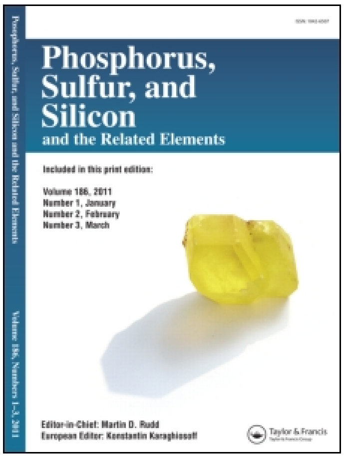

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SYNTHESIS AND PROPERTIES OF NEW BISDITHIOLENE METAL COMPLEXES OF THE 1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE (DMIT) LIGAND

Hong-Qi Li[a]; Sheng-Min Zhao[a]; Min Wang[a]; Gan-Zu Tan[a]; Xian-Da Yu[a]; Yu Xu[b]; Sheng-Gao Liu[b]; Yun-Qi Liu[b]; Yong-Fang Li[b]
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SYNTHESIS AND PROPERTIES OF NEW BISDITHIOLENE METAL COMPLEXES OF THE 1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE (DMIT) LIGAND

HONG-QI LI[a]*, SHENG-MIN ZHAO[a], MIN WANG[a], GAN-ZU TAN[a], XIAN-DA YU[a], YU XU[b], SHENG-GAO LIU[b], YUN-QI LIU[b] and YONG-FANG LI[b]

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Two series of integer or non-integer oxidation-state metal complexes of the multi-sulfur donor ligand 1,3-dithiole-2-thione-4,5-dithiolate (DMIT) with Cd (II), Hg (II), Sn (II), Mn (II), Fe (II), Co (II), or Bi (III) have been prepared as tetraalkylammonium salts. The compounds are characterized by elemental analysis, ^{1}H NMR spectra, Fourier Transform IR spectra, and UV-Vis spectral analysis. The electrochemical properties of the complexes are also studied by cyclic voltammogram and conductivity measurements on the compressed pellets. A highly conducting LB film is constructed from one of the complexes cetylpyridinium-Cd(dmit)$_2$.

Keywords: Bisdithiolene metal complex; 4,5-dimercapto-1,3-dithiole-2-thione; synthesis; LB film; conductivity

INTRODUCTION

Metal complexes with the DMIT (1,3-dithiole-2-thione-4,5-dithiolate) ligand are of considerable interest, in which electrical conduction is expected to occur through two- or three-dimensional pathways constructed from intermolecular sulfur-sulfur and sulfur-metal contacts.[1,2] Particularly, some complexes such as $[Me_4N][Ni(dmit)_2]_2$ were reported to become superconductor under pressure.[3] Various complexes of the DMIT ligand have been studied so far, including not

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*Corresponding author.

only transition metal complexes[4–6] but more recently main group metal DMIT complexes, e.g. DMIT complexes of zinc, cadmium and mercury,[7] $[Q]_2[M(dmit)_2]$ (M = Zn, Cd, or Hg), of antimony,[8] $[Q][Sb^{III}(dmit)_2]$, of tin,[9–11] and lead,[12] as well as tris-dmit complexes of tin, $[Q][Sn(dmit)_3]$, of antimony,[14] $[Q][Sb^{V}(dmit)_3]$, and indium and thallium,[15] $[Q]_3[M(dmit)_3]$ (M = In or Tl).

Since the first report of the conducting Langmuir-Blodgett (LB) films based on DMIT-metal complexes by Japanese workers,[16] extensive studies have been devoted to this new kind of LB films because they are promising candidates for high conductivity LB films and high dimensionality.[17–24] We have synthesized, in order to provide a more complete series of DMIT samples and to obtain highly conducting LB films based on them, ten new DMIT-metal complexes of two series, one of which has the same cation (tetraethylammonium, TEA) and different central metal ion (Mn, Fe, Co, Cd, Hg, Sn, Bi) and the other the same central metal ion (Cd) and different cation (TEA, BTMA (benzyltrimethylammonium), CTMA (cetyltrimethylammonium), or CPy (cetylpyridinium)). In the present paper we report the synthesis, characterization and electrical as well as LB film properties of the above two series of DMIT complexes.

EXPERIMENTAL

Melting points were determined on a PHMK micro melting point apparatus with the thermometer uncorrected; Elemental analyses were performed on the Carlo-Erba model 1106 elemental analyzer; ^1H NMR spectra were recorded on a FT-80A-NMR instrument, chemical shifts were given in ppm relative to TMS and CD_3COCD_3 was used as solvent: FT-IR spectra were recorded on a 10DX FTIR spectrometer in the region of 4000–400 cm^{-1} as KBr pellets: UV-Vis spectra were obtained on a UV-365 spectrophotometer in trichloromethane.

Cyclic voltammetric measurements were performed with a EG & G PARC Model 175 Universal Programmer and Model 174A Polarographic Analyzer and Model RE0074 X-Y Recorder at room temperature using dimethylformamide (DMF) solutions containing the DMIT complex (1×10^{-3} mol/L) and a supporting electrolyte (n-Bu_4NBF_4, 0.1 mol/L). A platinum disc (3 mm in diameter) was used as a working electrode, the counter electrode was a platinum plate which was immersed directly in the electrolyte solution. A saturated calomel electrode (SCE) was used as the reference electrode and also directly immersed in the electrolyte solution. Scan rate was 100 mV/s.

Powder conductivity measurements were performed by the usual two-probe technique on compressed pellets (5 mm in diameter, 0.1–0.2 mm thickness, pressed under a pressure of 350–400 kg cm^{-2}).

The measurement of surface pressure-area isotherms and the deposition of the LB films were carried out in a KSV 5000 twin-compartment Langmuir trough. The subphase was double-distilled water or dilute solution (5×10^{-4} mol/L) of $CdCl_2$ in double-distilled water. The temperature was 25 ± 1°C and the compression speed was 5 mm/min when the surface pressure-area isotherms were measured. The surfaces of the substrates were cleansed with $CHCl_3$, C_2H_5OH, CH_3COCH_3, and ultrasonic wave successively. Monolayers were transferred onto glass substrates with or without two aluminium electrodes at a surface pressure of 24 mN/m for measurement of in-plane conductivity and X-ray diffraction, respectively. The speed for the up and down stroke was in a range of 0.5–10 mm/min. The transfer ratio was 1.0 ± 0.1 for both up and down stroke. Y-type deposition was achieved. X-ray diffraction was determined using a D/MAX-RB automatic instrument. Electrical conductivity of the LB film was measured in air using a Solartron 7081 Precision Voltmeter by the standard two-contact method using silver contacts. The doping of the LB films was carried out by exposure to iodine vapour for several minutes in a sealed vessel.

Preparation of 4,5-bis(Benzoylthio)-1,3-Dithiole-2-Thione

The compound $(PhCO)_2(dmit)$ was prepared according to a general procedure by addition of dimethylformamide to a refluxing mixture of carbon disulphide and sodium.[25] It had a m.p. of 141–143°C (lit. value[25] 145°C).

General Experimental Details for the Preparation of M-DMIT Complexes

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (812 mg, 2 mmol) was dissolved in a methanol solution (20 mL) containing sodium metal (138 mg, 6 mmol) and stirred for 30 min at room temperature. To the resulting solution was added a methanol solution (20 mL) of 1 mmol inorganic salt ($CdCl_2 \cdot 2.5H_2O$, $HgCl_2$, $SnCl_2 \cdot 2H_2O$, $MnSO_4 \cdot H_2O$, $FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, or $BiCl_3$). Then a methanol solution (20 mL) containing 2.2 mmol of tetraalkylammonium halide (TEA, BTMA, CTMA, or CPy) was added. Immediately, a solid of deep color precipitated and was collected by filtration, washed with water and methanol and then dried in vacuo. Recrystallization from acetone gave the product as cube-shaped crystal or powder of deep color.

Compound **1**: Anal. Calc. for $C_{22}H_{40}N_2CdS_{10}$: C, 34.51; H, 5.27; N, 3.66; Cd, 14.68. Found: C, 34.53; H, 5.05; N, 3.66; Cd, 14.52%. FT-IR spectra (KBr,

ν, cm^{-1}): 2974.4(w), 2935.9(w), 1475.6(w), 1456.4(m), 1412.0(s), 1396.6(w), 1294.3(m), 1174.7(s), 1057.1(w), 1037.8(s), 985.7(w), 898.9(m), 870.0(m), 785.1(s), 563.3(w), 524.7(m), 457.2(s), 420.5(m). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 209, 240, 440. ^1H NMR spectra (CD_3COCD_3, δ, ppm): 1.38(t, 24H), 3.40(q, 16H).

Compound **2**: Anal. Calc. for $C_{22}H_{40}N_2HgS_{10}$: C, 30.95; H, 4.72; N, 3.28; Hg, 23.50. Found: C, 29.95; H, 4.49; N, 3.10; Hg, 23.42%. FT-IR spectra (KBr, ν, cm^{-1}): 2974.4(s), 2920.4(w), 1475.6(m), 1458.3(m), 1404.3(s), 1327.1(m), 1255.7(m), 1172.8(s), 1095.0(m), 1059.0(m), 1039.7(m), 993.4(m), 922.0(m), 897.0(m), 870.0(m), 781.2(s), 709.9(w), 601.8(w), 567.1(w), 522.8(w), 501.5(m), 457.2(s), 416.7(w). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 257, 288, 495. ^1H NMR spectra (CD_3COCD_3, δ, ppm): 1.36(t, 24H), 3.43(q, 16H).

Compound **3**: Anal. Calc. for $C_{18}H_{30}N_{1.5}SnS_{10}$: C, 30.59; H, 4.28; N, 2.97; Sn, 16.79. Found: C, 30.86; H, 4.17; N, 2.84; Sn, 16.89%. FT-IR spectra (KBr, ν, cm^{-1}): 2972.5(m), 2924.1(w), 1479.5(s), 1440.9(s), 1415.8(s), 1385.0(s), 1358.0(m), 1253.8(s), 1168.9(s), 1053.2(s), 1030.1(s), 995.3(m), 925.9(m), 891.2(s), 819.8(m), 779.3(s), 518.9(s), 486.1(m), 463.0(s). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 253, 280, 385, 460. ^1H NMR spectra (CD_3COCD_3, δ, ppm): 1.38(t, 18H), 3.32(q, 12H).

Compound **4**: Anal. Calc. for $C_{15.6}H_{24}N_{1.2}MnS_{10}$: C, 31.02; H, 4.01; N, 2.78; Mn, 9.10. Found: C, 31.06; H, 3.97; N, 2.92; Mn, 9.10%. FT-IR spectra (KBr, ν, cm^{-1}): 2978.3(m), 2922.5(w), 1479.5(w), 1402.3(m), 1300.1(s), 1242.2(w), 1170.9(w), 1122.6(m), 1060.9(s), 1024.3(w), 1001.1(w), 914.3(m), 787.0(m), 621.1(m), 545.9(m), 511.2(m), 472.6(m), 447.5(m). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 251. ^1H NMR spectra (CD_3COCD_3, δ, ppm): 1.43(t, 14.4H), 3.55(q, 9.6H).

Compound **5**: Anal. Calc. for $C_{14}H_{20}NFeS_{10}$: C, 29.05; H, 3.48; N, 2.42; Fe, 9.65. Found: C, 30.54; H, 3.31; N, 2.70; Fe, 9.68%. FT-IR spectra (KBr, ν, cm^{-1}): 2968.7(w), 2924.3(w), 1442.8(m), 1386.9(m), 1294.3(m), 1176.7(m), 1059.0(s), 908.5(m), 777.4(m), 601.8(m), 507.3(m), 464.9(m), 407.0(m). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 263, 292, 380. ^1H NMR spectra (CD_3COCD_3, δ, ppm): 1.42(t, 12H), 3.47(q, 8H).

Compound **6**: Anal. Calc. for $C_{15.6}H_{24}N_{1.2}CoS_{10}$: C, 30.82; H, 3.98; N, 2.76; Co, 9.69. Found: C, 30.66; H, 3.95; N, 2.92; Co, 9.68%. FT-IR spectra (KBr, ν, cm^{-1}): 2980.2(m), 2931.7(w), 1477.6(w), 1454.4(w), 1394.6(m), 1226.8(m), 1141.9(m), 1103.4(m), 1053.2(s), 1022.3(m), 997.3(w), 895.0(w), 781.2(m), 617.3(m), 513.1(m), 472.6(m). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 252. ^1H NMR spectra (CD_3COCD_3, δ, ppm): 1.50(t, 14.4H), 3.54(q, 9.6H).

Compound **7**: Anal. Calc. for $C_{15.6}H_{24}N_{1.2}BiS_{10}$: C, 24.72; H, 3.19; N, 2.22; Bi, 27.57. Found: C, 24.49; H, 3.16; N, 2.25; Bi, 27.41%. FT-IR spectra (KBr,

ν, cm^{-1}): 2972.5(m), 2930.1(w), 1473.7(w), 1425.5(m), 1392.7(m), 1348.3(m), 1302.0(m), 1261.5(m), 1170.9(m), 1053.2(m), 1028.1(s), 916.3(m), 868.0(m), 819.8(m), 781.2(m), 727.2(m), 611.5(m), 522.8(m), 459.1(m).

Compound **8**: Anal. Calc. for $C_{26}H_{32}N_2CdS_{10}$: C, 38.76; H, 4.00; N, 3.48; Cd, 13.95. Found: C, 38.59; H, 3.88; N, 3.46; Cd. 13.89%. FT-IR spectra (KBr, ν, cm^{-1}): 2969.7(w), 2924.3(w), 1475.6(m), 1454.4(w), 1410.0(m), 1377.3(w), 1288.5(s), 1140.0(m), 1055.1(w), 1032.0(s), 974.1(m), 927.8(m), 881.5(m), 835.2(w), 779.3(m), 725.3(m), 700.2(m), 611.5(m), 459.1(m). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 246. ^{1}H NMR spectra (CD_3COCD_3, δ, ppm): 1.34(s, 18H), 4.77(s, 4H), 7.56–7.66(m, 10H).

Compound **9**: Anal. Calc. for $C_{44}H_{84}N_2CdS_{10}$: C, 49.20; H, 7.88; N, 2.61; Cd, 10.46. Found: C, 49.25; H, 7.83; N, 2.59; Cd, 10.52%. FT-IR spectra (KBr, ν, cm^{-1}): 2918.5(s), 2851.0(s), 1471.8(m), 1410.9(w), 1379.2(w), 1290.5(m), 1257.7(m), 1234.5(w), 1215.2(m), 1136.1(m), 1060.9(w), 1035.8(m), 1012.7(s), 962.6(m), 931.7(m), 908.5(w), 833.3(m), 719.5(m), 630.8(m), 594.1(s). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 244. ^{1}H NMR spectra (CD_3COCD_3, δ, ppm): 1.30(s, 18H + t, 6H), 3.20(q, 60H).

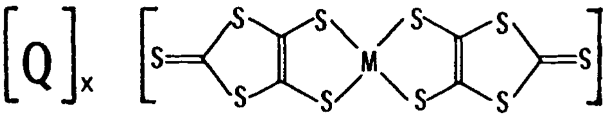
Compound **10**: Anal. Calc. for $C_{27}H_{38}NCdS_{10}$: C, 40.05; H, 4.73; N, 1.73; Cd, 13.88. Found: C, 39.99; H, 4.63; N, 1.76; Cd, 13.81%. FT-IR spectra (KBr, ν, cm^{-1}): 2922.4(s), 2849.1(s), 1483.4(s), 1462.1(m), 1375.3(w), 1290.5(s), 1172.8(w), 1140.0(m), 1037.8(s), 927.8(s), 873.8(m), 833.3(s), 767.7(m), 725.3(s), 679.0(s), 630.8(m), 463.0(m). UV-Vis spectra ($CHCl_3$, λ_{max}, nm): 243. ^{1}H NMR spectra (CD_3COCD_3, δ, ppm): 1.30(t, 3H), 3.56(q, 30H), 7.67(s, 5H).

RESULTS AND DISCUSSION

Preparation of DMIT-metal Complexes

Table I shows the physical data of the as-prepared DMIT-metal complexes. As can be seen from Table I, most of the complexes of the multi-sulfur ligand DMIT with main group or transition metal ions were obtained in high yield. In fact, most of the metal ions studied so far, either main group or transition metal ion, can form stable complexes with DMIT.[4,5] However, when we attempted to prepare the DMIT complexes with the rare-earth metal ions such as La^{3+} and Ce^{3+} under the same conditions as preparing other DMIT-metal compounds, no solid product was obtained. It suggests that the coordinating ability of the rare-earth metal ion with the multi-sulfur ligand DMIT was poor or that the complexes of DMIT with the rare-earth metal ions were unstable even in solution.

TABLE I Complexes of the type $[Q]_x[M(DMIT)_2]$, i.e.,



Compound	*Q*	*X*	*M*	*Abbreviation*	*Yield (%)*	*M.p. (°C)*	*Colour*
1	TEA	2.0	Cd	$[TEA]_2[Cd(DMIT)_2]$	93	197 (dec.)	red
2	TEA	2.0	Hg	$[TEA]_2[Hg(DMIT)_2]$	93	136 (dec.)	brown
3	TEA	1.5	Sn	$[TEA]_{1.5}[Sn(DMIT)_2]$	92	140 (dec.)	brown
4	TEA	1.2	Mn	$[TEA]_{1.2}[Mn(DMIT)_2]$	75	143–145	brown
5	TEA	1.0	Fe	$[TEA][Fe(DMIT)_2]$	63	148–150	black
6	TEA	1.2	Co	$[TEA]_{1.2}[Co(DMIT)_2]$	82	> 250	black
7	TEA	1.2	Bi	$[TEA]_{1.2}[Bi(DMIT)_2]$	87	102–103	black
8	BTMA	2.0	Cd	$[BTMA]_2[Cd(DMIT)_2]$	85	82–83	brown
9	CTMA	2.0	Cd	$[CTMA]_2[Cd(DMIT)_2]$	90	179–180	brown
10	CPy	1.0	Cd	$[CPy][Cd(DMIT)_2]$	87	75–77	brown

For the as-prepared DMIT complexes, the oxidation state varies from 1 to 2 with the change of the central metal ion. The DMIT complexes with Cd (II) or Hg (II), which has full-filled d orbitals ($4d^{10}$ or $5d^{10}$) in the outest layer like Zn (II, $3d^{10}$), are difficult to be oxidized by aerial oxidation. While the DMIT complexes with other metal ions which do not have the full-filled d orbitals in the outermost layer are susceptible to aerial oxidation and show oxidation states of 1 ~ 1.5. Although the $[M(dmit)_2]^{2-}$ (M = Cd or Hg) complexes are stable to aerial oxidation, they can be oxidized by iodine. For example, we find that complex **2** can be oxidized by iodine to give a new complex with non-integral stoichiometry of $[TEA]_{0.6}[Hg(dmit)_2]$ (determined based on elemental analysis).

IR Spectral Characteristics

Table II presents some characteristic IR spectral data of the as-prepared complexes. Apart from the common absorption bands due to the cation such as the stretching vibration peaks at about 2960, 2920 and 2850 cm^{-1}, the compounds show several characteristic absorptions of the C = C, S-C-S, C = S, and M-S (M = metal) bonds in the regions of 1480–1380, 1060–870, 1040–1020, and 490–400 cm^{-1}, respectively.[26] The complexes show two absorption bands in the

TABLE II Some characteristic IR spectral data* of the M-DMIT complexes

Complex	$\nu_{C\text{-}H}$	$\nu_{C=C}$	$\nu_{S\text{-}C\text{-}S}$	$\nu_{C=S}$	$\nu_{M\text{-}S}$
1	2974.4(w) 2935.9(w)	1475.6(w) 1456.4(m) 1412.0(s) 1396.6(w)	1057.1(w) 985.7(w) 898.9(m)	1037.8(s)	457.2(s) 420.5(m)
2	2974.4(s) 2920.4(w)	1475.6(m) 1458.3(m) 1404.3(s)	1059.0(m) 993.4(m) 897.0(m)	1039.7(m)	457.2(s) 416.7(w)
3	2972.5(m) 2924.1(w)	1479.5(s) 1440.9(s) 1415.8(s) 1385.0(s)	1053.2(s) 995.3(m) 891.2(s)	1030.1(s)	486.1(m) 463.0(s)
4	2978.3(m) 2922.5(w)	1479.5(w) 1402.3(m)	1060.9(s) 1001.1(w) 914.3(m)	1024.3(w)	472.6(m) 447.5(m)
5	2968.7(w) 2924.3(w)	1442.8(m) 1386.9(m)	1059.0(s) 908.5(m)		464.9(m) 407.0(m)
6	2980.2(m) 2931.7(w)	1477.6(w) 1454.4(w) 1394.6(m)	1053.2(s) 997.3(w) 895.0(w)	1022.3(m)	472.6(m)
7	2972.5(m) 2930.1(w)	1473.7(w) 1425.5(m) 1392.7(m)	1053.2(m) 916.3(m) 868.0(m)	1028.1(s)	459.1(m)
8	2969.7(w) 2924.3(w)	1475.6(m) 1454.4(w) 1410.0(m) 1377.3(w)	1055.1(w) 974.1(m) 881.5(m)	1032.0(s)	459.1(m)
9	2918.5(s) 2851.0(s)	1471.8(m) 1410.9(w) 1379.2(w)	1060.9(w) 1012.7(s) 908.5(w)	1035.8(m)	
10	2922.4(s) 2849.1(s)	1483.4(s) 1462.1(m) 1375.3(w)	927.8(s) 873.8(m)	1037.8(s)	463.0(m)

*Unit: cm^{-1}; s: strong; m: middle; w: weak.

region of 1060–1020 cm^{-1}. According to the normal vibration analysis of the DMIT complexes,[27] the peak at about 30 cm^{-1} higher frequency than that of the vibration of C = S was assigned to the coupling vibration of S-C-S bonds. The peaks at 1060–1050 cm^{-1} are attributed to the coupling vibration of S-C-S bonds while the peaks at about 1030 cm^{-1} are assigned to the vibration of C = S.

Electronic Spectral Analysis

Figure 1 shows the electronic absorption spectra of complex **1** (a) and **3** (b). UV-Vis spectra of the complexes show one to four characteristic bands at about 210–260, 280–290, 380, and 440–500 nm range, respectively. The former two bands may be assigned to the characteristic absorptions of the thione group and

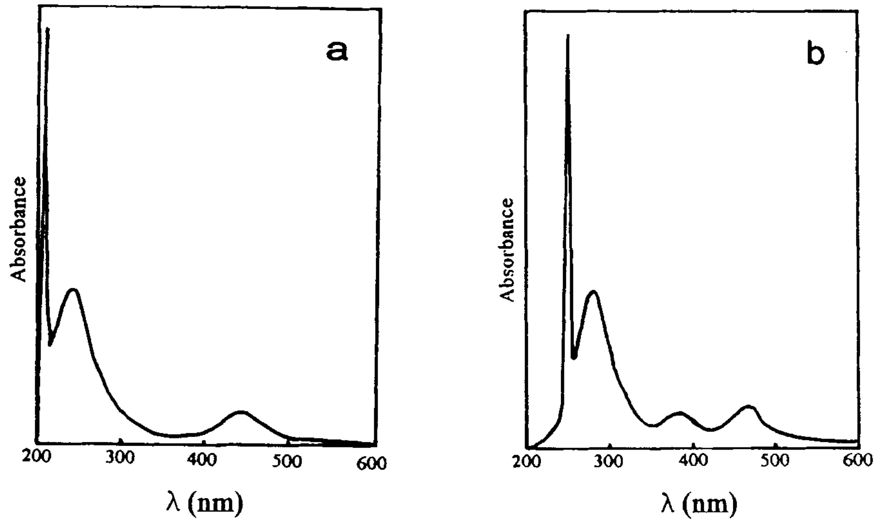


FIGURE 1 Electronic absorption spectra of complex **1** (a) and **3** (b)

the other two may come from the π-electronic delocalization over the ligand through π-d interactions.[26]

Cyclic Voltammetric Studies

The electrochemical properties of the DMIT complexes were studied by cyclic voltammograms (Figure 2) and the peak potentials were listed in Table III. The complexes show two or three irreversible oxidation peaks which could be tentatively assigned to the oxidation to intermediate states or finally to neutral or partially anodic species. Unlike $[Bu_4N]_2[M(dmit)_2]$ which has low oxidation potentials: −30 and +170 mV for M = Ni,[1,28] and −80 and +110 mV vs. SCE in acetonitrile for M = Pt,[29] the first and second oxidation potentials of the as-prepared complexes, corresponding to $[M(dmit)_2]^{2-}/[M(dmit)_2]^{-}$ and $[M(dmit)_2]^{-}/[M(dmit)_2]^{0}$, respectively, are irreversible and more positive. While the first oxidation potentials of the complexes show small differences (230–310 mV, except for complex **8** at 450 mV), the second ones vary significantly from 330 mV to 750 mV, rather similar to the results reported by Matsubayashi.[30,31]

Electrical Conductivity

The room temperature conductivities of compressed pellets of the complexes **1**–**10** are measured by the usual two-probe method and are at a range of 10^{-7} – 10^{-10} S/cm. It is anticipated that they are semiconductors or insulators. The

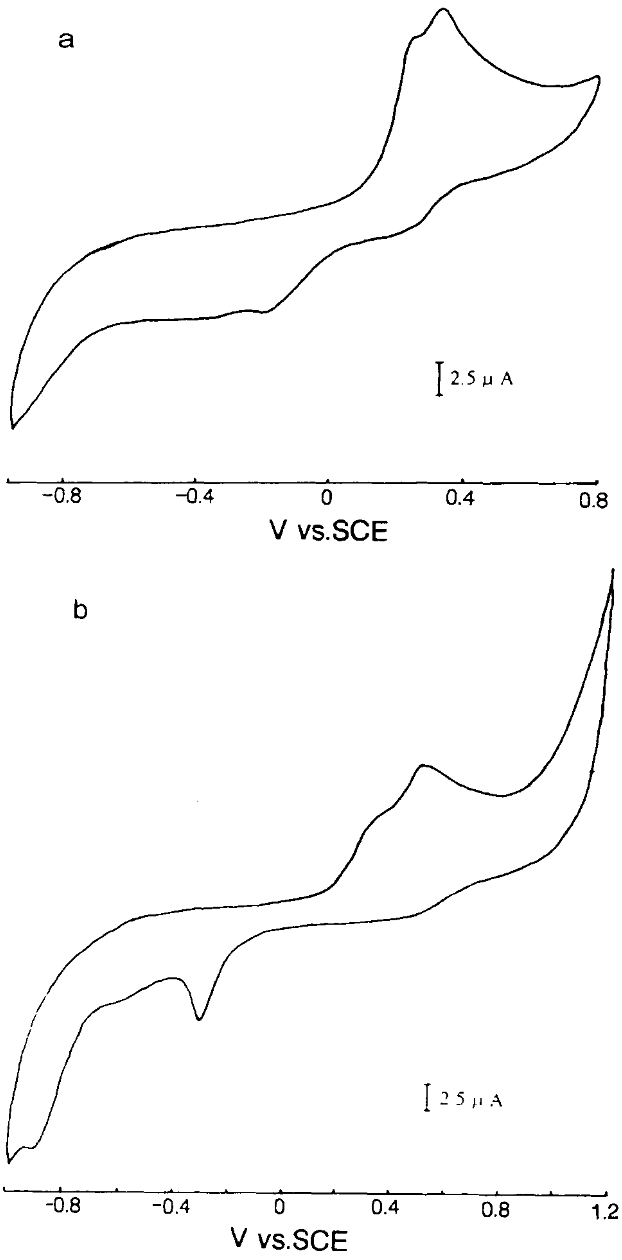


FIGURE 2 Cyclic voltammograms of complex **1** (a) and **2** (b)

TABLE III Peak potentials of the as-prepared complexes (mV, 100 mV/s, *vs.* SCE)

No.	*Compound*	*Peak potentials*
1	$[TEA]_2[Cd(dmit)_2]$	E_{ox} 240 330 E_{red} −400 −210 220
2	$[TEA]_2[Hg(dmit)_2]$	E_{ox} 310 530 E_{red} −850 −260 440
3	$[TEA]_{1.5}[Sn(dmit)_2]$	E_{ox} 300 660 900 E_{red} −620 −400 −180
5	$[TEA][Fe(dmit)_2]$	E_{ox} 260 380 E_{red} −980 −830 −150 230
8	$[BTMA]_2[Cd(dmit)_2]$	E_{ox} 450 750 E_{red} −850 −340
9	$[CTMA]_2[Cd(dmit)_2]$	E_{ox} 250 740 E_{red} −860
10	$[CPy][Cd(dmit)_2]$	E_{ox} 230 660

powder conductivities do not show substantial differences among the complexes with different counter cations or central metal ions and thus it is difficult to determine the effects of the counter cation and the central metal ion on the electrical properties of the DMIT complexes. To investigate the above effects and to obtain good conducting materials, the complexes have to be further oxidized. The oxidation of these complexes to partially oxidized or charge transfer complexes with tetrathiafulvalene (TTF) donors such as tetrakis(*p*-halobenzylthio)tetrathiafulvalene[32,33] is now under progress.

LB Film

Surface pressure-area isotherms of the complexes showed that all of the complexes **1–10** could form a relatively stable monolayer at the air-water interface. Though the film-forming ability of the complexes with different central metal ion (**1–7**) did not show substantial difference, the effect of the cations in the complexes (**1, 8–10**) were striking. The longer of the alkyl chains in the cation, the better of the film-forming ability for the corresponding complex. Complex **10** with the longest alkyl chain in the cation had the best film-forming ability (Figure 3). To facilitate the transfer of the monolayers for the achievement of the LB films, an equimolar arachidic acid (AA) was added to complex **10** to form a floating monolayer with better stability and greater susceptibility to be transferred onto solid substrates. The X-ray diffraction of a 34-layered LB film thus obtained from **10**/AA (1:1, molar ratio) was shown in Figure 4. Results from X-ray diffraction patterns of the pristine LB film demonstrated that the LB film had an ordered lamellar structure with a thickness per layer of 2.83 nm (Table IV). In-plane conductivity measurement on the 32-layered **10**/AA LB film showed that the LB film had a room temperature conductivity of 4.4 ×

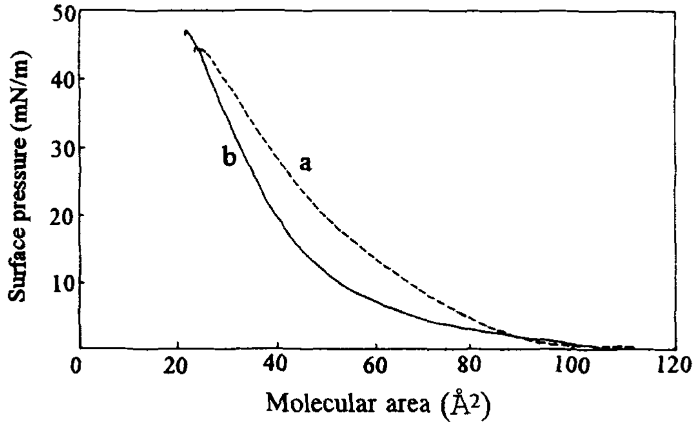


FIGURE 3 Surface pressure-area isotherm of complex **10** in water subphase (a) and **10**/AA (1:1, molar ratio) in $CdCl_2$ subphase

10^{-3} S/cm, and iodine doping resulted in a conductivity of 3.1×10^{-1} S/cm. The conductivity of **10**/AA LB film was larger by 4 orders of magnitude than that of the compressed pellet of complex **10** (ca. 10^{-7} S/cm) due to the highly close and ordered lamellar structure of the LB film. More detailed studies on the structural characterization and physical properties of the LB films from the complexes will be published elsewhere in due course.

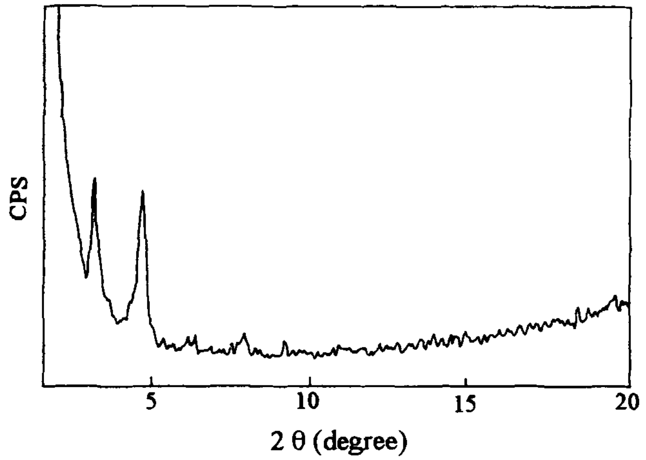


FIGURE 4 X-ray diffraction patterns of the 34-layered **10**/AA (1:1, molar ratio) LB film

TABLE IV Data and results from X-ray diffraction patterns of the 34-layered **10**/AA (1:1, molar ratio) LB film

hkl	*2θ (degree)*	*D (nm)*	*d (nm)*
002	3.16	5.59	2.79
003	4.70	5.64	2.82
004	6.18	5.72	2.86
005	7.92	5.58	2.79
006	9.20	5.76	2.88
Mean value		5.66	2.83

CONCLUSIONS

Two series of metal complexes of the multi-sulfur ligand DMIT with Cd (II), Hg (II), Sn (II), Mn (II), Fe (II), Co (II), or Bi (III) have been prepared in high yields. The compounds are characterized by elemental analysis, ^{1}H NMR spectra, FT-IR and UV-Vis spectral analysis. Cyclic voltammetric studies reveal that the complexes are relatively difficult to be oxidized. The room temperature conductivities of the complexes as compressed pellets are at a range of 10^{-7} – 10^{-10} S/cm. Surface pressure-area isotherm measurements show that the complexes had a good film-forming ability. A highly conducting LB film is constructed from cetylpyridinium-Cd(dmit)$_2$ by admixing with an equimolar of arachidic acid. X-ray diffraction of the pristine LB film demonstrates that the film has an ordered lamellar structure with a thickness per layer of 2.83 nm. The LB film show high conductivity values of 4.4×10^{-3} and 3.1×10^{-1} S/cm without and with iodine doping, respectively.

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