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Organoheterobimetallic complexes derived from bis(1-ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolatometalate(II) ion: synthesis and properties

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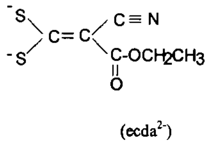
Abstract

A complex salt $[NEt_4]_2[Cu(ecda)_2]$ and six organoheterobimetallic complexes $[Bu_2Sn][Cu(ecda)_2]$, $[Ph_3Sn]_2[Ni(ecda)_2]$ and $[PhHg]_2[M(ecda)_2]$ (M = Ni(II), Cu(II), Zn(II) or Cd(II); $ecda^{2-}$ = 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate) have been prepared. Their characterization relies on analysis, spectroscopic methods, magnetic and conductivity measurements and cyclic voltammetric studies. The diamagnetic compounds $[PhHg]_2[Cu(ecda)_2]$ and $[Bu_2Sn][Cu(ecda)_2]$ are strongly antiferromagnetically coupled. Unshifted and unbroadened nature of ^{1}H-NMR signals show that $[PhHg]_2[Cu(ecda)_2]$ remains diamagnetic in solution while $[PhHg]_2[Ni(ecda)_2]$, which is paramagnetic in the solid state becomes square planar-diamagnetic in solution. In the case of $[Bu_2Sn][Cu(ecda)_2]$ the peak broadening shows absence of Cu–Cu interaction due to paramagnetic nature of the compound in solution. All the products exhibited σ_{rt} in the range of 10^{-10}–10^{-9} S cm^{-1}. Except $[Bu_2Sn][Cu(ecda)_2]$, $[PhHg]_2[Cu(ecda)_2]$ and $[Ph_3Sn]_2[Ni(ecda)_2]$, which show semi conducting behaviour in the range of 293–343 K, the remaining compounds are electrically insulating over the above temperature range. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dithiocomplexes; Organoheterobimetallic complexes; Spectroscopic studies; Semiconducting properties

1. Introduction

For over 40 years, transition metal 1,2-dithiolene complexes have been thoroughly investigated by many research groups [1] and a considerable number of these complexes have novel and interesting conducting [2–5] and magnetic properties [6–8]. The 1,1-dithioligand, isomaleonitriledithiolate (i-mnt^{2-}) which has been recently found useful in molecular electrical conductor exploration [9] like its 1,2-dithio analogue, mnt^{2-}, is quite similar to 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate (ecda^{2-}). Nevertheless, substitution of one of the C≡N groups by the ester group in i-mnt^{2-} is expected to influence the properties of the complexes [10]. Furthermore, despite some of their properties being common, 1,1- and 1,2-dithioligands that is where thiofunctions are on the same or neighbouring carbons differ significantly in their behaviour. 1,1-Dithioligands form four-membered strained chelate ring while 1,2-dithiolenes form less strained five-membered ring in their transition metal complexes. Also, the former shows smaller π-acceptor character as compared to metal 1,2-dithiolates. These features make huge difference in the structure and properties of the complexes.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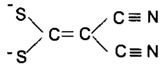
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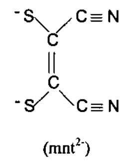
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The general interest of chemists in the investigation of organoheterobimetallics has sparked because of their significant properties, functions and applications in areas such as catalysis, material synthesis and bioorganometallics due to cooperative effect induced by two metal centers of varying electronic configuration. Organomercury compounds are important in organic synthesis on account of generation of radical precursors

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[11]. Higher propensity of mercurials towards sulfur containing ligands focus research interest because of topical problems of mercury poisoning while, organotin(IV) mono and di-cation complexes are antitumour active [12]. The tendency of dithioligands to form heterobimetallic complexes is well pronounced [4,5,13–15].

Taking together the chemistry and properties of organometallic and dithiocomplexes, this paper is devoted to the study of properties of newly synthesized organoheterobimetallic dithio complexes, using cationic organometallic species and anionic transition metal dithiolates at the border between organometallic and inorganic chemistry.

2. Experimental

2.1. Materials

Tetraethylammonium bromide, phenylmercuric acetate, triphenyltin chloride, dibutyltin chloride and ethylcyanoacetate (all Aldrich) were used as received. The ligand, potassium 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate (K_2ecda) was prepared according to the reported method [16] by reaction of ethylcyanoacetate, KOH and CS_2 in dioxane and characterized by analyses, IR and NMR spectra. All other metal salts and reagents were of BDH (AR) or equivalent grades. The solvents were purified by distillation and dried, where necessary, before use. All the syntheses were performed in open atmosphere.

2.2. Synthesis of complexes

2.2.1. [Ph$_3$Sn]$_2$[Ni(ecda)$_2$]

A reddish–brown solution of K_2[Ni(ecda)$_2$] was generated in situ by gradual addition (30 cm^3) of an ethanolic solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (0.248 g, 1 mmol) to a (20 cm^3) ethanol solution of Ph_3SnCl (0.77 g, 2 mmol), was filtered (50 cm^3) water–ethanol (50:50 v/v) solution of K_2ecda (0.52 g, 2 mmol) with vigorous stirring. To a stirred (10 cm^3) solution of K_2[Ni(ecda)$_2$] prepared above. The reaction mixture was stirred for 1 h and then water (20 cm^3) was added.

2.2.2. [PhHg]$_2$ [M(ecda)$_2$]{M = Zn(II) or Cd(II)}

Yellow solution of K_2[Zn(ecda)$_2$]–K_2[Cd(ecda)$_2$] was evolved in situ by slow addition of (30 cm^3) ethanolic solution of $Zn(CH_3COO)_{2.}2H_2O$–$Cd(CH_3COO)_2 \cdot 2H_2O$ (0.219 g, 1 mmol):(0.266 g, 1 mmol) to an (30 cm^3) ethanol–water (80:20 v/v) solution of K_2ecda (0.52 g, 2 mmol) with vigorous stirring. To the (60 cm^3) stirred solution of K_2[Zn(ecda)$_2$]–K_2[Cd(ecda)$_2$], was added a (10 cm^3) ethanolic solution of $PhHgCH_3COO$ (0.673 g, 2 mmol).

2.2.3. [PhHg]$_2$[Ni(ecda)$_2$]

To a (20 cm^3) stirring ethanolic solution of $PhHgCH_3COO$ (0.673 g, 2 mmol), was added a (50 cm^3) solution of K_2[Ni(ecda)$_2$] prepared as described above.

2.2.4. [PhHg]$_2$[Cu(ecda)$_2$] and [Bu$_2$Sn][Cu(ecda)$_2$]

A dark brown solution of K_2[Cu(ecda)$_2$] was prepared in situ by slow addition of a (30 cm^3) water–ethanol (80:20 v/v) solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.199 g, 1 mmol) to a (20 cm^3) aqueous solution of K_2ecda (0.52 g, 2 mmol) with constant stirring. To this (50 cm^3) solution, an ethanolic solution (20 cm^3) of $PhHgCH_3COO$ (0.673 g, 2 mmol)–Bu_2SnCl_2 (0.304 g, 1 mmol) was added with stirring.

2.2.5. [NEt$_4$]$_2$[Cu(ecda)$_2$]

To a stirred (50 cm^3) solution of K_2[Cu(ecda)$_2$] prepared as described above, was added (5 cm^3) aqueous solution of NEt_4Br (0.420 g, 2 mmol).

In general the reaction mixtures were stirred for another 30 min and the solid compounds thus formed in each case were filtered, washed with ethanol–water mixture followed by ethanol and diethyl ether and dried in vacuo over $CaCl_2$.

2.3. Analysis and physical measurements

The organic part of the complexes were decomposed with concentrated HNO_3–aqua-regia. Metals were determined following standard gravimetric procedures [17]. Sulfur was estimated as $BaSO_4$. Physical measurements dealing with solution and solid state conductivity and magnetic susceptibility measurements and recording of IR (4000–400 cm^{-1}) spectra were the same as described earlier [5]. Far IR (400–200 cm^{-1}) as polyethylene pellets were recorded on a PE 983/PE 781 spectrophotometer. The Raman spectra of selected samples were recorded on a Bruker IFS 66 V FT IR FRA 106 Raman module using YAG Laser. ^{1}H- and ^{13}C-NMR spectra were recorded in DMSO-d_6 on a JEOL FX 90Q spectrometer with δ measured relative to the internal reference Me_4Si. The X-band EPR spectra for the powder and DMSO solution of the samples were obtained at room temperature with a Varian E-112 spectormeter. Diphenylpicrylhydrazyl (dpph) powder ($g = 2.0036$) was employed as a field reference. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using m-nitrobenzyl alcohol as the matrix. For cyclic voltammetric experiments, a conventional three-electrode system was used in a single compartment cell. The working electrode was a platinum wire and the reference electrode was a saturated sodium chloride calomel electrode (SSCE) which was separated from the test solution by using Luggin capillary containing an agar salt (NaCl) bridge.

All the potentials were reported with respect to this electrode. The counter electrode was also a platinum wire. Cyclic voltammograms were obtained with a bipotentiostat model-AFRDE 4E, Pine instrument (USA) and recorded on a Houston Model 2000 X–Y recorder. Concentration of the complexes was 10^{-3} M in acetonitrile, containing 0.1 M $NaClO_4$ as a supporting electrolyte. The relevant analytical and physico–chemical data of the complexes are given in Tables 1 and 2.

3. Results and discussion

When an aqueous–ethanolic solution of $K_2[M(ecda)_2]$ was allowed to react with an ethanolic solution of $Ph_3SnCl–Bu_2SnCl_2–PhHgCH_3COO$ or an aqueous solution of NEt_4Br in appropriate molar ratio, the complex salt $[NEt_4]_2[Cu(ecda)_2]$ and the organoheterobimetallic complexes $[PhHg]_2[M(ecda)_2]$, $[Ph_3Sn]_2[Ni(ecda)_2]$ and $[Bu_2Sn][Cu(ecda)_2]$ were formed according to the following matathesis reactions:

$$M(CH_3COO)_2 + 2K_2ecda$$

$$\rightarrow K_2[M(ecda)_2] + 2CH_3COOK$$

$$K_2[Cu(ecda)_2] + 2NEt_4Br \rightarrow [NEt_4]_2[Cu(ecda)_2] + 2KBr$$

$$K_2[M(ecda)_2] + 2PhHgCH_3COO$$

$$\rightarrow [PhHg]_2[M(ecda)_2] + 2CH_3COOK$$

$$K_2[Ni(ecda)_2] + 2Ph_3SnCl \rightarrow [Ph_3Sn]_2[Ni(ecda)_2] + 2KCl$$

$$K_2[Cu(ecda)_2] + Bu_2SnCl_2 \rightarrow [Bu_2Sn][Cu(ecda)_2] + 2KCl$$

M = Ni(II), Cu(II), Zn(II) or Cd(II)

The complexes melt/decompose in the range of 110–140°C. Bimetallic complexes $[PhHg]_2[Ni(ecda)_2]$ and $[Ph_3Sn]_2[Ni(ecda)_2]$ are soluble in acetone while the remaining complexes are soluble in acetonitrile and DMSO. The conductivities (6.7–27.8 $cm^2\ \Omega^{-1}\ mol^{-1}$) of a 10^{-3} M acetone solution of the complexes (Table 1) show non-electrolytic behaviour [18] of $[PhHg]_2[Ni(ecda)_2]$, $[PhHg]_2[Cu(ecda)_2]$ and $[Ph_3Sn]_2[Ni(ecda)_2]$ while $[NEt_4]_2[Cu(ecda)_2]$ registered a conductivity of 108 $cm^2\ \Omega^{-1}\ mol^{-1}$ in 10^{-3} M DMSO consistent with 1:2 electrolytes [18]. Molar conductivities (85–90 $cm^2\ \Omega^{-1}\ mol^{-1}$) for the remaining complexes in DMSO solution indicate their complete dissociation.

In the positive ion FAB mass spectra of $[PhHg]_2[Ni(ecda)_2]–[PhHg]_2–[Cu(ecda)_2]$, the peaks at m/z (I%), 1091(15)/1021(40), 865(40/100), 743(100), 588(25/80), 467(10)/471(5), 244(25)/248(40), 232(30/15), 89(60)/94(20) and 77(75/40) correspond to $\{[PhHg]_2[Ni(ecda)_2] + S\}^+–\{[PhHg]_2[Cu(ecda)_2] + S\}^+$, $\{(PhHg)_2ecda + 2C_2H_5SH\}^+$, $[(PhHg)_2ecda]^+$, $[(PhHg)_2 + S]^+$, $[Ni(ecda)_2 + H_2S]^+–[Cu(ecda)_2 + H_2S]^+$, $[Ni(ecda)]^+–[Cu(ecda)]^+$, $[HgS]^+$, $[NiS]^+–[CuS]^+$ and $[C_6H_5]^+$ fragment ions and suggest identical environment around the metal ions. An intense peak at $m/z = 432$ in both the complexes may be accounted to the $m/2z$ of the peak at $m/z = 865$ or $[Ni(ecda)_2]^+–[Cu(ecda)_2]^+$ moieties.

3.1. Magnetic moment, EPR and UV–visible spectra

The $\mu_{eff} = 2.93$ BM for $[PhHg]_2[Ni(ecda)_2]$ suggests that geometry around nickel(II) center is not square planar but involvement of a solid state interaction through coordinatively unsaturated sulfurs of $ecda^{2-}$ groups and also the proposed non-linearity for the S–Hg–Ph interactions result into an octahedral environment around nickel(II). The electronic spectral data for the complexes are summarized in Table 2. The absorption band centered at around 600 nm, is most likely assigned to a d–d transition, characteristic for square planar environment [19] around nickel(II) and suggests that solid state interactions responsible for the octahedral environment around nickel(II) are not preserved in solution. The absorption peak at 450 nm is attributed to $Ni \leftarrow S(ecda^{2-})$ MLCT transition [19] while the high energy absorptions are mainly associated to the intraligand ($\pi–\pi^*$) transitions. The diamagnetism together with electronic spectral bands at around 580 nm suggest square planar geometry [19] about nickel(II) in $[Ph_3Sn]_2[Ni(ecda)_2]$.

Magnetic moment 1.28 BM for $[NEt_4]_2[Cu(ecda)_2]$ is somewhat low for a single unpaired spin present on copper(II) center and shows some sort of metal–metal interaction in the solid state. In DMSO solution this gives an isotropic spectrum with $A_{av} = 56.25$ G and $g_{av} = 2.060$ which conforms to the values reported for the square planar cupric dithiolates [20]. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023) shows that the unpaired electron is present in the $d_{x^2-y^2}$ orbital [20] of copper(II). Complete quenching of paramagnetism at room temperature for $[Bu_2Sn][Cu(ecda)_2]$ and $[PhHg]_2[Cu(ecda)_2]$ is indicative of strong antiferromagnetic interaction between uncoupled spins at copper(II) centers. Features of RT powder EPR spectra for the diamagnetic $[PhHg]_2[Cu(ecda)_2]$ and $[Bu_2Sn][Cu(ecda)_2]$ belong to Cu(II), S = 1/2 monomeric impurities possibly incorporated during preparation. The complex salt $[NEt_4]_2[Cu(ecda)_2]$ and organoheterobinuclear complexes containing copper(II) show a weak broad d–d band at around 600 nm, characteristic of square planar geometry [21] about copper(II) while the intense high energy absorptions at around 300–350 nm and 398–450 nm are assigned to $\pi–\pi^*$ intraligand and $Cu \leftarrow S(ecda^{2-})$ charge transfer transitions.

Table 1
Analytical data, molar conductance and ^{1}H-NMR chemical shifts, δ ppm (proton/J) of the complexes [a]

Complex empirical formula	Colour (% yield)	M.p. (decomp.) (°C)	Λ_M (cm^2 Ω^{-1} mol^{-1}) in 10^{-3} M DMSO–acetone	Analysis, % found (calculated)			^{1}H-NMR		
				Hg/Sn	M	S	$\mathrm{OC}\mathit{H}_2\mathrm{CH}_3$	$\mathrm{OCH}_2\mathrm{C}\mathit{H}_3$	C_6H_5
$[\mathrm{Bu_2Sn}][\mathrm{Cu(ecda)_2}]$ $C_{20}H_{28}N_2O_4SnCuS_4$	Red (60)	115	87.4	17.71 (17.89)	9.40 (8.99)	19.09 (19.09)	4.22 (m, 4H)	(0.88–1.77)	
$[\mathrm{PhHg}]_2[\mathrm{Cd(ecda)_2}]$ $C_{24}H_{20}N_2O_4Hg_2CdS_4$	Yellow (65)	135	85.0	38.08 (38.19)	10.75 (10.89)	12.24 (12.30)	4.20 (q, 4H, $J = 7.5$ Hz)	1.26 (t, 6H, $J = 7.5$ Hz)	7.46 (m, 10H)
$[\mathrm{PhHg}]_2[\mathrm{Ni(ecda)_2}]$ $C_{24}H_{20}N_2O_4Hg_2NiS_4$	Yellowish green (72)	(140)	21.2	40.44 (41.05)	5.91 (5.90)	12.90 (12.89)	4.33 (q, 4H, $J = 6.6$ Hz)	1.53 (t, 6H, $J = 6.6$ Hz)	7.60 (m, 10H)
$[\mathrm{Ph_3Sn}]_2[\mathrm{Ni(ecda)_2}]$ $C_{48}H_{40}N_2O_4Sn_2CuS_4$	Reddish brown (78)	110	27.8	20.00 (19.81)	5.13 (5.09)	11.21 (11.29)	4.26 (q, 4H, $J = 7.0$ Hz)	1.24 (t, 6H, $J = 7.0$ Hz)	7.50 (m, 30H)
$[\mathrm{PhHg}]_2[\mathrm{Cu(ecda)_2}]$ $C_{24}H_{20}N_2O_4Hg_2CuS_4$	Yellowish brown (70)	(130)	6.7	40.15 (40.78)	6.30 (6.59)	13.84 (13.99)	4.22 (q, 4H)	1.24(t, 6H)	7.50 (m, 10H)
$[\mathrm{PhHg}]_2[\mathrm{Zn(ecda)_2}]$ $C_{24}H_{20}N_2O_4Hg_2ZnS_4$	Yellow (65)	129	90.5	40.16 (40.25)	6.54 (6.49)	12.81 (12.81)	4.22 (q, 4H, $J = 7.5$ Hz)	1.24 (t, 6H, $J = 7.4$ Hz)	7.50 (m, 10H)
$[\mathrm{NEt_4}]_2[\mathrm{Cu(ecda)_2}]$ $C_{28}H_{50}N_4O_4CuS_4$	Brown	155	108.5		9.10 (8.99)	18.35 (18.30)			

[a] Signals for –CH_3 of ecda and Bu groups are merged.

Table 2
Selected IR [Raman] bands (cm^{-1}) and UV–visible spectral data of the complexes

Complex	ν(C≡N)	ν(C=O)	ν(C=CS$_2$)	ν(C–S)	ν(Sn–C)–ν(Hg–C)	ν(M–S)	ν(Sn–S)–ν(Hg–S)	Solvent	λ_{max} (nm) (ε (dm^3 mol^{-1} cm^{-1}))
$[\mathrm{Bu_2Sn}][\mathrm{Cu(ecda)_2}]$	2210	1684	1458	1175	596, 460	375	280	Acetonitrile Acetone	230, 330, 432(1196), 600 (342) 430 (1435)
$[\mathrm{PhHg}]_2[\mathrm{Cd(ecda)_2}]$	2190 [2193]	1695 [1690]	1430 [1421]	1141 [1158]	670, 460 [660, 450]	350 [360]	260 [255]		
$[\mathrm{PhHg}]_2[\mathrm{Ni(ecda)_2}]$	2200	1689	1430	1140	675, 452	380	260	Acetonitrile Acetone	600 345 (25,000), 370 (30,100), 398 (23,840), 450 (1757), 600 (156)
$[\mathrm{Ph_3Sn}]_2[\mathrm{Ni(ecda)_2}]$	2190	1620	1429	1175	600, 450	375	300	Acetonitrile Acetone	220, 340, 440, 580 340, (13,560), 350 (13,550), 405 (5990), 442 (8934)
$[\mathrm{PhHg}]_2[\mathrm{Cu(ecda)_2}]$	2195	1665	1438	1140	660, 450	370	255	Acetonitrile	240, 330, 450
$[\mathrm{PhHg}]_2[\mathrm{Zn(ecda)_2}]$	2200 [2193]	1690 [1689]	1430 [1421]	1158 [1158]	670, 455 [660, 460]	360 [375]	255 [250]		
$[\mathrm{NEt_4}]_2[\mathrm{Cd(ecda)_2}]$	2192	1675	1460	1170		370		DMSO	342, 395, 620

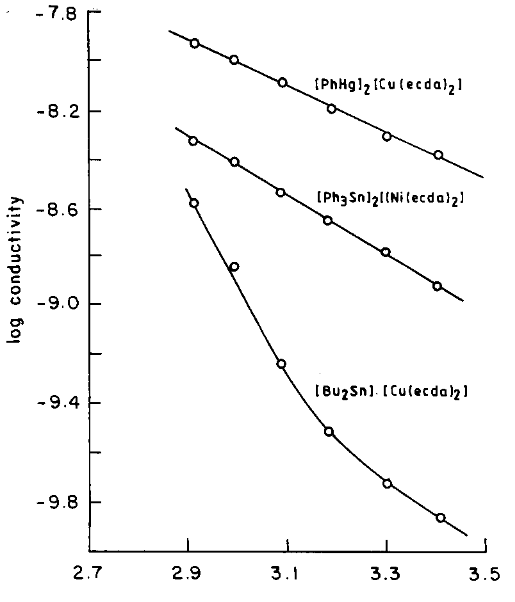


Fig. 1. Temperature dependence of the electrical conductivities of the complexes.

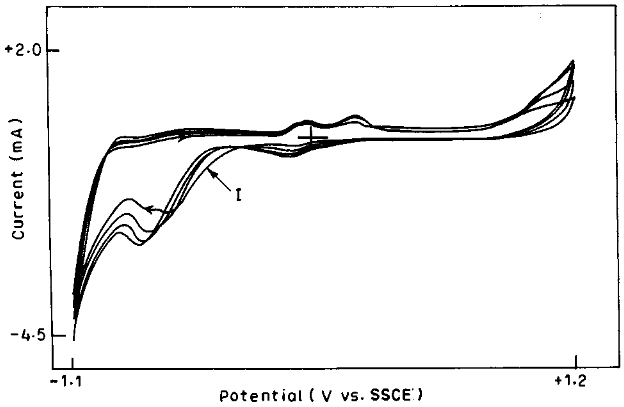
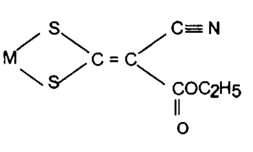


Fig. 2. Cyclic voltammogram of 1 mM $[NEt_4]_2[Cu(ecda)_2]$ in acetonitrile at Pt electrode recorded at different scan rates starting from 40 mV s^{-1} (curve I) and increasing in steps of 20 mV s^{-1}.

3.2. Vibrational spectra

Apart from the NEt_4^+ and coordinated Ph as well as Bu groups [22], the complexes exhibit strong IR absorptions (Table 2) near 2190–2210, 1660–1690, 1420–1460 and 1140–1175 cm^{-1} corresponding to $\nu(C≡N)$, $\nu(C=O)$, $\nu(C=C)$ and $\nu(C–S)$ modes characteristic of the $ecda^{2-}$ in a (S,S) chelating–chelating-bridging manner [10,14].



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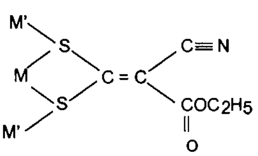

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The three important observations of the spectra are: (a) The high energy shift (52–92 cm^{-1}) of the strong $\nu(C=C)$ and a little variation (~ 15 cm^{-1}) in $\nu(C–S)$ from the free ligand, K_2ecda spectrum to that of the complexes. (b) The occurrence of Sn–C and Hg–C stretching vibrations at 596–670 and 450–460 cm^{-1} respectively in the organoheterobimetallic complexes [22]. (c) Appearance of a single sharp band near 2200 cm^{-1} in the complexes because of their higher symmetry compared to the splitted bands at 2160 and 2190 cm^{-1} in the ligand K_2ecda. In the lower frequency region (400–200 cm^{-1}), the absorptions occurring in 350–380 and 250–300 cm^{-1} region have been assigned to $\nu(M/Sn–S)$ modes, respectively [23].

A comparison of the infrared and Raman spectra obtained for $[PhHg]_2[Zn(ecda)_2]$ and $[PhHg]_2[Cd(ecda)_2]$ shows that Raman bands typically agree well with those obtained by infrared spectroscopy for $\nu(C≡N)$, $\nu(C=O)$, $\nu(C=C)$, $\nu(C–S)$, $\nu(Sn–C)$, $\nu(Hg–S)$ and $\nu(M–S)$ [24] frequencies. Both in the IR and Raman spectra, peaks corresponding to the phenyl group and its monosubstituted analogue [22] have been found at around 1500, 1600, 727 and 674 cm^{-1}.

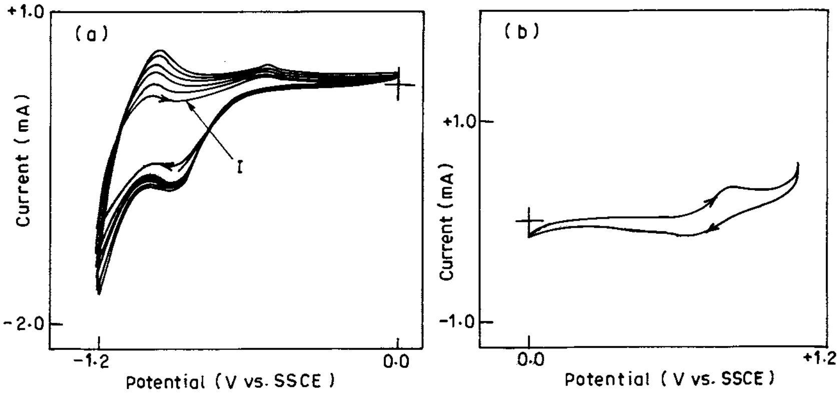

Fig. 3. (a) Cyclic voltammogram of 1 mM $[Bu_2Sn][Cu(ecda)_2]$ in acetonitrile at Pt electrode recorded at different scan rates (cathodic region) starting from 40 mV s^{-1} (curve I) and increasing in steps of 20 mV s^{-1}. (b) Scan in anodic region (20 mV s^{-1}).

3.3. NMR spectra

All the complexes show well resolved ^{1}H-NMR signals in the aliphatic and aromatic region (Table 1) and integrate well for the corresponding number of protons. As compared to the free ligand K_2ecda, the OCH_2 and CH_3 protons are marginally downfield shifted in the complexes. Consistent with UV–visible spectra, appearance of narrow and unshifted ^{1}H-NMR resonances show diamagnetic, square planar coordination around nickel(II) in [PhHg]$_2$[Ni(ecda)$_2$] in the solution. This indicates that the solid state interactions bringing octahedral geometry about nickel(II) exist no more in the solution. Consistent with magnetic behaviour and appearance of unbroadened and unshifted ^{1}H-NMR resonances for [PhHg]$_2$[Cu(ecda)$_2$] clearly indicates that dominant Cu–Cu interaction present in the solid state is preserved in the solution while the peak broadening for [Bu$_2$Sn][Cu(ecda)$_2$] shows that strong Cu–Cu interaction, responsible for its diamagnetism in the solid is not retained in the solution.

The ^{13}C-NMR spectra of the complexes show signals for CH_3 (18.4–23.68), OCH_2 (52.4), C=C (90), C≡N (120.8–122.4), C_6H_5 (128.8–129.6) and C=O (δ 174 ppm) carbons of the ecda^{2-} and phenyl group.

3.4. Solid state electrical conductivity

The conductivity measurements of the pressed pellets were made in the temperature range of 293–343 K using conventional two probe technique (on a Keithely 236 SMU). The room temperature conductivity, $\sigma_{rt} = 1.78\times10^{-9}$ to 1.41×10^{-10} S cm^{-1} for the compounds is low. In the case of [Bu$_2$Sn][Cu(ecda)$_2$], [Ph$_3$Sn]$_2$[Ni(ecda)$_2$] and [PhHg]$_2$[Cu(ecda)$_2$], the conductivity increases with the increase in temperature (Fig. 1) with energy band gaps, Ea, 0.39, 0.25 and 0.20 eV, respectively, showing their semiconducting behaviour. Interestingly organoheterobimetallic dithio complexes containing Ni(II) and Cu(II) which show greater tendency to form square planar π-delocalized extended S...S stacked structure, exhibit semiconducting behaviour compared to those electrically insulating materials containing Zn(II), Cd(II), or Hg(II) which possess preferential tetrahedral/octahedral geometry where a columnar stacked arrangement is less feasible.

3.5. Cyclic voltammetry

The electrochemical behaviour of [NEt$_4$]$_2$[Cu(ecda)$_2$] and [Bu$_2$Sn][Cu(ecda)$_2$] was measured by cyclic voltammetry in acetonitrile solution using NaClO$_4$ as supporting electrolyte. The cyclic voltammogram (Fig. 2) for [NEt$_4$]$_2$[Cu(ecda)$_2$] shows that this salt undergoes a quasi reversible reduction at −0.1 V for Cu(II/I) process. The second reduction near −0.7 V which is much stronger than the first reduction is probably ligand based since dithiolene complexes are well known to exhibit such processes [25]. In Fig. 3a the reduction peak at −0.90 V and its reoxidation peak at −0.53 V are too widely separated to be accounted due to one species. Probably, some chemical reaction must have occurred following the reduction at −0.90 V. The oxidation peak at +0.80 V and its corresponding reduction at +0.65 V seems to have involved metal

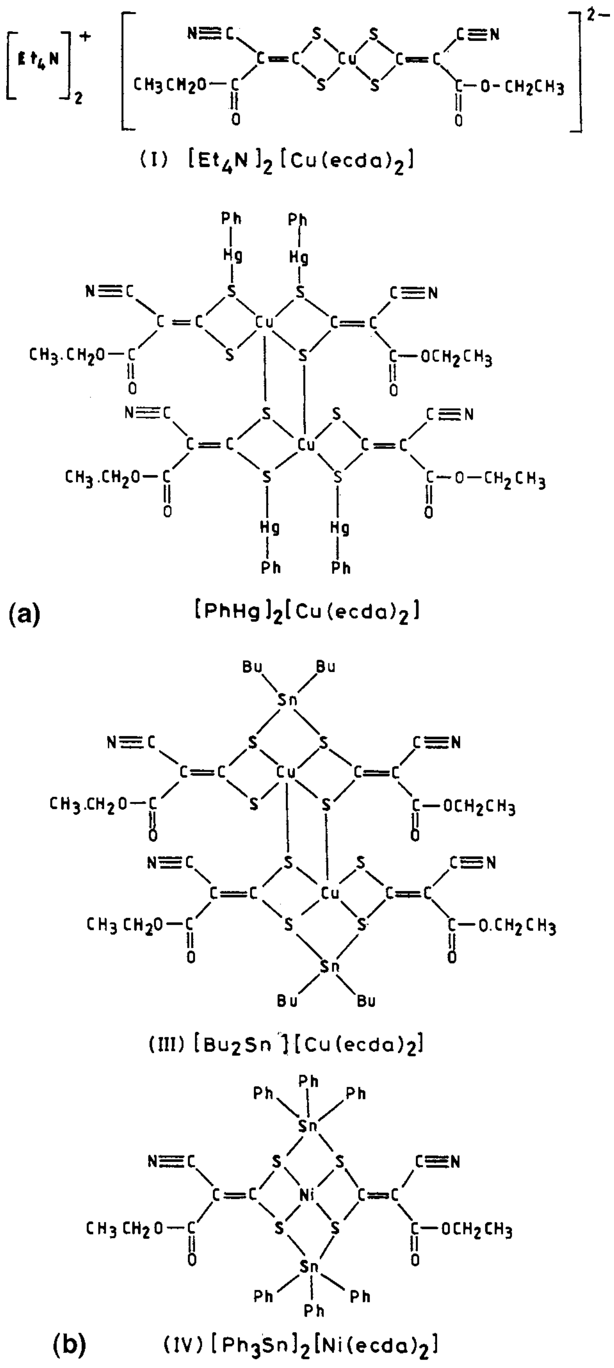

Fig. 4. Suggested structure of the complexes.

induced oxidation of the ligand moiety. Consistent with EPR and UV–visible spectra, these findings indicate that the copper is present as Cu(II), d^9 in these complexes.

Despite our best efforts, we could not grow single crystals of the complexes for their structural characterization. On the basis of foregoing discussion the ionic, and stacked dimeric structure (Fig. 4a and b) have been tentatively suggested for the complex salt $[NEt_4]_2[Cu(ecda)_2]$ and the organoheterobimetallic dithiolates. In the case of bimetallic complexes, lone pairs present on the coordinated sulfurs of the $ecda^{2-}$ have been shown to be involved [19] in the bonding with organomercury(II)/organotin(IV) Lewis acid moieties having higher propensity for the sulfur donors.

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