

Synthesis and characterization of [PPh₄][M(diod)₂], M = Ni, Pd, Cu or Au; crystal structure of [PPh₄][Cu(diod)₂]

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Abstract—The complexes $[P(C_6H_5)_4][M(diod)_2]$ [where M = Ni, Pd, Cu or Au (**2a**, **b**, **c**, **d**)] have been prepared and characterized spectroscopically, electrochemically and by X-ray structure determination for **2c**. Preparation of **2d** involved isolation of an intermediate complex with only one diod ligand. The Ni complex **2a** forms semiconducting charge transfer complexes with TTF and BEDT-TTF. Copyright © 1997 Elsevier Science Ltd

Keywords: dithiolene; crystal structure; charge-transfer salt.

Metal bis-1,2-dithiolene complexes have been widely studied due to potential applications as molecular conductors [1,2], the observation of large third order optical non-linearities [3] and the occurrence of unusual magnetic properties [4,5] in salts of these compounds. In order to extend the range of such compounds available for study, we recently prepared and structurally characterized TBA[Ni(diod)₂] (diod = 1,4-dithia-6-oxa-2,3-dithiolate, Fig. 1) from which a charge-transfer complex with BEDT-TTF was prepared [6]. We have also reported preliminary studies on analogous Cu and Au complexes [7]. These complexes have a structure related to that of the organic donor molecule OTT [bis(2-oxatrimethylenedithio)tetrathiafulvalene or BOBMT-TTF]



Fig. 1. X = O, TBA[Ni(diod)₂]; X = S, TBA[Ni(dtdt)₂].

RESULTS AND DISCUSSION

determination of the Copper salt 2c.

conducting charge transfer salts.

The preparation of the complexes $[TPP][M(diod)_2]$ (where M = Ni, Pd, Cu) is outlined in Scheme 1. The thione 1 was readily prepared by reaction of $[TEA]_2[Zn(dmit)_2]$ (dmit = 1,3-dithiol-2-thione-4.5dithiolate), a convenient source of the $C_3S_5^2$ unit, with bischloromethyl ether. The dipotassium salt of the ligand precursor was prepared by reaction of the thione 1 with KOH in warm ethanol and was obtained as a yellow precipitate which could be isolated. The potassium salt was allowed to react in methanol with the appropriate metal chloride and finally [TPP]Br was added to give a precipitate of the product. This procedure is analogous to that used by Kato *et al.* for the preparation of the analogous complex with a terminal sulfur rather than oxygen atom (Fig. 1) [9].

[8], which has been shown to be capable of forming

We now report an improved synthesis of these com-

pounds which has led to the isolation of TPP salts of

Ni, Pd, Cu and Au complexes (2a, b, c, d) of the diod

ligand and their spectroscopic and electrochemical

characterization together with an X-ray structure

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The analogous gold complex was not obtained by the above scheme due to formation of a brown precipitate after reaction of the ligand precursor with K[AuCl₄]. This product was believed to be K[Au-(diod)Cl₂] by analogy with the complex K[Au(dtdt)Cl₂], which was isolated in a related study [10]. It was not possible to purify the product by recrystallization due to the almost complete lack of solubility, however, elemental analysis of the brown precipitate 3 was not inconsistent with this formula. Further evidence for the structure of 3 was obtained by the successful reaction of 3 with a further portion of K₂diod over 2 days in methanol to give the gold bis diod salt 2d after addition of [TPP]Br (Scheme 2).

The synthesis of **2a**, **b**, **c**, **d** contrasts with the method used previously for the preparation of TBA[Ni (diod)₂] [6], in which the thione **1** was deprotected with refluxing NaOEt/EtOH and the soluble sodium salt formed reacted *in situ* with the metal chloride. This method was found to be unreliable over many repetitions as a mixture of products were often obtained which proved difficult to separate. It is believed that side products arose from the further degradation of the thione to $C_2S_4^{4-}$ fragments, which could bridge between metal centres to give rise to dimeric or polymeric products. This was supported by elemental analyses which showed a higher sulfur content and lower carbon content than that expected for the monomeric species and consistent with monoanionic salts of bridged species. In addition, an indication of interacting metal centres was detected electrochemically. The formation of the dipotassium salt of the ligand as a precipitate in the method described here, however, avoids the possibility of further degradation in solution.

The structure of [PPh₄][Cu(diod)₂] (2c) was determined by single-crystal X-ray diffraction and consists of [PPh₄]⁺ cations and [Cu(diod)₂]⁻ anions held together by Van der Waals forces (Fig. 2). The shortest inter-ionic contact involving non-hydrogen atoms is 3.347 Å $[O(1) \cdots C(8)$ at 1 + y, z], which indicates fairly close packing of the cationic and anionic species in the crystal. The anions are arranged in more or less parallel layers, but they are separated by the [PPh₄]⁺ cations in a way that excludes any possibility of stackinteractions between them. The ing tetraphenylphosphonium cation is sited on а crystallographic two-fold axis with bond lengths and angles expected for this type of species. One of the angles at P(1) [C(5)-P(1)-C(5')], however, is considerably narrowed compared with the others $[104.5(3) vs 109.2(3)-111.1(2)^{\circ}]$ probably as a result of packing requirements.

The $[Cu(diod)_2]^-$ moiety (Fig. 3) is centro-





Fig. 2. The unit-cell contents of [PPh₄][Cu(diod)₂] projected along b.



Fig. 3. The structure of the centrosymmetric $[Cu(diod)_2]^-$ anion showing the atom labelling scheme. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

symmetric with the Cu atom showing an exactly planar configuration. The unique Cu—S distances, 2.1800(13) and 2.1874(11) Å, are the same within experimental error. The *trans* angles are 180° by symmetry, whilst the *cis* angles show slight deviations (1.16⁻) from 90.0°, which may be attributed to the requirement of the bite angle of the chelating diod ligand. Similar angular distortions were also observed

in the square planar $[Ni(diod)_2]^-$ anion in $[NBu_4]$ $[Ni(diod)_2]$ [6] and also in the complexes $[Ni(S_2C_2S_2R_2)_2]$ (R = butyl or hexyl) [11], $[Ni\{S_2C_2S_2(RR')\}_2]$ (R = Ph, R' = Bu; R = Ph, R' = cyclopentylmethyl) [12] and $[Ni(S_2C_2S_2(CH_2)_2C$ ==CH₂)₂] [13]. Other geometrical parameters of the central CuS₄C₄S₄ core are typical for this class of compound [14]. The C—C bond length in the chelate ring [1.331(5) Å] is comparable with those in other similar species and indicative of the nature of the bonding. delocalized The S(1)S(2)C(1)C(2) fragment of the diod ligand is planar within 0.009 Å, with the Cu(1), S(3) and S(4) atoms lying, respectively, -0.381, -0.071 and 0.014A away from this plane. As observed in [NBu₄] $[Ni(diod)_2]$ [6], the seven-membered C₄OS₂ ring in the present case also has a chair conformation, with fold angles of 61.2 and 65.9° along the $S(3) \cdots S(4)$ and $C(3) \cdots C(4)$ lines, respectively. A similar conformation of the seven-membered C₅S₂ ring was also observed in [Ni(dpdt)₂] [13], but in this case the twofold angles above were nearly equal at 62.7 and 61.9 (see Tables 1 and 2).

The electrochemical properties of **2a, b, c, d** were studied by cyclic voltammetry against SCE in acetonitrile and the results are presented in Table 3.

The values obtained for the nickel complex 2a are in agreement with those previously observed for the related TBA salt and show a 1-/0 couple similar to that of other metal dithiolene complexes with a proven ability to form molecular metals [6]. The separation between the 1 - 0 and 2 - 1 - couples however, is large and indicates a poorer ability to delocalize charge than $[Ni(dmit)_2]^{x-1}$. These observations are reflected in the inability to prepare molecular conductors with $[Ni(diod)_2]^{x-}$ as the sole conducting component, although the use of this complex as a counter ion for TTF or BEDT-TTF has shown greater utility towards the preparation of conducting solids. The palladium complex 2b shows a similar reversible 1-0 couple to **2a**, but differs in that the reduction to a dianionic state occurs irreversibly, again presumably reflecting the reduced ability of the diod ligand to delocalize charge. Compared with dmit therefore, the dianionic diod complex with Pd is destabilized such that no analogue of the isolable salts of $[Pd(dmit)_2]^{2-}$ is available.

The results obtained for the Cu and Au complexes 2c, d reflect the double occupation of the HOMO for the monoanions of these complexes, which cause reduction to be disfavoured as it involves introduction of an electron into a higher energy molecular orbital. The Cu complex 2c therefore, showed reduction at -1.4 V with an associated oxidation whose position and peak height was dependant on sweep rate, suggesting that this process would be chemically reversible if a high enough sweep rate could be attained. For the gold complex 2d, no reduction was observed up to -1.5 V. The oxidation observed for 2d occurred at +0.64 V and was irreversible. A recent study [15] has demonstrated that the oxidation process in related gold dithiolene complexes can become reversible at high sweep rates (50–2000 V s⁻¹). This, however, could not be investigated for 2d due to instrumental limitations.

The UV-vis and near IR spectra of complexes **2a, b, c, d** were recorded in methylene chloride solution and results are presented in Table 4. The nickel complex **2a** shows an intense absorption at 950 nm typical for this class of compound and consistent with the results previously observed for the related TBA salt. The Pd complex **2b**, which also has a singly occupied HOMO displays a low energy band at 1200 nm. The large difference in the values observed for **2a** and **2b** indicates the strong influence of the central metal on the frontier orbitals of the complex. This is expected if the ligand is strongly electron-withdrawing and this may reflect the presence of the electron-withdrawing oxygen atom in the diod ligand. The Cu and Au analogues, however, possess an additional valence elec-

$C_{11}(1) = S(1)$	2 1800(13)	$C_{\mu}(1) - S(2)$	2.1874(11)
S(1) - C(2)	1.756(4)	S(2) - C(1)	1.754(5)
S(3) - C(2)	1.759(4)	S(3)—C(3)	1.814(5)
S(4) - C(1)	1.759(4)	S(4)—C(4)	1.799(5)
P(1) - C(5)	1.796(5)	P(1) - C(11)	1.800(4)
O(1) - C(3)	1.402(5)	O(1)—C(4)	1.407(6)
C(1)C(2)	1.331(5)		
$S(1) - Cu(1) - S(1')^{i}$	180.0	$S(2) - Cu(1) - S(2)^{i}$	180.0
S(1)Cu(1)S(2)	91.16(4)	$S(1) - Cu(1) - S(2')^{i}$	88.84(4)
C(2) - S(1) - Cu(1)	102.77(13)	C(1) - S(2) - Cu(1)	102.56(14)
C(2) - S(3) - C(3)	102.3(2)	C(1) - S(4) - C(4)	103.5(2)
$C(5')^{ii} - P(1) - C(5)$	104.5(3)	$C(5')^{ii} - P(1) - C(11)$	111.1(2)
C(5) - P(1) - C(11)	110.4(2)	$C(11) - P(1) - C(11')^{ii}$	109.2(3)
C(3) - O(1) - C(4)	113.9(4)	C(2) - C(1) - S(4)	124.5(3)
C(2) - C(1) - S(2)	120.9(3)	S(4) - C(1) - S(2)	114.6(2)
C(1) - C(2) - S(3)	125.3(4)	C(1) - C(2) - S(1)	120.3(3)
S(3) - C(2) - S(1)	114.3(2)	O(1) - C(3) - S(3)	116.1(4)
O(1) - C(4) - S(4)	116.5(4)		
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Table 1. Selected bond lengths (Å) and angles ([¬]) for [PPh₄][Cu(diod)₂]

The primed atoms are related to the unprimed ones by the symmetry: (i) 0.5-x, 0.5-y, -z; (ii) -x, y, 0.5-z.

Table 2. Crystal data and details of data collection and structure refinement for [PPh4][Cu(diod)2]

Empirical formula	$[C_{2}H_{2}P][C_{*}H_{*}CuO_{2}S_{*}]$
Formula weight	795.53
Temperature (K)	298(2)
$\lambda(Mo-K_{\alpha})$ (Å)	0.71069
Crystal system	Monoclinic
Space group	C2/c
Unit-cell dimensions	a = 25.607(4) Å
	b = 7.282(3) Å
	c = 21.183(5) Å
	$\beta = 119.02(3)^{\circ}$
Volume (Å ³)	3454(2)
Ζ	4
Density (calculated) (Mg m^{-3})	1.530
Absorption coefficient (mm ⁻¹)	1.192
<i>F</i> (000)	1632
Crystal size (mm)	$0.32 \times 0.12 \times 0.10$
θ range for data collection (°)	2.06-24.88
Index ranges	$-29 \le h \le 16, -7 \le k \le 8, -20 \le l \le 24$
Total data collected	5752
Independent reflections	2252 $[R_{int} = 0.0788]$
Absorption correction factors	0.798-1.107
Refinement method	Full-matrix least-squares on F^2
Data/parameters	2252/201
Goodness-of-fit on F^2	0.857
Final R indices (all 2252 data) ^a	$R_1 = 0.0584, wR_2 = 0.0897$
R indices [1563 data with $I > 2\sigma(I)$] ^a	$R_1 = 0.0383, wR_2 = 0.0871$
Largest diff. peak and hole (e $Å^{-3}$)	0.494 and -0.284

 ${}^{a}R_{1} = \Sigma(\Delta F)/\Sigma(F_{0}); wR_{2} = [\Sigma\{w(F_{0}^{2} - F_{c}^{2})^{2}\}/\Sigma\{w(F_{0}^{2})^{2}\}]^{1/2}; w = [\sigma^{2}(F_{0})^{2} + (0.0325P)^{2}], \text{ where } P = [Max(F_{0})^{2} + 2F_{c}^{2}]/3.$

Table 3.

Compound	1 – /0 (V)	2 - 1 - (V)
[TPP][Ni(diod) ₂]	+0.27 (reversible)	-0.65 (reversible)
[TPP][Pd(diod) ₂]	+0.26 (reversible)	-1.24 (irreversible)
[TPP][Cu(diod) ₂]	+0.56 (irreversible)	- 1.40 (quasi-reversible)
[TPP][Au(diod) ₂]	+0.64 (reversible)	not observed

Table 4.		
Complex	λ (max)	$\varepsilon (M^{-1} cm^{-1})$
[TPP][Ni(diod) ₂]	950	7300
	450	6610
	325	16,700
[TPP][Pd(diod) ₂]	1200	4370
	315	16,700
[TPP][Cu(diod) ₂]	450	28,400
	350	12,500
[TPP][Au(diod) ₂]	500 (broad)	

tron and, therefore, have a fully occupied HOMO and cannot exhibit a low-energy excitation. These observations are consistent with the electrochemical behaviour of these species.

The copper complex 2c shows a visible colour

change from green to red upon dissolution in methylene chloride and comparison of the solid-state reflectance and solution spectra showed additional broad bands at 1350 and 650 nm in the solid state. As the crystal structure of this complex indicates no significant intermolecular interactions, it appears that the colour change arises from some intramolecular rearrangement. It has been previously observed that in the complex [N-ethyl pyridinium][Cu(dmit)₂] the dihedral angle between the ligand planes is 57.3° around the central metal in the solid state structure [16]. This suggests that copper complexes are able to adopt a tetrahedral arrangement of the sulfur donor atoms in solution and that the colour change in 2c may be associated with a change from tetrahedral to square-planar geometry.

In the IR spectrum of 2a, a band was observed at 1386 cm⁻¹ corresponding to a weakened C==C bond. For 2b, c, d, this band could not be unambiguously assigned due to the presence of broad bands in this region associated with the TPP cation. C—S bond stretching was observed for complexes 2a, b, c, d at around 1040 cm⁻¹ and at around 905 cm⁻¹. The gold complex 3 showed bands at 1399 and 1048 cm⁻¹, consistent with the presence of a diod ligand in the proposed structure.

Electrochemical crystallization of the TPP, TBA and TMA salts of the nickel complexes were attempted in order to obtain partially oxidized salts of this complex with TPP, TMA or TBA present as counterion. These studies, however, seemed only to lead to isolation of the neutral complex [Ni(diod)₂], which has also been previously prepared by reaction of 2a with I_2 [6]. Electrocrystallizations were also attempted in the presence of TTF and BEDT-TTF in order to obtain charge-transfer complexes involving these organic donors. Highly conducting solid-state products were obtained from these experiments which appeared from elemental analysis data to have a composition approximate to that of neutral [Ni(diod)₂], but clearly contained some other component as the conductivity was several orders of magnitude higher (Table 5). We postulate that these products contain a small ratio of the organic donor to the nickel complex although it is not possible to ascertain the true stoichiometry in the absence of better quality crystals which could lead to structural data.

Conclusions

A series of monanionic metal complex salts of the ligand diod have been prepared and characterized, including a crystal structure of the copper complex. Preparation of the gold complex involved isolation of an intermediate which appeared to contain only one diod ligand and may have potential as a precursor towards the preparation of asymmetric metal dithiolene containing complexes. Conducting charge-transfer complexes have been prepared from TTF or BEDT-TTF with $[Ni(diod)_2]^{x-}$, but a detailed understanding could not be obtained due to lack of high quality crystals.

EXPERIMENTAL

Bischloromethyl ether [17], $TEA_2[Zn(dmit)_2]$ [18] and thione [6] were prepared by previously described methods. NiCl₂·6H₂O, PdCl₂(NCPh)₂, CuCl₂ and

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Complex	$\sigma_{\rm RT}~({\rm S~cm^{-1}})$
[Ni(diod) ₂]	9×10^{-6}
[TTF],[Ni(diod) ₂]	2×10^{-3}
[BEDT-TTF] _x [Ni(diod) ₂]	3×10^{-1}

 $K[AuCl_4]$ were used as purchased without further purification. Ethanol was distilled from Mg/I₂ prior to use and stored over molecular sieve. IR spectra of samples pressed as KBr discs were recorded on a Perkin–Elmer 1600 series FTIR spectrometer. Near IR, UV-vis and reflectance spectra were recorded on a Beckman DK-2A instrument. Electrocrystallization experiments were carried out by methods analogous to those described previously [6].

Preparation of TPP[M(diod)₂] (2a, b, c)

(i) 2a: The thione 1 (1.078 g, 4.49 mmol) was stirred in dry ethanol (50 cm³) with KOH (2.0 g, 36 mmol) for 2 h in a water bath at 45–50°C. A pale yellow precipitate was formed which was filtered off under nitrogen and washed with ethanol. The salt was dried in vacuo and dissolved in dry methanol (20 cm³). $NiCl_2 \cdot 6H_2O$ (0.309 g, 1.30 mmol) dissolved in dry methanol (20 cm³) was added and stirring continued for 16 h at room temperature under nitrogen. Air was bubbled through the solution for 20 min and the mixture filtered to remove a pale yellow residue. TPPBr (2.524 g, 6.02 mmol) dissolved in methanol was added to the filtrate dropwise with stirring. The brown precipitate formed was filtered off, washed with methanol and dried in air. The product was recrystallized by dissolving in acetone, filtering to remove any undissolved solid, addition of IPA and reduction of the volume until the solution became cloudy. The crystalline product was allowed to form over 2 h, filtered off, washed with IPA and dried in air. Yield = 0.37 g, 0.47 mmol, 36%. Found : N, 0.0; C, 46.9; H, 3.5; S, 32.4. Requires: N, 0.0; C, 46.6; H, 2.4% S, 31.1. IR : v_{max}/cm^{-1} 3433, 1480, 1434, 1386, 1305, 1184, 1107, 1038.

(ii) **2b,c**: These were formed by a procedure identical to that for **2a** but substituting $NiCl_2 \cdot 6H_2O$ for $PdCl_2(NCPh)_2$ and $CuCl_2$, respectively.

2b: Yield = 5%. Found: N, 0.1; C, 46.0; H, 2.6; S, 24.9. Requires: N, 0.0; C, 45.9; H, 3.3; S, 30.6%. IR: v_{max}/cm^{-1} 3446, 2361, 1702, 1482, 1436, 1301, 1108, 1043, 996, 972, 906.

2c: Yield = 7%. Found: N, 0.0; C, 48.1; H, 3.1; S, 31.8. Requires: N, 0.0; C, 48.3; H, 3.5; S, 32.2%. IR: v_{max}/cm^{-1} 1481, 1434, 1305, 1108, 1035, 904.

Preparation of 3

The thione 1 (0.411 g, 1.71 mmol) and KOH (0.856 g, 15.26 mmol) were dissolved in dry ethanol (20 cm³) and stirred under nitrogen at 45°C for 2.5 h. A pale yellow precipitate was formed and filtered off under nitrogen. The yellow solid was stirred in methanol (20 cm³) under nitrogen along with K[AuCl₄] (0.20 g, 0.52 mmol) and stirred overnight. A dark brown solid was formed which was filtered off and washed with methanol. Found : N, 0.0; C, 7.3; H, 0.5; S, 24.2. Requires :

N, 0.0.; C, 9.5; H, 0.8; S, 25.5%. IR : ν_{max}/cm^{-1} 1399, 1048.

Preparation of 2d

The thione 1 (0.20 g) and KOH (0.41 g) were reacted in dry ethanol over 2.5 h and the resultant yellow precipitate filtered off, washed with ethanol and dried under nitrogen. This solid was dissolved in dry methanol (50 cm³) and reacted with 3 over 2 days at 50°C under nitrogen then filtered to remove any undissolved solid. To the filtrate was added TPPBr (0.813 g) in dry methanol (20 cm³) dropwise with stirring forming a yellow/brown precipitate. This was filtered off, washed with methanol and dried in air. Yield = 0.113 g, 0.12 mmol, 24%. Found : N, 0.0; C, 40.7; H, 2.9; S, 28.7. Requires : N, 0.0; C, 41.4; H, 3.0; S, 27.6%. IR : v_{max}/cm^{-1} 3448, 1638, 1548, 1484, 1436, 1382, 1304, 1108, 1037, 905, 723, 688, 618.

X-ray structure determination of [PPh₄][Cu(diod)₂]

All crystallographic measurements were made at 298(2) K on a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator using $Mo-K_{\alpha}$ radiation $(\lambda = 0.71069 \text{ Å})$ by following procedures described elsewhere [19]. The structure was solved by Patterson methods (SHELXS86) [20] and difference syntheses, and refined on F^2 by full-matrix least-squares (SHELXL93) [21] using all unique data corrected for Lorentz and polarization factors and also for absorption effects (DIFABS) [22]. The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were included in calculated positions (riding model) with $U_{\rm iso}$ tied to the $U_{\rm eq}$ of the parent carbons. Sources of scattering factors as in reference [21]. The diagrams were drawn with SNOOPI [23]. The calculations were done on a Pentium P5-90 personal computer. Important bond lengths and angles are given in Table 1, and the crystal data and details of data collection and structure refinement are presented in Table 2. The atomic coordinates, thermal parameters, full lists of bond lengths and angles, and structure factor tables have been deposited with the Editor as supplementary material.

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