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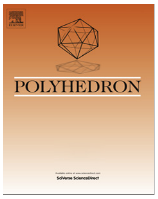

Synthesis and structures of perthio- and polymeric metal complexes with the tetrathio- and dithioterephthalate ligands

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ABSTRACT

The thioterephthalate anions $[1,4\text{-}(CS_2)_2C_6H_4]^{2-}$, TTT, (**I**); $[1,4\text{-}(CS_2)(CO_2)C_6H_4]^{2-}$, DTT, (**III**); and, $[1,4\text{-}(COS)(COS)C_6H_4]^{2-}$, DCT, (**IV**) have been synthesized and isolated as tetraphenylphosphonium $(Ph_4P)^+$ salts, (**I**, **III**, **IV**), tetra *n*-butylammonium $(n\text{-}Bu_4N)_2$TTT (**II**) and tetra-ethyl ammonium $(Et_4N)_2$TTT salts (**IIa**). **I**, **IIa** and **IV** have been characterized structurally. The $S_2C{-}C_6H_4$ dihedral angles Φ vary from 7° to 44°. The electronic spectra of the green Ph_4P^+ (**I**) ($\Phi = 16$) and the red Et_4N^+ (**IIa**) ($\Phi = 44$) salts in CH_3CN solution are identical and indicate a low energy barrier to rotation about the $S_2C{-}C_6H_4$ bond. The $(-CS_2)$ groups in **I** and **III** react with either Cu(I)/S or with Cu(II) and undergo a sulfur addition reaction to give the "sulfur-rich" $(-CS_3)^-$ units that are coordinated to Cu(I) as bidentate chelates in the diamagnetic $[ClCuS_3C{-}C_6H_4{-}CS_3CuCl]^{2-}$, (**V**) and $[XCuS_3C{-}C_6H_4{-}CO_2]^{2-}$, (**VI**), ($X = Cl^-$, Br^-) complexes. In the latter the Cu(I) ions are bound to halide ligands and display a distorted trigonal planar coordination. Generation of S^{2-}, or S_2^{2-}, by cleavage of the C–S bonds, also occurs in the solid state synthesis of the unique $[(n\text{-}BuS)_2Ni_{12}(S)_8(S_2)_6]^{2-}$ cluster (**IX**), at 140 °C, by the reaction of $Ni(OAc)_2{\cdot}4H_2O$ with **II**. The $[Ni_{12}(S)_8(S_2)_6]$ core in **IX** is best described as a distorted S_8 cube with 12 Ni(II)S_4 square planar units located at the centers of the cube edges. Six S_2^{2-} ligands one on each of the six, S_8, cube faces, are quadruply bridging the Ni ions. Two *n*-Bu^+ groups are bound, to two of the S^{2-} ligands that define one of the S_8 cube diagonals. A bridging mode of **IV** and **III** is found in $\{[Cu(DCT)(PPh_3)]^-\}_n$, (**X**) and $\{Ni(DTT)_3Zn_2(DMSO)_6\}_n$, (**XI**), respectively. In the polymeric **X**, the trigonal planar Cu(I) ions are bound to the S donors of two **IV** ligands and one PPh_3. In **XI**, the Ni(II) ion is octahedrally coordinated by three CS_2 groups from two "bridging" and one "terminal" type DTT ligands. The CO_2 groups of the "bridging" ligands are bound in a mono-dentate bridging fashion to one of the four-coordinate Zn(II) ions and the "terminal ligand" is coordinated in a bi-dentate fashion to a non-bridging six-coordinate Zn(II) ion. Dimethylsulfoxide molecules complete the coordination spheres around the Zn(II) ions.

1. Introduction

Crystalline, microporous, solids obtained by connecting metal clusters with multifunctional bridging ligands have received great attention in recent years. The basic Zn acetate core Zn_4O or the dinuclear L_2Cu_2 unit, are found in the acetate cluster $Zn_4O(OAc)_6$ and in $L_2Cu_2(OAc)_4$. The carboxylate groups in these compounds, as well as in other carboxylate clusters, such as $[M_3(\mu_3\text{-}O)(O_2CR)_6$, ($M = Cr^{+3}$, Fe^{+3}, Al^{+3} etc.), the linear $M_3(O_2CR)_6$, the oxo-centered, $M_4(\mu_4\text{-}O)((O_2CR)_8$ with a square planar M_4O core and others [1] can be replaced by the carboxylate units in multi-carboxylate phenyl ligands to form polymeric materials. Many of these, often low density, metal organic frameworks, MOFs, contain solvent molecules within the lattice voids [2]. Upon desolvation they have been found effective in the storage of small molecules such as N_2, CO_2 CH_4 and H_2 [3]. The storage of H_2 is of particular interest given the potential use of H_2 as a fuel. The interactions of relatively inert guest molecules within the MOF lattice voids determine the strength of physi-sorption and the temperatures at which these materials can be effective as storage media. A ΔH of adsorption between 15 and 20 kJ mol^{-1} is desirable for effective H_2 storage at room temperature [4].

The use of MOFs based on metal carboxylate clusters with multifunctional carboxylate bridges (such as terephthalates), as H_2 storage materials, often is characterized by weak interactions and consequently these materials function best at cryogenic temperatures [4]. As a result of M–O bonding between oxophilic metal ions and the carboxylate ligands, the porous framework products, in terephthalate-based MOFs, potentially may be susceptible to hydrolysis. Hydrolysis would have an adverse effect in the utility of these extended frameworks as materials for the storage of gases. An increase in the ΔH of adsorption of H_2 may be expected for

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materials that contain coordinatively unsaturated metal centers within the organic linkers [4].

We suggest that a class of bridging connectors that may satisfy some of the requirements for optimal adsorption of H_2 are those that contain Ni^{+2}, Cu^{+2}, Rh^{+} or Pt^{+2} complexes of S,S coordinated, multitopic thiocarboxylate ligands that may serve as terephthalic acid substitutes in MOFs. The conductivity, doping and redox chemistry of a dithiolene based metal organic framework has been reported [4b]. The effective use of the TTT dianion as a bridging connector has been reported in the synthesis of the isomorphous polymeric M(TTT)(DMF) 2 complexes M = Zn(II), Mn(II)). The structure of the Zn complex consists of one dimensional "zig-zag" chains [5].

Our interest in the design of extended frameworks with thiocarboxylate complexes as bridging ligands has led us to a structural/synthetic study of the tetrathioterephthalate, TTT, (Fig. 1, **I**) [6], dithioterephthalate, DTT, (Fig. 1, **III**) [7], and the 1,4-thioacyl benzene, DCT, (Fig. 1, **IV**) [8], ligands, their chelating properties and their ability to serve as ditopic linkers. The TTT, DTT, and DCT, ligands (pK_a's of the dithiobenzoic, thiobenzoic and benzoic acid at 1.92, 2.48 and 4.20 respectively [9]) were prepared by modified procedures of the previously reported syntheses [6–8]. In this paper we report on certain unique reactivity characteristics of the thioterephthalate ligands. The latter include: (a) facile C–S bond cleavage with generation of elemental sulfur and subsequent formation of "sulfur-rich" thiocarboxylates and also of sulfido and polysulfido ligands. (b) The ability of the thio-carboxylate ligands to serve bi-functionally as homo-metallic or hetero-metallic bridges.

Herein we report on the syntheses and structural characterization of the "sulfur-rich" $(PPh_4)_2$[ClCu(SDTT)] and $(PPh_4)_2$[ClCu(STTTS)CuCl] complexes, (Fig. 2, **V**, **VI**) the polymeric $\{[Cu(DCT)(PPh_3)](Ph_4P){\cdot}Et_2O\}_n$ (Fig. 2, **X**) and $\{Ni(DTT)_3Zn_2(DMSO)_6\}_n$ (Fig. 2, **XI**) complexes. The solvo-thermally obtained, n-Bu_4N^+ salt, of the $[(n\text{-}BuS)_2Ni_{12}(S)_8(S_2)_6]^{2-}$ cluster (Fig. 2, **IX**) also was the product of the reaction between $Ni(OAc)_2{\cdot}4H_2O$ and **II** and was structurally characterized.

2. Experimental

All reactions have been performed under aerobic conditions. Ligands TTT [6] DTT [7] and DCT [8] were prepared by modified procedures.

IR spectra were obtained on a Perkin Elmer BX FT-IR spectrometer (mid-IR) and a Nicolet 740 FT-IR spectrometer (Far-IR) in KBr pellets. Mass spectra were collected on a Micromass LCT Time-of-Flight mass spectrometer.

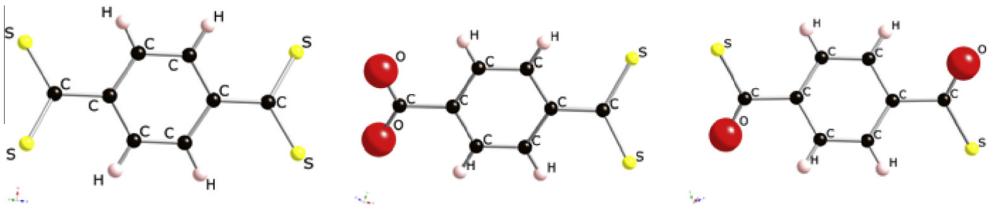
2.1. Crystallography

Single crystal X-ray diffraction data for all compounds except **XI** were collected on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 Å) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities for **XI** were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal or on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 1500 W power (50 kV, 30 mA).

Yellow needles of $\{[Cu(CDT)(PPh_3){\cdot}(Ph_4P){\cdot}Et_2O]\}_n$, **X** were grown from a diethyl-ether solution of the compound at 23 °C. A crystal of dimensions 0.28 × 0.09 × 0.02 mm was mounted. A total of 3542 images were collected with an oscillation width of 1.0° in ω. The exposure time was 2 s. for the low angle images, 8 s. for high angle. The integration of the data yielded a total of 56650 reflections to a maximum 2θ value of 136.48° of which 8322 were independent and 6850 were greater than $2\sigma(I)$. The final cell constants Table 1) were based on, using the space group $P\bar{1}$ with $Z = 2$ for the formula C52H45.5O3.25P2S2Cu. Full matrix least-squares refinement based on F^2 converged at $R_1 = 0.0755$ and $wR_2 = 0.2304$ [based on $I > 2\sigma(I)$], $R_1 = 0.0835$ and $wR_2 = 0.2442$ for all data. Additional details are presented in Table 1 and are given as Supporting information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Red-brown needles of $\{Ni(DTT)_3Zn_2(DMSO)_6\}_{n,}$ **XI**, were grown from a dimethylsulfoxide solution at 23 °C. A crystal of dimensions 0.13 × 0.09 × 0.03 mm was mounted. The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 2966 frames were collected with a scan width of 0.5° in w and 0.45° in phi with an exposure time of 80 s/frame. The crystal was determined to be a non-merohedral twin with indexing preformed with CELL_NOW. Reflections from the primary component were used as the basis of an HKLF 4 input file. The integration of the data yielded a total of 28359 reflections to a maximum 2θ value of 37.84° of which 4695 were independent and 3781 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 5981 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with TWINABS (CELL_NOW: SHELDRICK, G. v.2008/2, Program For Indexing Twins) and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package (Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.) using the space group $P\bar{1}$ with $Z = 2$ for the formula C35H45O12S12NiZn2. Disordered lattice solvates, presumably DMSO and possibly water were treated as contributing to diffuse scatter by the SQUEEZE subroutine of the PLATON program suite, (A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands).

All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at $R_1 = 0.1910$ and $wR_2 = 0.4654$ [based on $I > 2\sigma(I)$], $R_1 = 0.2062$ and $wR_2 = 0.4737$ for all data. Additional details are presented in Table 1 and are given as Supporting information in a CIF file.



I **III** **IV**

Fig. 1. Structures of the thioterephthalate salts. **I**, $(Ph_4P)_2$(TTT); **III**, $(Ph_4P)_2$(DTT); **IV**, $(Ph_4P)_2$(DCT).

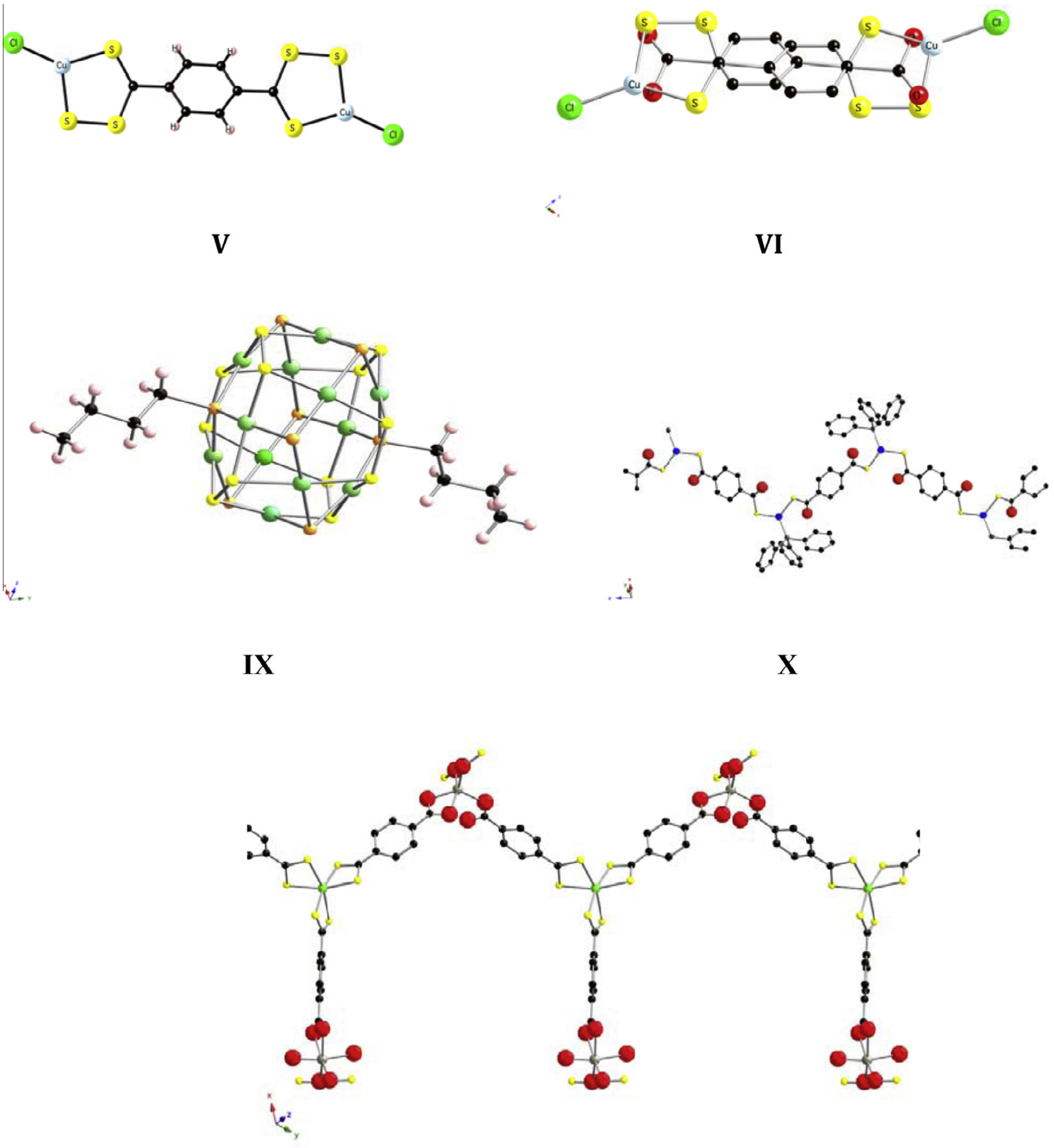


Fig. 2. Structures of the thioterephthalate derivatives. $(Ph_4P)_2[ClCuS_3C–C_6H_4–CS_3CuCl]$ **V**, the positionally disordered $(Ph_4P)_2[XCuS_3C–C_6H_4–CO_2]$ **VI**, $(n\text{-}Bu_4N)_2[(n\text{-}BuS)_2Ni_{12}(S)_8(S_2)_6]$ **IX**, $\{[Cu(DCT)(PPh_3)]\ (Ph_4P)\cdot Et_2O\}_n$ **X**, and $\{Ni(DTT)_3Zn_2(DMSO)_6\}_n$ **XI**.

2.2. Syntheses

2.2.1. Bis-tetraphenylphosphonium tetrathioterephthalate, (**I**, **Ia**)

2.2.1.1. *$[Ph_4P]_2[1,4\text{-}(CS_2)_2C_6H_4]$; $[Ph_4P]_2(TTT)$.* To a solution of sodium methoxide (10.8 g, 0.20 mol) in 300 ml of dry methanol, sulfur (6.40 g, 0.20 mol) was added and refluxed for 3 h. Then *p*-xylyl chloride, $(H_3C–C_6H_4–CH_2Cl)$ (8.75 g, 0.05 mol) was added in small portions for 1.5 h and refluxed overnight. The solution was filtered and the solvent was partially evaporated to give a dark-brown residue which was treated with a large excess of dilute HCl to give a green precipitate of the tetrathio acid (5.5 g). The above precipitate was isolated and dissolved in 150 ml of 10% NaOH solution and then added to 150 ml of a hot aqueous solution of tetraphenyl phosphonium bromide (20 g, 0.047 mol).

The dark red-brown precipitate was recrystallized either from methanol–water or from hot ethanol to give the desired compound with water or ethanol as solvent of crystallization.

The methanol–water recrystallized product, (**I**), is red in the solid state whereas the ethanol recrystallized product (**Ia**) is green in the solid state. Yield for **I**, (22 g, 48.5%). mp: 160–162 °C. *Anal.* Calc. for $C_{56}H_{44}P_2S_4$: (**I**) M.W. = 907.16. C, 74.14; H, 4.89. Found: C, 73.22; H, 5.29%. IR (cm^{-1}) 3432(m), 3050(w), 3004(w), 1584(m), 1437(vs), 1433(vs), 1393(w), 1376(w), 1335(w), 1310(w), 1184(m), 1106(vs), 1009(s), 996(s), 888(m), 858(m), 752(m), 722(vs), 688(s), 608(w), 526(vs). FAR-IR. UV–visible spectrum (DMF): $\lambda_{max(nm)}$, 521, 330. NMR(CD_3CN): δ7.9–7.6(br, 44H); 3.6(q, 2H); 1.1(t, 3H). MS: (ESI+) *m*/*z* 339.1; MS: (ESI−) *m*/*z* 227.8.

2.2.2. Bis-tetrabutylammonium tetrathioterephthalate, ***II***

2.2.2.1. *$(n\text{-}Bu_4N)_2$ $[1,4\text{-}(CS_2)_2C_6H_4]$; $(n\text{-}Bu_4N)_2TTT$.* It was prepared following the above procedure by using tetrabutyl ammonium chloride (13.06 g, 0.047 mol) instead of tetraphenyl phosphonium bromide. The color of this compound is pink-red. Yield (15 g, 42%). mp 68–69 °C. *Anal.* Calc. for $C_{40}H_{76}N_2S_4$: M.W. = 713.31. C, 67.35; H, 10.74; N, 3.93. Found: C, 66.88; H, 9.82; N, 3.24%. IR(cm^{-1}): 3432(m), 2960(vs), 2934(m), 2873(m), 1483(s), 1462(m), 1379(m), 1219(w), 1150(w), 1100(w), 1013(vs), 890(s), 834(s), 798(s), 738(s), 496(s). NMR(CD_3CN): δ 8(s, 4H); 3.1(t, 16H); 1.62(m, 16H); 1.35(m, 16H); 0.96(t, 24H). MS: (ESI+) *m*/*z* 242.3; MS: (ESI−) *m*/*z* 227.8.

Table 1
Crystallographic and refinement data.

	I	**Ia**	**III**	**V**	**VI**
	$(PPh_4)_2TTT$	$(PPh_4)_2TTT·2EtOH$	$(PPh_4)_2DTT·2EtOH$	$(PPh_4)_2[Cu_2TTT)Cl_2$	$(PPh_4)_2[CuDTT)Cl]$
Color	green	brown	red		
Size (mm)	0.34 × 0.24 × 0.2	0.40 × 0.10 × 0.07	0.28 × 0.16 × 0.14	0.16 × 0.12 × 0.035	0.41 × 0.14 × 0.12
Formula	$C_{56}H_{44}P_2S_4$	$C_{60}H_{56}O_2P_2S_4$	$C_{60}H_{56}O_4P_2S_2$	$C_{56}H_{44}Cl_2P_2S_6Cu_2$	$C_{56}H_{44}ClO_2P_2S_3Cu$
Weight	907.16	999.23	967.11	1169.29	1006.09
Space group	$P2_1/n$	$P2_1/n$	Pc	$P\bar{1}$	$P\bar{1}$
Unit Cell dimensions					
a (Å)	10.0469(7)	12.6773(9)	12.7345(8)	9.3608(6)	9.1629(6)
b (Å)	15.7502(11)	15.9314(11)	15.3061(10)	9.6370(6)	9.2845(6)
c (Å)	14.6751(10)	14.225(1)	13.4780(9)	15.4408(10)	15.4553(10)
α (°)	90.00	90.00	90.00	105.067(1)	78.1250(10)
β (°)	90.412(1)	112.892(1)	108.377(1)	102.685(1)	73.6810(10)
γ (°)	90.00	90.00	90.00	93.993(1)	89.1180(10)
V (Å^3)	2322.1(3)	2646.8(3)	2493.1(3)	1300.27(14)	1233.59(14)
Z	4	2	2	2	1
T (K)	85(2)	293(2)	85(2)	85(2)	85(2)
Absorption coefficient	0.312	0.282	0.220		
$F(000)$	948	1052	1020		
θ range (°)	1.90–28.35	1.83–19.24	169–28.4		
Reflections	5805	2211	12414	6489	6182
R_1	0.0516	0.0492	0.0388	0.0264	0.0413
wR_2 $[I > 2\sigma(I)]$	0.1357	0.1241	0.0999	0.0718	0.1096
R_1	0.0662	0.0662	0.0409	0.0304	0.0501
wR_2 (all data)	0.1467	0.1367	0.1014	0.0792	0.1153
Goodness-of-fit (GOF) (F^2)	1.057	1.021	1.033	1.112	1.090

Table 1
Crystallographic and refinement data (continued).

	IV	**X**	**IX**	**XI**
	$(PPh_4)_2DCT$	$[Cu(DCT)(PPh_3)]^-(Ph_4P).(Et_2O)_{1.5}$	$[Ni_{12}S_{18}(n\text{-}BuS)_2]^{2-}$ $[Bu_4N]_2$	$Ni(DTT)_3Zn_2(DMSO)_6$
Size (mm)	0.20 × 0.11 × 0.23	0.28 × 0.09 × 0.02	0.21 × 0.18 × 0.18	0.13 × 0.09 × 0.03
Formula	$C_{56}H_{44}O_2P_2S_2$	$C_{52}H_{45.5}O_{3.25}P_2S_2Cu$	$C_{41}H_{51}C_{12}N_2S_{20}Ni_{12}$	$C_{35}H_{45}O_{12}S_{12}NiZn_2$
Weight	875.03	911.98	1988.46	1231.88
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
λ (Å)	1.54178	1.54178	1.54178	0.71073
Unit cell dimension				
a (Å)	9.0494(6)	10.3820(2)	13.7145(3)	12.478(3)
b (Å)	9.5133(7)	12.2861(2)	14.2809(3)	15.366(4)
c (Å)	14.0642(10)	19.461(1)	19.462(1)	17.808(5)
α (°)	75.137(1)	74.927(5)	84.909(6)	113.841(4)
β (°)	71.765(1)	86.02(6)	79.705(6)	100.781(4)
γ (°)	80.838(1)	74.435(5)	73.947(5)	98.954(4)
V (Å^3)	1107.4(1)	2309.06(18)	3601.0(3)	2964(7)
Z	1	2	2	2
T (K)	85.2	85.2	85.2	85.2
Absorption coefficient	0.237	0.250		
$F(000)$	458	949	2002	1262
θ range (°)	1.56–29.65	6.59–68.24	2.31–50.43	2.25–18.92
Reflections	12449	8322	2211	4695
Limit. indices	$-12 < h < 12$	$-12 < h < 12$	$-13 < h < 13$	$-11 < h < 11$
	$-13 < k < 13$	$-14 < k < 14$	$-14 < k < 14$	$-13 < k < 13$
	$-19 < l < 19$	$-23 < l < 23$	$-19 < l < 19$	$-16 < l < 16$
R_1	0.0336	0.0755	0.0839	0.1910
wR_2, $[I > 2\sigma(I)]$	0.0892	0.2304	0.2409	
R_l (all data)	0.0391	0.0835	0.0907	0.2062
wR_2 (all data)	0.0940	0.2442	0.2480	
Goodness-of-fit (GOOF) (F^2)	1.046	1.207	1.035	1.070

2.2.3. Bis-tetraphenylphosphonium dithioterephthalate, *III*

2.2.3.1. $[Ph_4P]_2[1,4\text{-}(CS_2)(COS)C_6H_4]$; $[Ph_4P]_2$ DTT. 1.17 g of Potassium (0.03 mol) was dissolved in 100 ml dry ethanol. To this solution 0.64 g of sulfur (0.02 mol) was added followed by 4-Bromomethylbenzoic acid (2.15 g, 0.01 mol) and the mixture was refluxed overnight. The solution was filtered and the solvent was evaporated to give a yellow-brown color precipitate of bis-potassium dithioterephthalate. The precipitate was dissolved in 100 ml of water and the solution was added to 100 ml of a hot aqueous solution of tetraphenyl phosphonium bromide (4.02 g, 0.0096 mol). A green precipitate formed, was isolated and was recrystallized from ethanol-ether to give the desired product with ethanol as solvent of crystallization.

Yield (3.41 g, 39%). *Anal.* Calc. for $C_{56}H_{44}O_2P_2S_2$: M.W. = 875.03. C, 76.87; H, 5.07. Found: C, 75.92; H, 4.80%. mp 197–199 °C. IR(cm^{-1}): 3399(m), 3051(w), 2954(w), 1581(s), 1543(m), 1482(m), 1437(vs), 1361(vs), 1312(m), 1185(m), 1108(vs), 1052(w), 1004(s), 993(s), 903(w), 878(w), 819(w), 793(m), 757(m), 722(vs), 689(vs), 614(w), 525(vs). $\lambda_{max(nm)}$ DMF MS: (ESI−) m/z 197.7.

2.2.4. Bis-tetraphenyl phosphonium 1,4-dithiocarboxybenzene, *IV*

2.2.4.1. $[Ph_4P]_2[1,4\text{-}(COS)(COS)C_6H_4]$; $[Ph_4P]_2DCT$. 2 g of terepthaloyl chloride (9.85 mmol) was dissolved in 30 ml of dichloromethane. To the above solution N,N′-dimethylthioformamide (1.75 ml, 20.2 mmol) was added dropwise under stirring. H_2S gas was passed in the solution at 25 °C, at a moderate rate, for 1 h. Then the solvent was removed in a rotary evaporator to give a yellow solid which was washed with dichloromethane and water (1.77 g, 8.96 mmol). The above acid was dissolved in 30 ml of 10% NaOH solution and to it 2 equivalents of tetraphenyl phosphonium bromide (7.5 g, 17.92 mmol) in hot water was added and the mixture stirred for 30 min to give a dark yellow solid. Yield (6.97 g, 89%). *Anal.* Calc. for $C_{56}H_{44}O_2P_2S_2$: M.W. = 875.03. C, 76.87; H, 5.07. Found: C, 76.02; H, 5.29%. IR (cm^{-1}) 3453(m), 3394(m), 3055(w), 1620(w), 1583(m), 1550(w), 1513(vs), 1480(m), 1432(vs), 1310(w), 1170(s), 1104(vs), 993(m), 927(s), 857(w), 750(m), 720(vs), 687(s), 669(m), 525(vs). Uv–Vis (DMF): 328 nm. NMR ($CDCl_3$): δ 7.8–7.4(m, 52H). MS: (ESI+) *m/z* 339.1; MS: (ESI−) *m/z* 195.8, 1178.9, 162.9.

2.2.5. $(PPh_4)_2[ClCu(STTTS)CuCl]$, *V*

Method A: To a 10 ml DMF solution of the $[Ph_4P]_2(TTT)$ ligand, (0.5 g, 0.55 mmol), a $CuCl_2{\cdot}2H_2O$ solution (0.093 g, 0.55 mmol in 5 ml DMF) was added drop-wise under stirring and the stirring continued for 2 h. The solution was filtered and layered with 75 ml of diethyl ether. Upon standing, brown colored crystals formed. Yield (0.263 g, 41%). *Anal.* Calc. for $C_{56}H_{44}Cl_2P_2S_6Cu_2$: M.W. = 1169.29. C, 57.52; H, 3.79. Found: C, 56.90; H, 3.42%. IR(cm^{-1}): 3429(m), 3054(w), 1664(w), 1584(w), 1572(w), 1482(w), 1440(s), 1434(vs), 1400(w), 1338(w), 1313(w), 1234(w), 1184(w), 1163(w), 1107(vs), 1015(s), 1005(s), 996(s), 974(w), 895(vs), 842(m), 760(m), 750(m), 724(vs), 689(vs), 578(s), 561(s), 525(vs). $\lambda_{max(nm)}$ (DMF): 506, 382. NMR (DMSO): δ 8–7.5(m, 44H). MS: (ESI+) *m/z* 339.1; MS: (ESI−) *m/z* 390.9, 354.9,327, 290.9, 223.9, 134.9.

Method B: To a 10 ml DMF solution of the $[Ph_4P]_2(TTT)$ ligand, (0.5 g, 0.55 mmol), S powder (0.036 g, 1.1 mmol) was added and was immediately followed by the addition of CuCl (0.108 g, 1.1 mmol) under stirring and the stirring continued for 2 h. A violet color solution was obtained and was filtered. It was layered with 50 ml of diethyl ether and upon standing gave a red-brown crystalline product. Yield (0.39 g, 60%). The compound was found identical to that obtained by method A.

2.2.6. $(PPh_4)_2[Cu(SDTT)Cl]$, *VI*

Method A: To a 10 ml DMF solution of the $[Ph_4P]_2(DTT)$ ligand, (0.5 g, 0.55 mmol), a $CuCl_2{\cdot}2H_2O$ solution (0.050 g, 0.28 mmol in 5 ml DMF) was added slowly with stirring and the stirring continued for 2 h. The solution was filtered and layered with 75 ml of diethyl ether to give red colored crystals. Yield (0.229 g, 40%). *Anal.* Calc. for $C_{56}H_{44}ClO_2P_2S_3Cu$: M.W. = 1006.09. C, 66.85; H, 4.41. Found: C, 66.12; H, 4.18%. IR (cm^{-1}): 3417(m), 3051(w), 2324(m), 1687(s0, 1584(w0, 1482(w), 1434(vs), 1400(w), 1374(w0, 1312(w), 1224(s0, 1178(w), 1108(vs), 1004(m), 994(s), 864(w), 776(m), 754(m), 722(vs), 689(vs), 667(w), 559(w), 526(vs), 456(vs). $\lambda_{max(nm)}$ DMF: 491, 356. NMR (DMSO): δ 8–7.7(m, 44H). MS: (ESI+) *m/z* 339; MS: (ESI−) *m/z* 326.9, 291, 263, 247, 134.9.

Method B: The same compound is obtained from S/CuCl as describd above for the synthesis of **V.**

2.2.7. $(Ph_4P)_2$ [(TTT)Ni(STTT], *VII*

Procedure: To a DMF solution of the $(PPh_4)_2TTT$ ligand (1 g, 1.1 mmol in 20 ml DMF), a $[Ni(MeCN)_6](BF_4)_2$ solution (0.263 g, 0.55 mmol in 5 ml DMF) was added drop wise under stirring to give a brown precipitate. Elemental Sulfur powder (0.070 g, 2.2 mmol) was added to the above mixture and allowed to stir for 2 h. The precipitate slowly dissolved to give a brown color solution along with a minor precipitate. The solution was filtered to isolate a small amount of black precipitate and brown colored filtrate was layered with ca. 150 ml ether, affording a brown precipitate. Yield, 60% based on ligand.

The insoluble black precipitate obtained is insoluble in organic solvents.

The brown product shows the presence of tetraphenyl phosphonium cation in the FT-IR spectrum.

Elemental *Anal.* Calc. for $C_{64}H_{48}S_9P_2Ni$: C, 62.69, H, 4.08. Found: C, 62.78, H, 4.61%.

2.2.8. $(Ph_4P)_2$ $Ni(SDTT)_2$, *VIII*

To a DMF solution of $(PPh_4)_2DTT$ (1 g, 1.14 mmol in 15 ml DMF) a $NiCl_2{\cdot}6H_2O$ solution (0.135 g, 0.57 mmol in 5 ml DMF) was added drop wise under stirring to give a brown precipitate. Elemental Sulfur powder (0.037 g, 1.1 mmol) was added and the mixture was allowed to stir for 2 h. The precipitate slowly dissolved to give a violet color solution. The resulting solution was filtered and layered with ca. 200 ml ether, affording a violet colored crystalline material. Yield 0.77 mmol, 68% based on ligand. Elemental *Anal.* Calc. for $C_{64}H_{54}S_6P_2O_7Ni$: C, 61.59, H, 4.33. Found: C, 61.07, H, 4.35%. FT-IR: 3394(w),3052(w), 1583(w), 1480(w), 1436(s),1235(vs), 1107(vs), 1018(vs), 993(m), 761(m), 723(vs), 691(vs), 600(vs), 525(vs). λ_{max} DMF: 485, 377 nm.

2.2.9. $[Ni_{12}(n\text{-}C_4H_9S)_2(S)_6(S_2)_6][(n\text{-}C_4H_9)_4N]_2{\cdot}CH_2Cl_2$ *IX*

$(n\text{-}Bu_4N)_2TTT$ (0.7 g) and $Ni(OAc)_2{\cdot}4H_2O$ (0.244 g), were intimately mixed (in the air) and placed in a 5 mL glass ampoule. The ampoule was evacuated, sealed and heated in an oven to 140 °C for 3 days. A brown-black oil formed. The oil was dissolved in 10 mL of CH_2Cl_2 the solution filtered and layered with 15 mL of diethyl ether. Upon cooling to 3 °C for 5 days (or until fully diffused) a small amount of dark green crystals formed on the wall of the crystallization test tube. The experiment was repeated successfully three times. The small amounts of this compound did not allow for an elemental analysis but a crystal gave a satisfactory Ni:S ratio of 3:5 by microprobe analysis. MS: (ESI+) *m/z* 242.2; MS: (ESI−) *m/z* 1699.7, 1457.4, 671.5, 639.5, 325.2. FT-IR: 2956.0(s), 2926.2(s) 2868.4(m), 1635.6(w), 1458.4(m), 1383.1(m), 1262.5(w), 1166.8(w), 1106.1(w), 1032.6(w), 881.7(w), 741.7 (m) 509.0(w).

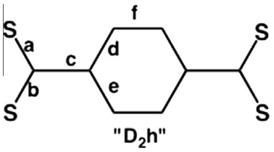
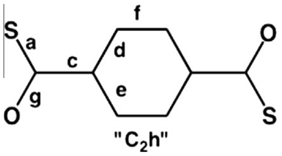
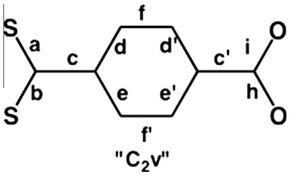
2.2.10. $\{[Cu(DCT)(PPh_3)]^{-}[Ph_4P]\ Et_2O\}_n$

To a 12 mL CH_3CN solution of $(Ph_4P)_2(DCT)$, (0.36 g, 0.44 mmol) was added a 5 mL solution of $Cu(CH_3CN)_4PF_6$ (0.28 g, 0.44 mmol). An insoluble red-orange precipitate formed instantly suspended in an essentially colorless solution. The precipitate was filtered, washed with diethyl-ether, Et_2O, and dried. It was suspended in 20 mL of dimethylformamide, DMF, and Ph_3P was added (2.6 g, 10 mmol). The red-orange solid dissolved rapidly and a yellow solution was obtained. A layer of Et_2O (20 mL) was carefully deposited on top of the DMF solution. Upon standing for 24 h. at room temperature, yellow crystals formed. Microprobe analysis showed a S:Cu:P ratio of 2:1:1. The reaction was reproducible (as established by single crystal X-ray diffraction), however the quantity of 373(w), 340(w). $\lambda_{max(nm)}$ DMSO: 291, 356 these crystals was insufficient for elemental analysis.

2.2.11. $\{Ni(DTT)_3Zn_2(DMSO)_6{\cdot}CH_2Cl_2\}_n$ *XI*

*Method A (from preformed $(Ph_4P)_2[Ni(DTT)_2]$); see synthesis of **VIII** above):* An amount of $(Ni(CH_3CN)_6)(BF_4)_2$ (0.1 g, 0.21 mmol) in 15 mL of CH_3CN was added dropwise to 20 mL of a CH_3CN solution of $(Ph_4P)_2DTT$ (0.37 g, 0.42 mmol). A precipitate formed immediately and the suspension was stirred for 10 min. The brown solid

Table 2
Structures of the thioterephthalate ligands.

	$(Et_4N)_2$TTT **IIa**	$(Ph_4P)_2$TTT **I**	$(Ph_4P)_2$TTT **Ia** – 2EtOH	$(Ph_4P)_2$DCT **IV**	$(Ph_4P)_2$DTT **III** 2EtOH
					
Color of crystals	red	green	brown	yellow	yellow-brown[c]
Φ[a] S–C–S/Ph S–C–O/Ph O–C–O/Ph	43.96°	23.11°	16.08°	25.07°	28.85[d]; 28.33[e]; 7.12[d]; 8.47[e]
a	1.688(1)	1.684(3)	1.617(6)	1.721(1)	1.691(1); 1.692[e]
b	1.683(1)	1.640(3)	1.659(6)[b]		1.679(1): 1.677[e]
c	1.496(4)	1.501(6)	1.497(9)	1.510(5)	1.490(4) 1.521(4)
d	1.399(4)	1.397(6)	1.391(8)	1.395(5)	1.397(4) 1.386(4)
e	1.397(4)	1.400(6)	1.382(9)	1.395(6)	1.401(4) 1.394(4)
f	1.389(4)	1.385(6)	1.362(9)	1.385(4)	1.384(4) 1.390(4)
g				1.238(4)	
h					1.250(2); 1.249[e]
i					1.261(2);1.271[e]
S–C–S	124.96(7)°	123.4(1)°	122.6(4)°		124.3(4(11)
S–C–O				124.74(8)	
O–C–O					126.64(16)

[a] The dihedral angle between the SCX unit and the phenyl ring.
[b] Sulfur H-bonded to EtOH.
[c] Themolecule occupies the site in two orientations, differering by 180°, at occupancies of 79% and 21%.
[d] For the ligand at the 79% orientation.
[e] For the ligand at the 21% orientation.

was filtered and washed with CH_3CN, diethyl-ether and air dried. (yield 0.19 g, 80% of $(Ph_4P)_2[Ni(DTT)_2]$). This solid (0.19 g) was added to 20 mL of dimethylsulfoxide, DMSO, and the suspension was stirred slowly until most of the solid had dissolved. The solution was filtered to remove a small amount of undissolved solid and to it was added 1.399 g of $Zn(NO_3)_2{\cdot}6H_2O$. The mixture was stirred for 10 min to give a homogeneous brow red solution. Two mL portions of the solution were placed into a wide-mouth jar that contained 15 mL of chloro-benzene and 0.2 mL of NEt_3. The jar was capped and allowed to stand at room temperature. After 2 days a small amount of red crystals formed, were filtered washed with acetone and air dried. Microprobe analysis, qualitatively showed: S, Ni, and Zn in a 8:1:2 ratio. FT-IR spectra: 3419(m), 2962(w) 1652(m) 1616(m) 1539(m), 1495(w), 1402(vs), 1380(vs), 1306(w), 1265(m), 1224(m), 1170(w), 1133(w), 1100(w), 1016(vs), 989(s), 949(m), 933(m), 838(m), 785(m), 701(w), 665(w), 580(w), 527(w), 508(w), 417(w).

Method B: An amount of $Zn(NO_3)_2{\cdot}6H_2O$ (0.219 g, 0.74 mmol) and $(Ph_4P)_2$DTT) (0.215 g, 0.25 mmol) were dissolved n 10 mL DMSO to give a red solution. To this solution, a solution of $(Ni(CH_3CN)_6)(BF_4)_2$ (0.1 g, 0.21 mmol) in 5 mL DMSO was added and the color changed to a deep red-brown. 1 mL of this solution was layered with 2 mL of CH_3CN. Upon standing overnight, at room temperature, a small amount of red crystals formed. The IR spectra and microprobe analysis data show these crystals to be the same as those obtained by method A. Due to the poor quality of the best crystals obtained, the determined structure of **XI** was of unsatisfactory precision and is reported herein only to support the stoichiometry and atomic connectivity.

3. Discussion

3.1. The thioterephthalate ligands

The structures of the TTT, DTT and DCT ligands (Fig. 1) have been determined (Tables 1 and 2).

In TTT (Fig. 1, **I**) the planar dithio groups make different dihedral angles with the central phenyl rings at (156.89°, 163.92° and, 136.04° in the $(Ph_4P^+)_2$ (Fig. 1, **I**) $(Ph_4P^+)_2$2EtOH, and $(Et_4N^+)_2$ salts, respectively. The S=C–S bond angles are in the range of 122.7(4)–124.95(7)°. The IR spectra of the free TTT ligands show characteristic C=S stretches around 1009 cm^-.

Single crystals of the $(PPh_4)_2$DTT·2EtOH ligand (Fig. 1, **III**) were obtained from EtOH-Ether. The anionic ligand is positionally disordered. The C=S and C–S bond distances are 1.679(2) and 1.691(2) Å, whereas the C=O and C–O bond distances are 1.250(2) and 1.261(2) Å respectively. The S=C–S and O=C–O bond angles are 124.34(11)° and 126.64(16)°. The S=C–S group makes a dihedral angle of 151.28° whereas the O=C–O group makes a dihedral angle of 172.19° with the central phenyl ring indicating that the O=C–O unit is almost planar with the phenyl ring but the S=C–S is unit is non planar. The solvent of crystallization, EtOH, forms hydrogen bonding interaction with the ligand carboxylate ends, (H–OH, 1.45, 1.50 Å). The dithioterephthalate ligand shows the C=O stretching vibration at 1543 cm^{-1} and the C–O vibration at 1361 cm^{-1}. The C=S stretch appears at 1004 cm^{-1}.

Single crystals of $(PPh_4)_2$DCT (Fig. 1, **IV**) were obtained from EtOH-Ether. The C–S bond distances are 1.720(2) whereas the C=O bond distances are 1.238(2) Å. The O=C–S bond angles are

124.74(10)°. The dihedral angle between the O═C–S groups and central phenyl ring is 153.75°.

Crystal and structural details are presented in Tables 1 and 2.

3.2. Sulfur-rich" Cu(I) complexes with the TTT and DTT ligands, **V** and **VI**, respectively

3.2.1. The Cu(I) complexes

The TTT dianion reacts readily with $CuCl_2$ to give the neutral Cu^I complex $(STTT)(CuCl)_2$,**V** (Fig. 2, **V**; Scheme 1) which can be isolated in crystalline form as a tetraphenyl phosphonium salt**.** The additional S is generated from the TTT ligand. **V** also is obtained in the reaction of TTT with CuCl and elemental S (Scheme 1).

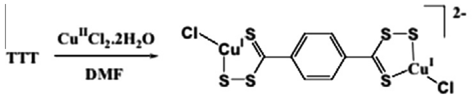
A procedure, similar to the one used in the synthesis of **V** (scheme 1), was used to obtain the $(PPh_4)_2[Cu(SDTT)Cl]$ complex. **VI**, (scheme 2).

The incorporation of the extra sulfur in the Cu(I)-coordinated TTT and DTT ligands at present is difficult to understand. We can only speculate that the apparent stability of the Cu(I)SSCS five-member ring, promotes oxidation of the TTT and DTT, Cu(I)-coordinated, ligands and subsequent reductive cleavage of the C–S bond. The identification of ligand-dissociation by-products will be necessary to determine the validity of this speculation.

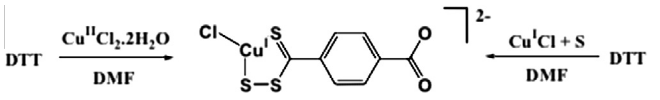
The dicopper complex of the STTT ligand shows the characteristic S–S vibration at 561 cm^{-1}. Mass spectrum shows no molecular ion peak but at 390.9(–CuCl), 354.9(–Cl), 327(–S), 290.9(per-tetrathio ligand only), 223.9, 134.9.

Single crystals of $(PPh_4)_2[Cu_2(STTTS)Cl_2]$·**V**, can be obtained from dimethylformamide-diethyl-ether mixtures and the crystal structure of **V** was determined by X-ray diffraction (Fig. 1, **V**, Table 3). The complex dianion contains two per-tetrathioterephthalte ligands which bind two Cu(I) ions, one each, at the two ends of the ligand. Two chlorides serve as Cu-bound terminal ligands.

The bonds around the Cu(I) are [Cu–S(C═S): 2.2046(5) Å; Cu–S(C–S): 2.2387(5) Å and Cu–Cl: 2.1790(4) Å]. The C═S and C–S bonds are 1.6811(16) and 1.6964(16) Å respectively. The S–S bond is 1.9989(5) Å. The bond angles around the Cu(I) are [S–Cu–S: 99.838(16)°; S–Cu–Cl: 121.087(18)° and 139.050(18)°]. The S═C–S bond angle is 126.26(9)°. The Cu(I) can be best described as having a distorted trigonal planar coordination.



Scheme 1.



Scheme 2.

Table 3
Cu(I) complexes of the STTT and SDTT ligands.

	$(Ph_4P)_2[ClCu(STTTS)CuCl]$	$(Ph_4P)_2Cu(SDTT)X$
Cu–S	2.2046(5); 2.3875(5)	2.201(1); 2.238(2)
Cu–Cl	2.1790(4)	2.2790(8)[a]
S–Cu–S	99.84(2)°	99.56(6)
S–Cu–Cl	121.09(2); 139.05(2)	118.67(6); 141.68(4)
S–S	1.9989(5)	1.999(2)
C–S	1.681(2); 1.696(2)	1.554(3); 1.668(2)
C–O		1.205(8); 1.325(6)
S–C–S	126.3(1)[a]	138.2(2)[a]
O–C–O		125.3(5)

[a] Dihedral angle between the CuS_2CS and phenyl ring: 32.04°.

The oxidative generation of aromatic perthiocarboxylates from dithiobenzoate and dithiotoluate ligands has been observed previously with the bis Ni(II) [10] bis Zn(II) [11] and tris Fe(III) [12] complexes of these ligands.

The structure of **V** demonstrates the utility of the STTT ligand as a bridge for thiophilic ions. We anticipate that the additional sulfur in the STTT ligand would be easily removed by Ph_3P. This reaction has been established in 1,1-dithiolate chemistry [13] and also with "sulfur-rich" dithio-benzoate ligands.

Single crystals of **VI** were obtained from DMF-Ether. The dianion in **VI** (Fig. 1, **VI**, Tables 1 and 3) is positionally disordered and also contains a "sulfur-rich" dithioterephthalate ligand which binds one Cu(I) at the dithiolate end, as the carboxylate end remains free. The geometry around Cu(I) can be best described as distorted trigonal planar with bond lengths around the Cu(I) at [Cu–S(C═S): 2.2008(11) Å; Cu–S(C–S): 2.2382(19) Å and Cu–Cl: 2.2790(8) Å]. The C═S and C–S bonds in the ligand are 1.554(3) and 1.668(2) Å respectively whereas the C═O and C–O bond distances are 1.205(8) and 1.325(6) Å. The bond angles around the Cu(I) are [S–Cu–S: 99.56(6); S–Cu–Cl: 118.67(6) and 141.68(4)]. The S═C–S and O═C–O bond angles are 138.2(2)° and 125.3(5)° respectively. The unusually long Cu–Cl bond in **VI** at 2.279 Å is 0.1 Å longer than the Cu–Cl bond in **V** but still shorter than the Cu–Br bond length in $[CuL^{Et}(Br)$, 2.316(2) Å [14]]; $[[PPh_4]_2[(\eta^5-C_5Me_5)MoS_3Cu_3Br_3]_2$, 2.291 Å [15] and in $[(t\text{-}BuNC)_4Mo(\mu\text{-}t\text{-}BuS)_2CuBr$, 2.317 Å [16] (see Table 4)

Table 4
Structural Details of the $[Ni_{12}(n\text{-}C_4H_9S)_2(S)_6(S_2)_6]^{2-}$, **IX**, cluster.

Distances (#)	Distance[a]	Range	$[Ni_{12}(S)_8(S_2)_6][Et_4N]_3$[b]
Ni–Ni	2.794(7,12)	2.754 (2)–2.825(2)	2.821 2.763(2)–2.915(2)
Ni–S (24)	2.181(5,24)	2.139(3)–2.219(3)	
$Ni–S_2$ (24)	2.173(4,24)	2.137–2.205	
$Ni–S_{nBu}$ (6)	2.200(6,6)	2.185–2.211	
Ni–S (all, 54)	2.179(3,54)	2.137(3)–2.219(3)	2.190(2) 2.142(3)–2.244(3)
$S^2–S^{2-}$ (cube, 12)	4.343(11,12)	4.302(8)–4.376(8)	
S–S S_2^{2-}, 6)	2.105(8,6)	2.069(8)–2.128(8)	
C–S	1.821; 1.848		
$Ni–S–Ni_{corners}$[c]	74.4(5)–112.7 (5)		77–106

[a] The first number in parenthesis represents the larger of the individual standard deviations or the standard deviation from the mean $\sigma = [\Sigma_{i=1}N(x_i - x)_2N(N-1)]^{1/2}$, the second represents the number of chemically equivalent bonds averaged out.

[b] From Ref. [15].

[c] See footnote of Fig. 5 above.

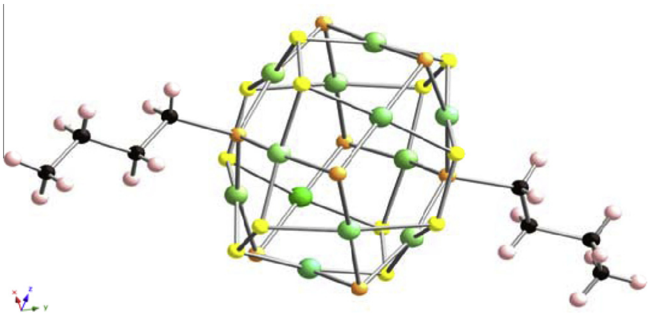


Fig. 3. The $[Ni_{12}(n\text{-}C_4H_9S)_2(S)_6(S_2)_6]^{2-}$, IX, Cluster.

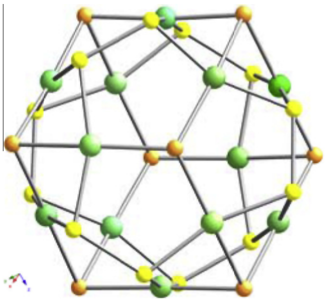


Fig. 4. The $Ni_{12}S_{20}$ framework. The yellow spheres are the S_2^{2-} and the Orange Spheres the S^{2-} Ligands.

Refinement with Br^- present at the same site as Cl^-, converged to a Br^- occupation of 60% The presence of Br^- also was qualitatively verified by microprobe analysis. The structure of **VI** demonstrates that, with a "free" carboxylate unit, the SDTT ligand may serve as a bridge between thiophilic and oxophilic metal ions, and **VI** conceptually may be considered a functionalized benzoate ligand.

The "sulfur-rich" complexes $(Ph_4P)_2$[(TTT)Ni(STTT], **VII** and $(Ph_4P)_2Ni(SDTT)_2$, **VIII**, also can be obtained (see experimental) by the reactions of $(PPh_4)_2$TTT and $(PPh_4)_2$DTT with $[Ni(MeCN)_6](BF_4)_2$ or $NiCl_2{\cdot}6H_2O$ and elemental sulfur in DMF solution.

3.2.2. $[Ni_{12}(n\text{-}C_4H_9S)_2(S)_6(S_2)_6][(n\text{-}C_4H_9)_4N]_2$, **IX**

The synthesis of **IX** was accomplished by the reaction of Ni acetate tetrahydrate and **II** in a sealed tube at 140° for 3 days. The molten **II** served as a solvent for the reaction and also as a source for *n*-Bu^+ that adds to S^{2-} to form the *n*-BuS^- ligands. The formation of the S^{2-} and S_2^{2-} anions from the decomposition of the coordinated TTT ligand demonstrates the propensity of the dithioaryl group to undergo reductive cleavage of the C–S bond. This reaction in the synthesis of **IX** undoubtedly is promoted by the thermodynamic stability of the Ni-S cluster.

The cuboctahedral $Ni_{12}(n\text{-}BuS)_2(S)_6(S_2)_6]^{2-}$ core in **IX** (Figs. 5–7) is structurally similar to the $[Ni_{12}(S)_8(S_2)_6]^{3-}$ core in the $[Ni_{12}(S)_8(S_2)_6][Et_4N]_3$ cluster [17], **XII**.

The latter was obtained by a lengthy hydrothermal reaction between GeS2, Ni(OAc)2·4H2O, and Et4HCO3 in a 10:1:17 ratio. In this cluster the S2 ligands are related by three mutually perpenticular 2-fold axes (D2 symmetry) and the overall charge suggests a Ni(II)11(Ni(III) formulation. By comparison, the S2 ligands in IX (described as a Ni(12) cluster are related by a center of symmetry. The electronic description of XII was chosen on the basis of spectroscopic evidense for an intravalence charge transfer absorption. The addition of two n-Bu+ groups to S2− ligands and formation of two n-BuS− ligands, in the synthesis of IX, may support the presence of an SH− ligand in XII. The distortion of the [Ni12(S2)6S8]3− framework in XII can be seen in the range of Ni–S–Ni bond angles, 77.0–105.8°, that define the S8 corners. In IX the Ni–S–Ni range is

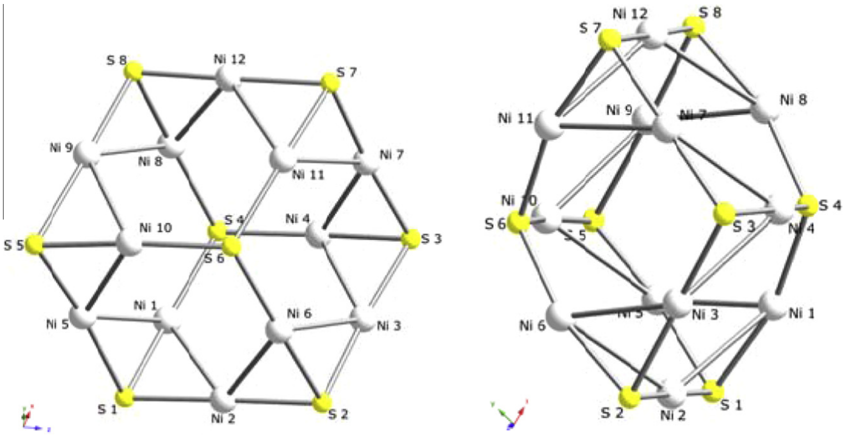


Fig. 5. Two Views of the $Ni_{12}S_8$ Core. Three sets of Ni–S–Ni angles define the S_8 distortion. (Left) Six Ni–SR–Ni angles around: S_6, S_4, range: 110–113°. (Right) Six Ni–S–Ni angles around: S_1, S_2, S_3, S_7, S_8, S_5, range: 95–103° (Right) 12 Ni–S–Ni angles around: S_1, S_2, S_3, S_7, S_8, S_5 range: 74–82°.

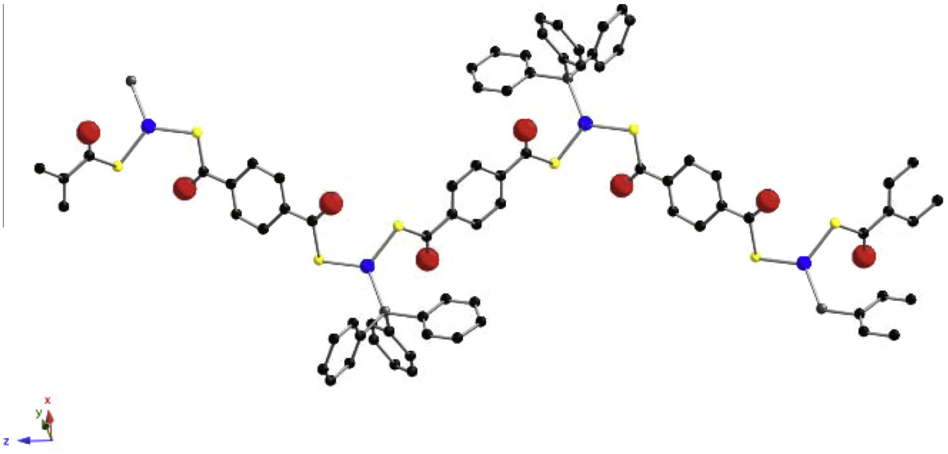


Fig. 6. The $\{[Cu(DCT)(PPh_3)]^{-1}\}_n$ polymer.

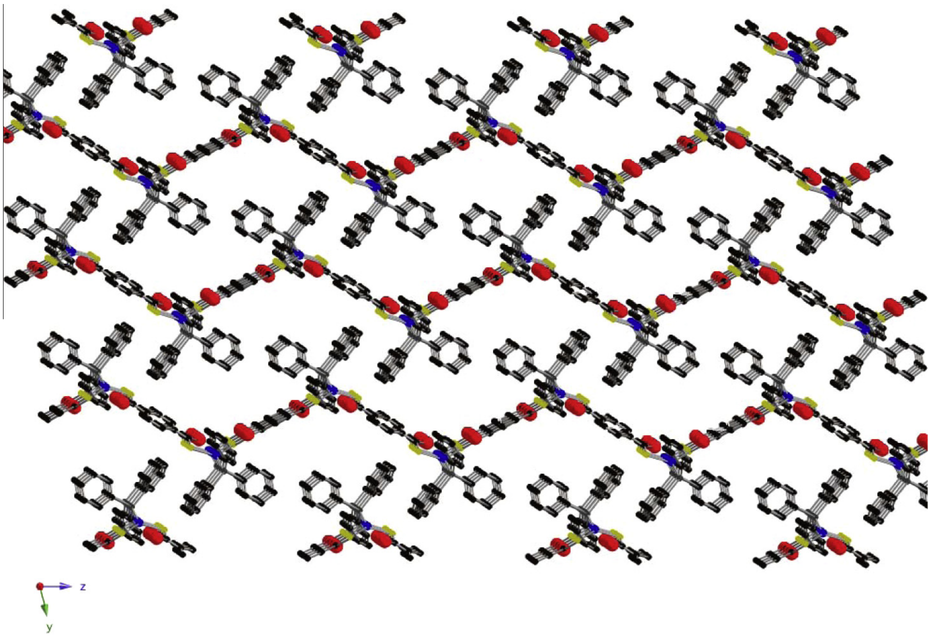


Fig. 7. Packing of the $\{[Cu(DCT)(PPh_3)](Ph_4P)\}_n$ chains parallel to the y–z plane.

Table 5
Structural data for the $\{Cu(DCT)(PPh_3)^{-1}\}_n$ polymer.

Distances		Angles	
Cu–S	2.2417(11); 2.2425(13)	S–Cu–S	120.20(5)
Cu–P	2.2204(12)	S–Cu–P	120.87(4)
$Cu–Cu_{inter}$	21.7690(1)	S–Cu–P	118.62(5)
$Cu–Cu_{intra}$	17.8012(1)		
S–O	2.607(3); 2.610(3)		
Cu–O	3.211(2); 3.267(2)		

74.4(5)–112.7°. The larger of these angles are the Ni-n-BuS-Ni angles that range from 110° to 112.6°.

The μ3-S-n-Bu ligands in IX are located on the S8 cube body diagonal and as a result the Ni12S20 cube is compressed along this diagonal.

The Ni–Ni distances in IX range from 2.754(2) to 2.825(2) Å, with an average value of 2.794(7) Å and are comparable to values found in XII. They are approximately 0.30 Å longer than the average Ni-Ni distance in metallic nicke1 [18], 0.02 Å shorter than found in millerite [19] and 0.27 Å longer than the Ni–Ni distance in hazelwoodite [20]. The Ni–S distances range from 2.137(3) to 2.219(3) Å with an average of 2.179 Å as opposed to averages of 2.272 and 2.306 Å in hazelwoodite and millerite, respectively.

The $Ni_{12}S_8$ core in **IX** is similar to the M/S cores in $[Cu_{12}S_8]^{4-}$ [21] and $[NaAu_{12}S_8]^{3-}$ [22]. The latter do not contain the bridging S_2^{2-} ligands. (Figs. 3 and 4).

3.2.3. *$\{[Cu(CDT)(PPh_3)](Ph_4P)\cdot Et_2O\}_n$*, ***X***

The reaction of $(Ph_4P)_2DCT$ with $Cu(CH_3CN)_4PF_6$ in CH_3CN solution in a 1:1 M ratio is fast and complete. The orange-red precipitate that forms is insoluble in most solvents and most likely a polymer. The analytical data support the 1:1 formulation. The structure of this compound is not known but the polymer reacts with Ph_3P to give the neutral **X** (Fig. 6) which is now soluble, and crystallizes from DMF. The polymer chains stack in the y-z plane

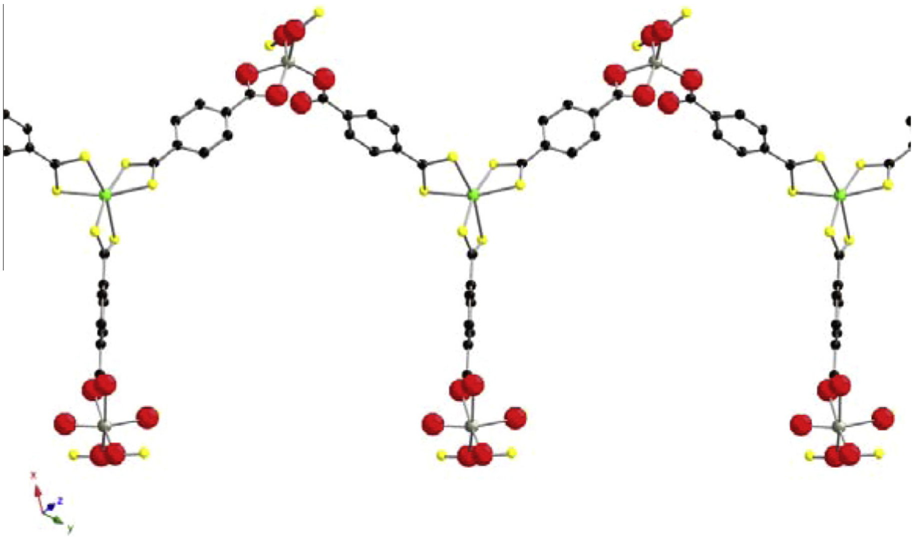


Fig. 8. The polymeric structure of the $\{Ni(DTT)_3Zn_2(DMSO)_6\}_n$ complex. The methyl groups in the Zn-bound DMSO ligands have been omitted for clarity.

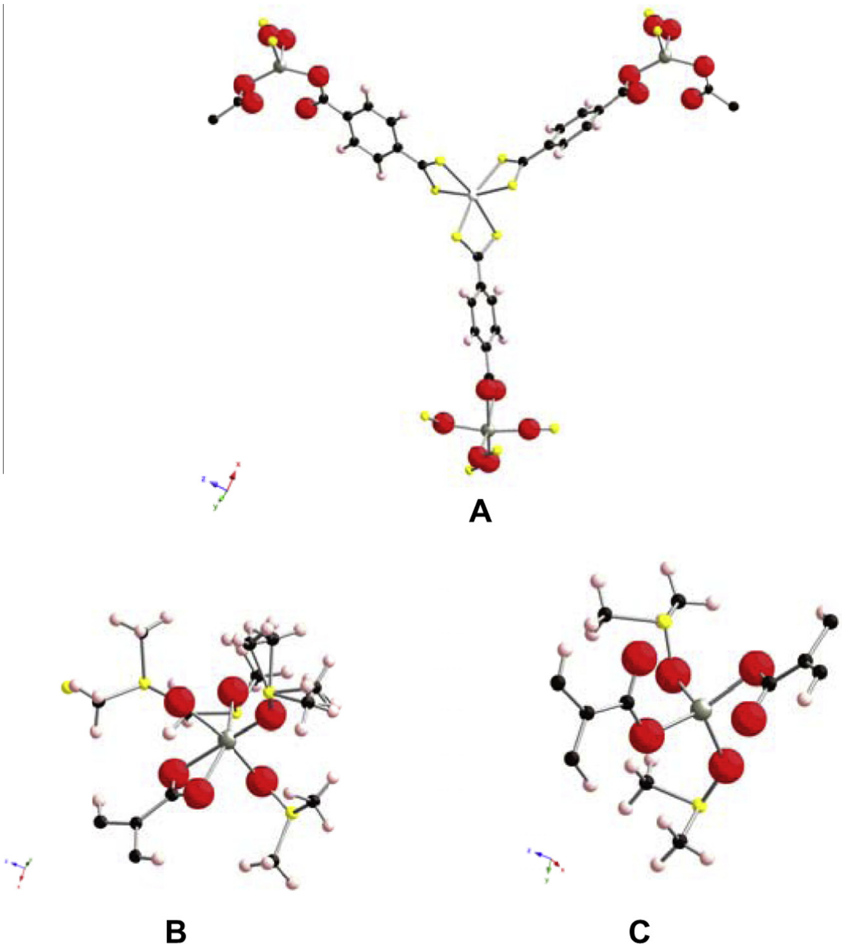


Fig. 9. The coordination environments of A: the Ni Site, B: the "terminal" Zn Site and C: the "bridging" Zn site.

Table 6
Structural details in the $\{Ni(DTT)_3Zn_2(DMSO)_6\}_n$ complex.

Distance (#)	Range	Mean*	Distance
Ni–S (6)	2.41–2.43	2.42(1,6)	Ni-Zn_2 11.08(1)
Zn_2–O_{DMSO} (4)	1.92–2.20	2.06(13,4)	Ni–Zn_1 11.12(1)
Zn_2–O_{DTT} (2)	2.23; 2.21		Ni–Ni 18.22(1)
Zn_1–O_{DMSO} (2)	2.03; 2.03		Zn_1–Zn_1 18.22(1)
Zn_1–O_{DTT} (2)	1.93–1.98		Zn_1–Zn_2 19.83(1)

The first number in parenthesis represents the standard deviation from the mean $\sigma = [\Sigma_{i=1}\mathrm{N}(x_i - x)_2\mathrm{N}(\mathrm{N} - 1)]^{1/2}$, the second represents the number of chemically equivalent bonds averaged out.

(Fig. 7). The properties of **X** in solution are under study. Structural details of **X** are presented in Table 5.

3.2.4. $\{Ni(DTT)_3Zn_2(DMSO)_6\}_n$, **XI**

The bifunctional DTT ligand is ideally suited to bind to both thio-philic and oxo-philic ions. The reaction of **III** with both Ni(II) and Zn(II) ions in solution, gives the S–S–Ni and O–O–Zn bridging mode not unexpected for the thiophilic Ni(II) and the oxophilic Zn(II) ions.

The structure of $Ni(DTT)_3Zn_2(DMSO)$ (Fig. 8) shows a polymeric array of six-coordinate Ni ions, S-bound to three DTT ligands (Fig. 9A) in a distorted octahedral geometry (N–S, 2.41(1) Å). Octahedral coordination by 1,1-dithio-ligands is rare, and to our knowledge is only known for the tris-ethyl-xanthato nickelate $[Ni(Et\text{-}xanth)_3]^-$ anion [23].

The "bridging" DTT ligands (Fig. 9C) are bound as monodentate ligands to the Zn(II) ions which complete their coordination sphere binding to two DMSO molecules. The Zn(II) ions on the "terminal" ligands show a distorted octahedral geometry, O–O bound to a bidentate DTT ligand, and four DMSO molecules (Fig. 9B). In the solid the polymeric assembly inter-digitizes to give sheets which stack. The stacked sheets are shown in the supplementary material. Structural details are shown in Table 6.

4. Conclusions

This preliminary synthetic study of the tetrathioterephthalate, TTT, dithio-terephthalate, DTT, and the 1,4-thioacyl benzene, DCT, ligands, demonstrates unique reactivity characteristics and their ability to serve as ditopic linkers. The TTT ligands show a facile C–S bond cleavage with generation of elemental sulfur and subsequent formation of "sulfur-rich" thiocarboxylates and also of sulfido and polysulfido ligands that subsequently form thiolate clusters. The general scope of these reactions will be investigated further. The DTT and DCT thio-carboxylate ligands serve bi-functionally as homo-metallic or hetero-metallic bridges and can be considered as functionalized carboxylate ligands. The SS-coordinated DTT ligands with thiophilic metal ions are metal functionalized terephthalates and their use as precursors for the synthesis of specific, highly porous, metal organic frameworks are presently under investigation.

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Appendix A. Supplementary data

CCDC 940488-940494; 940519, 940520; contains the supplementary crystallographic data for **I**, **Ia**, **III**, **IV**, **V**, **VI**, **IX**, **XI**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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