold complexes of related ligands (Tables 1 and 2).

Redox potentials of $(Bu^n_4N)[M(ttdt)_2]$ (M = Ni, Cu, Au)

Cyclic voltammetry measurements were carried out on **1a–c** in acetonitrile using a standard calomel electrode with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. The redox potential of these complexes and other complexes are shown in Table 3.

The nickel and gold complexes (**1a**, **1c**) showed reversible oxidation peaks at +0.21 and +0.46 V (*vs.* SCE) respectively, whereas the copper complex **1b** showed an irreversible oxidation peak at +0.45 V. The reversible oxidation waves observed for **1a** and **1c** disappeared on repetitive scans when the potential was increased to >1.5 V. Reversible reduction waves were observed for **1a–c** (−0.59, −0.63, −0.91 V, respectively).

The oxidation potential of the nickel complex **1a** is 0.61 V lower than that of $[Ni(mnt)_2]^-$, 0.15 V higher than that of $[Ni(dddt)_2]^-$ and is close to those of $[Ni(dmit)_2]^-$ and $[Ni(ddtdt)_2]^-$. It therefore appears that nickel complexes of ligands containing seven-membered outer rings are slightly more difficult to oxidise to the neutral complex than the

Table 1 Bond distances (Å) and bond angles (degrees) of some ammonium salts of nickel, copper and gold bis(dithiolene) complexes

complex	$M-S_1$	C_1-S_1	$C_1=C_2$	S_1-M-S_2	C_1-S_3	S_3-C_3	C_3-S_4
$[\mathrm{Ni(mnt)_2}]^-$ [a]	2.149	1.72	1.37	92.5			
$[\mathrm{Ni(dmit)_2}]^-$ [b]	2.156	1.72	1.35	93.2			
$[\mathrm{Ni(dddt)_2}]^-$ [c]	2.132	1.75	1.28	91.1	1.77	1.81, 1.89	
$[\mathrm{Ni(ttdt)_2}]^-$ [d]	2.141	1.72	1.37	91.3	1.76	1.81	1.81, 1.82
$[\mathrm{Cu(mnt)_2}]^-$ [e]	2.170	1.72	1.32	92.4			
$[\mathrm{Cu(dmit)_2}]^{2-}$ [f]	2.272	1.73	1.36	94.0	1.75		
$[\mathrm{Cu(dddt)_2}]^-$ [g]	2.181	1.73	1.39	91.5	1.76	1.75, 1.77	
$[\mathrm{Cu(ttdt)_2}]^-$	2.183(1)	1.752(5)	1.332(6)	91.68(6)	1.758(5)	1.805(5)	1.799(5)
$[\mathrm{Au(mnt)_2}]^-$ [h]	2.317	1.75	1.33	90.5			
$[\mathrm{Au(dmit)_2}]^-$ [i]	2.323	1.75	1.31	91.5	1.75		
$[\mathrm{Au(dddt)_2}]$ [c]	2.304	1.70	1.39	89.2	1.77	1.78, 1.88	
$[\mathrm{Au(ttdt)_2}]^-$	2.312(1)	1.750(5)	1.334(7)	89.35(6)	1.766(4)	1.810(5)	1.780(6) 1.809(6)

The numbering of the atoms is as shown in the compounds. References: [a]A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2650. [b]C. T. Vance, R. D. Bereman, J. Bordner, W. E. Hatfield and J. H. Helms, *Inorg. Chem.*, 1985, **24**, 2905. [c]A. J. Schultz, H. H. Wang, L. C. Soderholm, T. L. Sifter, J. M. Williams, K. Beckgaard and M.-H. Whangbo, *Inorg. Chem.*, 1987, **26**, 3757. [d]Ref. 4. [e]Ref. 6(*a*). [f]Ref. 6(*c*). [g]Ref 6(*b*). [h]P. Kuppusamy, N. Venkatalakshmi and P. T. Manoharan, *J. Cryst. Spectrosc. Res.*, 1985, **15**, 629. [i]G. Matsubayashi and A. Yokozawa, *J. Chem. Soc., Dalton Trans.*, 1990, 3535.

Table 2 Bond distances (Å) and bond angles (degrees) of $[\mathrm{Au(ttdt)_2}]^{x-}$ and $[\mathrm{Au(dddt)_2}]^{x-}$ complexes

complex	$M-S_1$	C_1-S_1	$C_1=C_2$	S_1-M-S_2	C_1-S_3	S_3-C_3	C_3-S_4
$(\mathrm{Bu^n{}_4N})[\mathrm{Au(ttdt)_2}]$	2.312(1)	1.750(5)	1.334(7)	89.35(6)	1.766(4)	1.810(5)	1.780(6) 1.809(6)
$\mathrm{TTF}[\mathrm{Au(ttdt)_2}]$	2.318(2)	1.754(5)	1.340(10)	90.78(6)	1.768(5)	1.810(5)	1.805(6)
$\mathrm{TTF}[\mathrm{Au(dddt)_2}]$ [a]	2.304	1.78	1.29	89.8	1.77	1.77, 1.93	
$\mathrm{TTF}[\mathrm{Au(dddt)_2}]$ [a]	2.303	1.76	1.37	89.8	1.76	1.68, 1.81	

Reference: [a]U. Geiser, A. J. Schultz, H. H. Wang, M. A. Beno and J. M. Williams, *Acta Crystallogr., Sect. C*, 1988, **44**, 259.

Table 3 Redox potentials of nickel, copper and gold bis(dithiolene) complexes

complex	E_1/V $-1\rightleftarrows 0$	E_2/V $-2\rightleftarrows -1$	$\Delta E/\mathrm{V}$ (E_1-E_2)	solvent, electrode
$[\mathrm{Ni(mnt)_2}]^-$ [a]	+0.82 (irr.)	−0.14	0.96	MeCN, $\mathrm{Ag/Ag^+}$
$[\mathrm{Ni(dmit)_2}]^-$ [b]	+0.22 (irr.)	−0.13	0.37	MeCN, SCE
$[\mathrm{Ni(dddt)_2}]^-$ [b]	+0.06	−0.69	0.75	MeCN, SCE
$[\mathrm{Ni(ddtdt)_2}]^-$ [b]	+0.16	−0.71	0.87	MeCN, SCE
$[\mathrm{Ni(ttdt)_2}]^-$	+0.21	−0.59	0.80	MeCN, SCE
$[\mathrm{Cu(mnt)_2}]^-$ [a]	+0.96 (irr.)	−0.03	0.99	MeCN, $\mathrm{Ag/Ag^+}$
$[\mathrm{Cu(dddt)_2}]^-$ [c]	+0.38 (irr.)	−0.49	0.87	DMF, $\mathrm{Ag/Ag^+}$
$[\mathrm{Cu(ttdt)_2}]^-$	+0.45 (irr.)	−0.63	1.08	MeCN, SCE
$[\mathrm{Au(mnt)_2}]^-$ [d]	+1.15	−0.88	2.03	$\mathrm{CH_2Cl_2}$, $\mathrm{Ag/Ag^+}$
$[\mathrm{Au(dmit)_2}]^-$	+0.35	−0.60	0.95	MeCN, SCE
$[\mathrm{Au(dddt)_2}]^-$ [e]	+0.41	−1.32	1.73	$\mathrm{CH_2Cl_2}$, SCE
$[\mathrm{Au(ttdt)_2}]^-$	+0.46	−0.91	1.37	MeCN, SCE

Irr. = irreversible. References: [a]L. Persaud and C. H. Langford, *Inorg. Chem.*, 1985, **24**, 3562. [b]Ref. 4. [c]Ref. [g] in Table 1. [d]J. C. Fitzmaurice, A. M. Z. Slawin, D. J. Williams, J. D. Woollins and A. J. Lindsay, *Polyhedron*, 1990, **9**, 1561. [e]Ref. *c* in Table 1.

complexes of ligands containing six-membered outer rings. The potentials are rather close to those of $[\mathrm{Ni(dmit)_2}]^-$ which contains a conjugated C=S bond. The difference between the oxidation and reduction potentials (ΔE) of **1a** is 0.80 V, which is considerably larger than ΔE of $[\mathrm{Ni(dmit)_2}]^-$, but is close to the values of $[\mathrm{Ni(dddt)_2}]^-$ and $[\mathrm{Ni(ddtdt)_2}]^-$ and smaller than that of $[\mathrm{Ni(mnt)_2}]^-$. The gold complex **1c** is more difficult to oxidise than $[\mathrm{Au(dmit)_2}]^-$ by 0.11 V and has a larger ΔE value than $[\mathrm{Au(dmit)_2}]^-$. The copper complex **1b** can be oxidised at a potential lower by 0.51 V compared with $[\mathrm{Cu(mnt)_2}]^-$, but ΔE of **1b** is similar to that of $[\mathrm{Cu(mnt)_2}]^-$.

Electrochemical oxidation of $(\mathrm{R_4N})[\mathrm{M(ttdt)_2}]$

The electrochemical oxidation of **1a–c** in the presence of alkali metal salts or TTF derivatives was investigated. A variety of solvent systems and current densities were investigated. No crystals were obtained in the electrochemical crystallisation of the nickel complex **1a** but an amorphous solid was obtained on the anode in every experiment. Electrochemical oxidation of the copper complex **1b** afforded only a small amount of a mixture of products on the anode. Experiments involving the gold complex **1c** resulted in the production of a polycrystalline product on the anode. The analytical results obtained for the products obtained from $(\mathrm{R_4N})[\mathrm{Ni(ttdt)_2}]$ suggested a stoichiometry close to that of the neutral $[\mathrm{Ni(ttdt)_2}]$ complex but containing a small quantity of the counter-cation. From the analytical data it was very difficult to determine whether or not partially oxidised products were obtained. For the nickel complexes, room temperature conductivities in the range 10^{-4}–10^{-5} S cm^{-1} were obtained for products produced by electrocrystallisation in the presence of alkali metal cations. A higher conductivity of 10^{-1} S cm^{-1} was observed for the product obtained in the presence of $\mathrm{Me_4N^+}$ ions and whose composition was close to $(\mathrm{Me_4N})_{0.5}[\mathrm{Ni(ttdt)_2}]$ from elemental analysis. These results are somewhat different from those reported by Cassoux who obtained the neutral nickel complex directly from electrochemical and chemical oxidation of **1a**.[5] For the gold complexes, conductivities of around 10^{-3} S cm^{-1} were obtained for products obtained in the presence of alkali metal, $\mathrm{Bu^n{}_4N^+}$, $\mathrm{Me_4N^+}$ cations and BEDT-TTF.

Partially oxidised salts of $[\mathrm{M(dmit)_2}]^-$ (M = Ni, Au) have been shown to exhibit high room temperature conductivities {room temperature conductivity = 10^1 S cm^{-1} for $(\mathrm{Bu^n{}_4N})_{0.29}[\mathrm{Ni(dmit)_2}]$,[7] 10^2 S cm^{-1} for $\mathrm{K_{0.5}}[\mathrm{Au(dmit)_2}]$,[8] 10^{-1} S cm^{-1} for $\mathrm{TTF_{0.67}}[\mathrm{Au(dmit)_2}]$[9]} whereas the partially oxidised salts of $[\mathrm{M(diod)_2}]^-$ and $[\mathrm{M(ttdt)_2}]^-$ **1** complexes show relatively lower conductivities {room temperature conductivity = 10^{-2} S cm^{-1} for BEDT-TTF$_{0.17}$[Ni(diod)$_2$] (compressed pellets)[10]}. It seems that the bulk or the flip motion of the peripheral chair-like seven-membered rings on these ligands interferes with the packing of the anions and makes the formation of partially oxidised products less likely.

Metathesis experiments

Diffusion controlled metathesis experiments involving (TTF)$_3$(BF$_4$)$_2$ and **1a–c** in acetonitrile were carried out.

Fine needle-shaped crystals were obtained for the nickel and gold complexes (**1a**, **1c**), but no crystals were obtained using the copper complex **1b**. The structure of the gold complex was successfully determined by X-ray crystallography and revealed that the product obtained was the 1:1 salt, TTF[Au(ttdt)$_2$]. Some of the structural parameters are shown in Tables 2 and 4. In the crystal, a pair of TTF molecules are surrounded by a pair of gold complexes (Fig. 4), an arrangement also seen in the crystal packing of TTF[Au(dddt)$_2$]. The structure of [Au(ttdt)$_2$]$^-$ is very similar to that in (Bu$^n{}_4$N)[Au(ttdt)$_2$] and the structure of the TTF molecule is similar to that found in TTF[Au(dddt)$_2$] (Tables 2 and 4).

Too little product was obtained from the experiment involving **1a** for elemental analysis and the crystals were too thin for an X-ray structure determination.

The electrical conductivity of the crystals of TTF$_x$[Ni(ttdt)$_2$] obtained from the metathesis experiment of **1a** was measured. The room temperature conductivity was *ca.* 4.7×10^{-4} S cm^{-1} and the band gap was 0.19 eV over the temperature range 295–210 K.

Conclusion

The preparation, redox electrical properties of [M(ttdt)$_2$]$^{x-}$ complexes (M = Ni, Cu, or Au) have been described. The crystal structure of the Cu and Au complexes have been determined. Attempts to prepare partially oxidised products by electrocrystallisation resulted in products which behaved as semiconductors from room temperature down to 200 K. The compound TTF[Au(ttdt)$_2$] was prepared by metathesis.

Experimental

All the reaction were carried out under nitrogen. All the solvents used in the experiments were purified by published methods. Melting points were uncorrected. A Perkin Elmer 1600 series FTIR spectrophotometer was used for IR measurement, a Carlo Erba elemental analyser 1106 was used for elemental analysis and a Bruker AC250 instrument was used for ^{1}H NMR measurements. UV–VIS spectra were recorded on Hitachi 200–10 spectrophotometer and near-IR spectra was recorded on a Perkin Elmer Lambda 9 spectrophotometer. Cyclic voltammograms was performed using a Polarographic Analyser Model 264A.

Preparation of (Bu$^n{}_4$N)[Ni(ttdt)$_2$] 1a

Thione **2** (0.51 g, 2 mmol) was allowed to react with potassium hydroxide (0.90 g, 16 mmol) in 10 ml ethanol for 1.5 h at 40–60 °C. The resulting gray precipitate of K$_2$(ttdt) was isolated by filtration under nitrogen. To a methanolic solution of the dipotassium salt was added a methanolic solution (10 ml) of NiCl$_2\cdot$6H$_2$O (133 mg, 0.85 mmol). After stirring the reaction mixture overnight at room temperature, air was bubbled through it for 15 min. The precipitate formed in the reaction was filtered off and the filtrate was added to a methanolic solution (20 ml) of tetrabutylammonium bromide (0.90 g, 2.8 mmol). The precipitate of **1a** was collected by filtration (190 mg, 31%). Dark green crystals of **1a** were obtained by recrystallisation from acetone and propan-2-ol under vacuum (mp 176.0–176.5 °C).

Anal. Calc. for C$_{24}$H$_{44}$NS$_{10}$Ni: C, 39.90; H, 6.11; N, 1.94; S, 44.17. Found: C, 40.28; H, 6.67; N, 1.92; S, 44.99%. IR (KBr disk): 1479, 1453, 1385, 1212, 1164, 1120, 886, 850, 719 cm^{-1}. UV–VIS (CH$_2$Cl$_2$): 395 nm (ε = 14 300 dm^3 mol^{-1} cm^{-1}), 340 (ε = 28 200). near-IR (CH$_2$Cl$_2$): 911 (ε = 8200).

Preparation of (Bu$^n{}_4$N)[Cu(ttdt)$_2$] 1b

A procedure similar to that used in the preparation of **1a** was adopted using CuCl$_2$ (130 mg, 1.0 mmol) instead of NiCl$_2\cdot$6H$_2$O. The reddish black powder of **1b** was obtained (508 mg, yield 72%). Deep red crystals were obtained by recrystallisation from acetone and propan-2-ol under vacuum (mp 140.5–141.0 °C).

Anal. Calc. for C$_{24}$H$_{44}$NS$_{10}$Cu: C, 39.44; H, 6.07; N, 1.92; S, 43.87. Found: C, 38.69; H, 6.12; N, 1.82; S, 42.98%. IR (KBr disk): 1481, 1452, 1373, 1213, 1164, 1120, 881, 850, 718 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.05(12 H, t), 1.45(16 H, m), 3.13(8 H, t), 4.01(8 H, s, SCH$_2$). UV–VIS (CH$_2$Cl$_2$): 441 nm (ε = 22 200 dm^3 mol^{-1} cm^{-1}).

Preparation of (Bu$^n{}_4$N)[Au(ttdt)$_2$] 1c

A procedure similar to that used in the preparation of **1a** was adopted using potassium tetrachloroaurate(III) (320 mg, 0.85 mmol) instead of NiCl$_2\cdot$6H$_2$O. Air was not bubbled through the solution. A black powder of **1c** was obtained (115 mg, yield 16%). Yellow crystals were obtained by recrystallisation of the product from acetone and propan-2-ol under vacuum (mp 197.0–198.5 °C). The yield of **1c** was improved to 35% when the reaction of K$_2$(ttdt) with KAuCl$_4$ was carried out at 50 °C over 2 days.

Anal. Calc. for C$_{24}$H$_{44}$NS$_{10}$Au: C, 33.36; H, 5.13; N, 1.62; S, 37.10. Found: C, 33.14; H, 4.88; N, 1.62; S, 38.46%. IR (KBr disk): 1482, 1374, 1213, 1164, 1120, 951, 872, 850, 719 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.03(12 H, t), 1.45(16 H, m), 3.12(8 H, t), 3.95(8 H, s, SCH$_2$). UV–VIS (CH$_2$Cl$_2$): 345 nm (ε = 27 000 dm^3 mol^{-1} cm^{-1}).

Preparation of (Me$_4$N)[M(ttdt)$_2$] (M = Ni, Cu, Au)

The tetramethylammonium salts were prepared by using a similar procedure to that used in the preparation of corresponding tetrabutylammonium salts **1a–c**. Tetramethylammonium bromide was used instead of tetrabutylammonium bromide [yield: 49% (M = Ni), 36% (M = Cu), 50% (M = Au)].

(Me$_4$N)[Ni(ttdt)$_2$]. mp: 182.5–184.0 °C. Anal. Calc. for C$_{12}$H$_{20}$NS$_{10}$Ni: C, 25.85; H, 3.62; N, 2.51; S, 57.50. Found: C, 26.68; H, 3.63; N, 2.30; S, 52.08%.

Table 4 Bond distances (Å) and bond angles (degrees) of TTF in TTF[Au(ttdt)$_2$] and TTF[Au(dddt)$_2$]

complex	C$_5$=C$_5$	S$_6$—C$_5$—S$_7$	C$_5$—S$_6$	S$_6$—C$_6$	C$_6$=C$_7$
TTF[Au(ttdt)$_2$]	1.40(1)	115.3(4)	1.705(8), 1.725 (8)	1.716(7)	1.33(2)
TTF[Au(dddt)$_2$][a]	1.51	115	1.63, 1.73	1.74	1.36

The numbering of the atoms is as shown in Fig. 4. Reference: [a]Ref. *a* in Table 2.

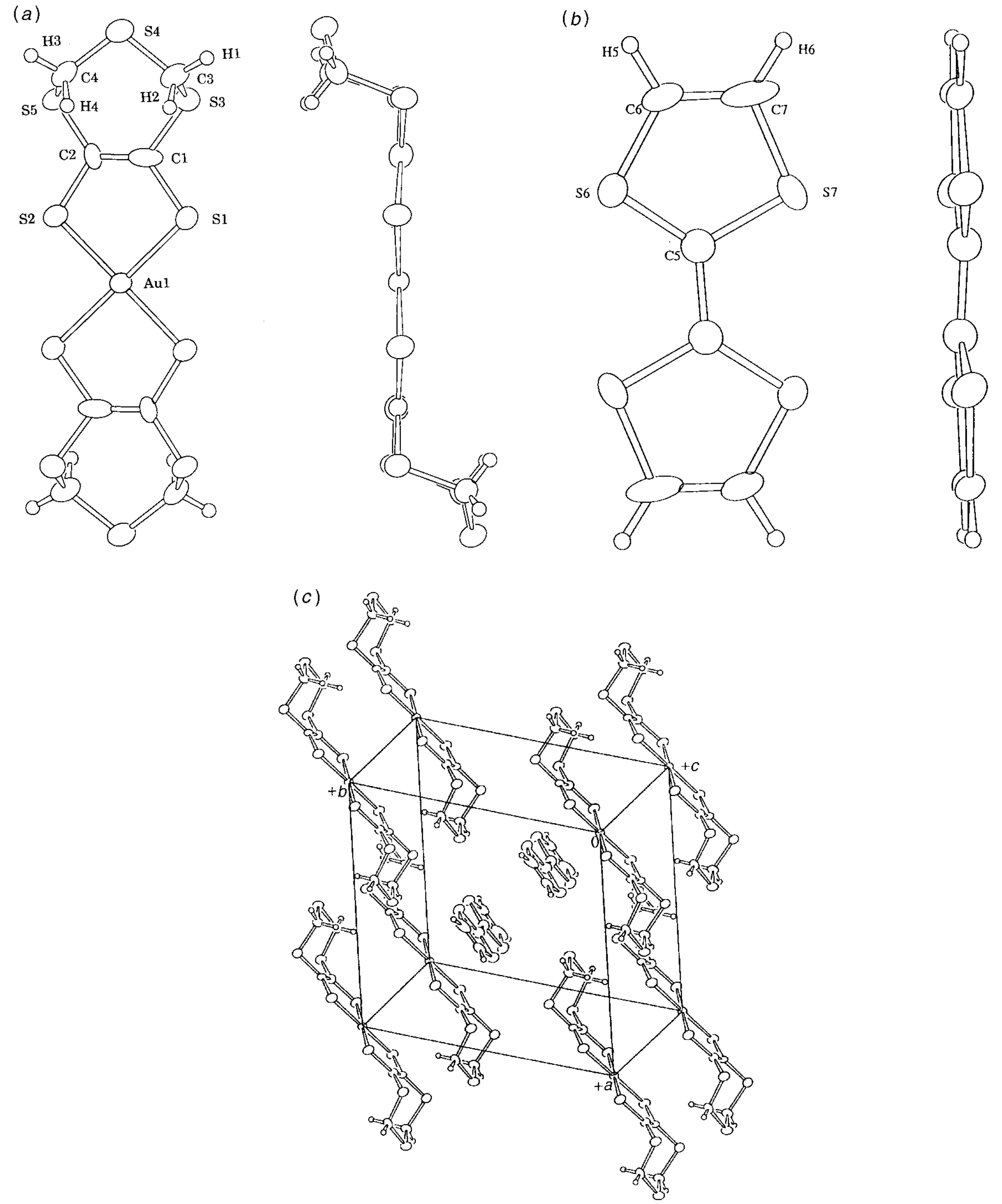

Fig. 4 Crystal structure of TTF[Au(ttdt)$_2$]: (*a*) molecular structure of [Au(ttdt)$_2$]$^{x-}$ in TTF[Au(ttdt)$_2$]; (*b*) molecular structure of TTF^{x+} in TTF[Au(ttdt)$_2$]; (*c*) crystal packing of TTF[Au(ttdt)$_2$]

(Me$_4$N)[Cu(ttdt)$_2$]. mp: 152.0–153.0 °C. Anal. Calc. for $C_{12}H_{20}NS_{10}Cu$: C, 25.62; H, 3.58; N, 2.49; S, 56.99. Found: C, 24.65; H, 3.45; N, 2.34; S, 55.23%.

(Me$_4$N)[Au(ttdt)$_2$]. mp: 145.0–146.0 °C. Anal. Calc. for $C_{12}H_{20}NS_{10}Au$: C, 20.71; H, 2.90; N, 2.01; S, 46.08. Found: C, 21.40; H, 2.96; N, 1.90; S, 47.85%.

X-Ray crystallography

Crystal data for 1b. $C_{24}H_{36}NS_{10}Cu$, $M = 722.70$, primitive monoclinic cell, space group $P2_1/n$ (no. 14), $a = 12.108(2)$, $b = 17.141(1)$, $c = 16.813(2)$ Å, $\beta = 102.16(1)°$, $V = 3411.1(8)$ Å^3, $Z = 4$, $D_c = 1.407$ g cm^{-3}, $\mu = 12.68$ cm^{-1}. The intensity data ($2\theta < 55°$) were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and 12 kW rotating anode generator. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorenz and polarization effects. The structure was solved by heavy atom Patterson methods (PATTY) and expanded using Fourier techniques. The refinement was carried out against *F*. The non-hydrogen atoms were refined anisotopically. The final cycle of full-matrix least squares refinement was based on 3141 observed reflections [$I > 3.00\sigma(I)$] and 325 variable parameters with $R(R_w) = 0.052$ (0.037). All calculations were performed using teXsan crystallographic software package of Molecular Structure Corporation.[11]

Crystal data for 1c. $C_{24}H_{44}NS_{10}Au$, $M = 864.18$, primitive monoclinic cell, space group $P2_1/n$ (no. 14), $a = 12.155(4)$,

$b=17.230(4)$, $c=16.974(3)$ Å, $\beta=102.51(2)°$, $V=3470(1)$ Å^3, $Z=4$, $D_c=1.654$ g cm^{-3}, $\mu=48.72$ cm^{-1}. The intensity data ($2\theta<55°$) were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda=0.710$ 69 Å). An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.6145 to 1.0000. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods (SAPI91) and expanded using Fourier techniques. The refinement was carried out against F. The non-hydrogen atoms were refined anisotopically. The final cycle of full-matrix least squares refinement was based on 3813 observed reflections [$I>3.00\sigma(I)$] and 325 variable parameters with $R(R_w)=0.046$ (0.036). All calculations were performed using teXsan crystallographic software package of Molecular Structure Corporation.[11]

Crystal data for TTF[Au(ttdt)$_2$]. $C_{14}H_{12}S_{14}Au$, $M=826.06$, primitive triclinic cell, space group $P\bar{1}$ (no. 2), $a=12.349(3)$, $b=13.438(3)$, $c=7.387(2)$ Å, $\alpha=124.54(2)$, $\beta=120.88(2)$, $\gamma=101.24(1)°$, $V=629(1)$ Å^3, $Z=1$, $D_c=2.179$ g cm^{-3}, $\mu=70.27$ cm^{-1}. The intensity data ($2\theta<55°$) were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda=0.71069$ Å) and 18 kW rotating anode generator. The linear absorption coefficient, μ, for Mo-Kα is 70.3 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.8003 to 0.9995. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELX86) and expanded using Fourier techniques. The refinement was carried out against F. The non-hydrogen atoms were refined anisotopically. The final cycle of full-matrix least squares refinement was based on 2723 observed reflections [$I>3.00\sigma(I)$] and 128 variable parameters with $R(R_w)=0.063$ (0.077). All calculations were performed using teXsan crystallographic software package of Molecular Structure Corporation.[11]

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 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/73.

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