Synthesis and spectral characterization of homo- and hetero-dinuclear complexes with a new septadentate Schiff base ligand

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Abstract. Reaction between 3-formylsalicylic acid and *bis*-(2-aminophenyl)-disulphide yields a septadentate Schiff base with N_2SO_4 donor frame of which the inner compartment is N_2SO_2 and the outer is O_2O_2 type. It forms several complexes with inner copper centre and outer nontransition/transition metal ions. The complexes have been characterised by elemental analyses, spectral (IR, absorption, diffused reflectance), thermal and magnetic data. Dinuclear copper complexes exhibit subnormal magnetic moments ($\approx 0\cdot80$ BM), showing magnetic exchange, and six-line solid-state ESR spectra at 77 K.

Keywords. Septadentate Schiff base; copper complexes; compartmental ligand; subnormal magnetic moment; spectral characterization; ESR spectra.

1. Introduction

The chemistry of multimetallic species has grown steadily because of their involvement in the area of homogeneous catalysis, magnetic exchange between paramagnetic centres, optically induced intrasystem charge transfer and bioinorganic chemistry[1–13]. The potential of the field can be gauged from the appearance of many reviews in the literature[1–3]. Considerable effort has thus been directed towards the synthesis of ligands that can generate polynuclear systems, particularly capable of holding two similar or dissimilar metal ions, subject to control by appropriate modification of the molecular topology[1–7]. The ligands are predominantly Schiff bases, popularly known as compartmental or polypodal ligands. The Schiff bases derived from 3-formylsalicylic acid (FSA) and diamines act as binucleating side-off acyclic ligands[9–14]. The compartment size and the number of donor centres are fully monitored by the use of diamines. *Bis*-(2-aminophenyl)disulphide is a potential diamine for synthesising the N_2SO_4 donor frame with FSA in which one compartment is a Schiff base of the N_2SO_2 type, whose chemistry is well-known[15,16] and the other compartment may be compared with keto-carboxylic acid and is designated O_2O_2 type. The subsequent metal incorporation may provide the opportunity to study the chemistry of binucleating systems. In this work, we report the synthesis of dinuclear stable, magnetically

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interacting metal complexes derived from acyclic chelators incorporating thioether function.

2. Experimental

$UO_2(OAc)_2 \cdot 2H_2O$, $Cu_2(OAc)_4 \cdot 2H_2O$ were BDH reagents. All other chemicals used were of AR grade and were used as received. Solvents were purified by reported procedure[17]. 3-Formylsalicylic acid (FSA)[18] and *bis*-(2-aminophenyl)disulfide[16] were prepared according to literature procedure. [Bu$_4$N][ClO$_4$] and MeCN for electrochemical work were synthesised and purified by a previously described process[19].

Microanalysis (C, H, N) were performed using a Perkin–Elmer 2400 CHN elemental analyser and copper analysis was carried out by iodometric titration method[20]. Spectroscopic measurements were carried out using the following instruments: IR spectra, JASCO FT-IR model 420; UV-VIS spectra, Shimadzu UV-160A; diffused reflectance spectra, Hitachi U-3501 UV-VIS-NIR spectrophotometer; and ^{1}H-NMR, Brucker 200 MHz FT-NMR spectrometers. Molar conductances (Λ_M) were measured in a Systronics conductivity meter 304 model using $\approx 10^{-3}$ M solutions in DMF. Thermoanalytical data were obtained using Shimadzu TG 50/DT 50. Bulk magnetic moments ($\boldsymbol{m}$, BM) were obtained from vibrating sample magnetometer PAR 155 model. Electrochemical measurements were made with a computer-controlled PAR model 270 VERSTAT electrochemical instrument using a glassy carbon disk working electrode. All measurements were made at 298 K and were referenced to the saturated calomel electrode (SCE) in DMF-MeCN with [Bu$_4$N][ClO$_4$] as a supporting electrolyte. The reported potentials are uncorrected for junction potential. ESR spectra were recorded at X-band on a Varian E-109C spectrometer. DPPH ($g = 2 \cdot 0037$) was used to calibrate the spectra.

2.1 *Preparation of the ligand (H$_4$L)*

To a stirred methanolic solution (15 ml) of 3-formylsalicylic acid (0·35 g, 2·11 mM) was added *bis*-(2-aminophenyl)disulphide (0·25 g, 1·01 mM) in the same solvent (10 ml) dropwise and stirred for 1h at room temperature. The yellow solid formed was filtered, washed with cold MeOH-water (1:1, *v/v*, 5 ml × 2) and dried *in vacuo*. Yield, 0·4 g (70%). MP 232 ± 1°C.

2.2 *Preparation of the complexes*

2.2a *Preparation of [Cu·H$_2$O]Na$_2$L·H$_2$O (**1**):* A solution (30 ml) of H$_4$L (0·55g, 1·01 mM) was added dropwise to a hot methanol solution (25 ml) of Cu$_2$(OAc)$_4$·2H$_2$O (0·2 g. 0·50 mM) in the presence of NaOH (0·18 g, 4·5 mM). The resulting mixture was refluxed for 4 h on a steam bath. The brown precipitate that formed was filtered hot and washed with methanol, ether and dried *in vacuo*. Yield, 0·44 g (64%).

2.2b *Preparation of [Cu·H$_2$O]ML·nH$_2$O (M = Ca(II) (**2**), Ba(II) (**3**), Zn(II) (**4**), n = 1; M = UO$_2$ (VI) (**5**)):* Cu$_2$(OAc)$_4$·2H$_2$O (0·11 g, 0·28 mM) in MeOH (10 ml) was added dropwise to a methanol solution (50 ml) of H$_4$L (0·3 g, 0·55 mM) in presence of LiOH (0·06 g, 2·5 mM), and refluxed over a steam bath for 2 h. A solution of MCl$_2$ + 2 NaOAc

(M = Ca, Ba)/Zn(OAc)$_2$/UO$_2$(OAc)$_2$·2H$_2$O (one equivalent) in MeOH (20 ml) was added to the suspension and refluxed for an additional 4 h. The dark precipitate that formed was filtered from the solution and washed with hot methanol (5 ml × 4). The product was dried over CaCl$_2$. Yield, 60–70%.

2.2c *Preparation of Cu$_2$L·H$_2$O (6)*: Cu$_2$(OAc)$_4$·2H$_2$O (0·22 g, 0·56 mM) in MeOH (10 ml) was added dropwise to a methanol solution (20 ml) of H$_4$L (0·3 g, 0·55 mM) in presence of LiOH (0·06 g, 2·5 mM), and refluxed over a steam bath for 2 h. The dark coloured precipitate was filtered and washed with hot methanol (5 ml × 4). The product was dried over CaCl$_2$. Yield, 0·31 g (82%).

2.2d *Preparation of (UO$_2$)$_2$L·H$_2$O (7)*: UO$_2$ (OAc)$_2$·6H$_2$O (0·48 g, 1·13 mM) was dissolved in MeOH (20 ml) and added dropwise to the methanolic solution (25 ml) of H$_4$L (0·3 g, 0·55 mM). The mixture was refluxed for 2 h over steam bath. The product was filtered at hot and washed with hot methanol. It was then dried over CaCl$_2$. Yield, 0·42 g (70%).

2.2e *Preparation of [Cu·S](UO$_2$)L (S = Py (8), DMSO (9))*: [Cu·H$_2$O](UO$_2$)L·H$_2$O (0·01 mM) was suspended in the solvent, S, and stirred for 8 h and then filtered. The filtrate was allowed to diffuse into MeOH upon layering for a week. Crystals formed were isolated and dried over CaCl$_2$. Yield, 40–50%.

3. Results and discussion

3.1 *Synthesis*

The ligand (H$_4$L) is obtained as a condensation product of *bis*-(2-aminophenyl)disulphide and 3-formylsalicylic acid (FSA) and has eight donor sites N$_2$S$_2$O$_4$. It acts however as a septadentate side-off ligand using two imine nitrogens, two phenolato oxygens, one disulphide sulphur and two carboxylato oxygens as donor sites. Thioether is not a good ligand to bind class of metal ions [21] and in this ligand it is located in an internal position within the complexing side chains. This has been specifically designed in order that the chelation by N and O enforces S coordination [15]. The ligand has two compartments; one resembles Schiff base N$_2$SO$_2$ type and the second site is O$_2$O$_2$ type.

The complexes were synthesised by direct reaction between pure isolated ligand (H$_4$L) and metal acetates in MeOH in presence of LiOH/NaOH with stoichiometric mole proportion to yield mono or dinuclear complexes. The complexes are listed in table 1 and their proposed structures are given in scheme 1. Hetero-dinuclear complexes with inner copper(II) core are [Cu·H$_2$O]ML·H$_2$O (M = Ca(II) (2), Ba(II) (3), Zn(II) (4), UO$_2$ (VI) (5)) ([Cu·H$_2$O] refers to the inner core metallated fragment). They were synthesised from 1 and the second metal salt in 1:1 mole proportion.

The composition of the complexes are supported from the elemental analyses. The molar conductances (Λ$_M$) were measured in DMF; the complex 1 shows conductivity 120 Ω^{-1}cm^{2}M^{-1} at 25°C and is 1:2 electrolyte in nature. All other complexes remain almost insoluble and are not measured.

Table 1. Physicochemical data of the compounds.

Compound	Colour	Found (Calc.) (%)				D^d (°C)	Electronic spectra l_{max}/nm
		C	H	N	Cu		
H_4L^a	Yellow	61·54 (61·76)	3·73 (3·68)	5·22 (5·15)		232 ± 1	353, 339, 280
$[Cu·H_2O][Na_2L·H_2O]^a$ (**1**)	Pale brown	48·87 (49·01)	3·03 (2·92)	4·00 (4·08)	8·73 (9·26)	>350	685, 620[c], 452[c], 360, 347, 300
$[Cu·H_2O]CaL·H_2O^b$ (**2**)	Brown	49·53 (49·44)	2·85 (2·94)	4·00 (4·12)	8·69 (9·34)	>350	672, 490[c], 385, 305
$[Cu·H_2O]BaL·H_2O^b$ (**3**)	Brown	43·13 (43·25)	2·70 (2·57)	3·67 (3·60)	8·35 (8·17)	>400	665, 470[c], 390, 325
$[Cu·H_2O]ZnL·H_2O^b$ (**4**)	Yellowish brown	47·79 (47·66)	2·73 (2·84)	4·09 (3·97)	8·52 (9·01)	>400	675, 485[c], 392, 310
$[Cu·H_2O](UO_2)L^b$ (**5**)	Orange brown	37·77 (37·69)	1·93 (2·02)	3·27 (3·14)	6·88 (7·12)	>400	600[c], 514, 445[c], 386, 347, 310
$Cu_2L·H_2O$ (**6**)	Black brown	48·89 (49·04)	2·55 (2·63)	4·00 (4·09)	17·86 (18·54)	>400	664, 480[c], 415, 389, 317
$(UO_2)L·H_2O$ (**7**)	Deep yellow	30·69 (30·60)	1·55 (1·64)	2·62 (2·55)		>400	476[c], 428, 380, 295
$[Cu·Py](UO_2)L^b$ (**8**)	Black brown	41·49 (41·57)	2·16 (2·21)	4·53 (4·41)	6·22 (6·67)	>350	630[c], 425, 400, 360, 300
$[Cu·DMSO](UO_2)L^b$ (**9**)	Black brown	37·77 (37·83)	2·39 (2·31)	3·05 (2·94)	6·26 (6·67)	>400	615[c], 410, 340, 290

[a] Solution spectra in DMF; [b] reflectance spectra; [c] shoulder; [d] decomposition temperature
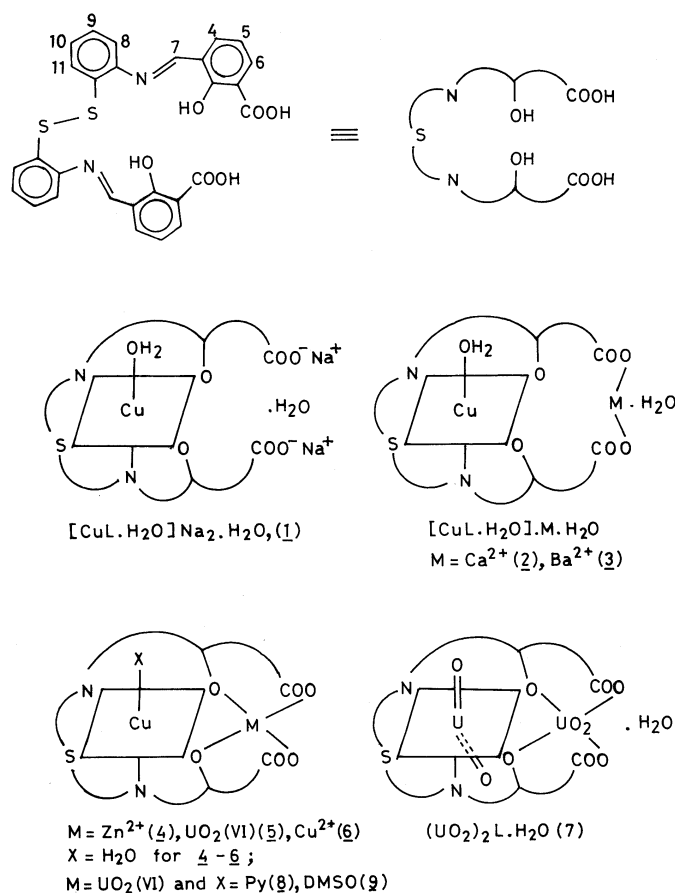
Scheme 1.

3.2 *Spectral studies*

IR spectrum of the ligand exhibits stretching at 1705 cm^{-1} corresponding to n(COOH). A broad vibration band at ≈ 3200 cm^{-1} is assigned to n(OH)[21] and n(C–O)(phenolic) is observed at 1510 cm^{-1}. The sharp intense band at 760 cm^{-1} is referred to n(C–S)[22] and the band at 1630 cm^{-1} is assigned to n(C=N). The ligand structure is established by ^{1}H-NMR data. The spectrum was taken in DMSO-d_6. The protons were assigned on the basis of spin–spin interaction and comparing with the previously reported results[19]. The singlet at the furthest downfield position is assigned to d(OH)(phenolic), 11·07 ppm followed by a signal at 9·70 ppm (singlet) for d(CH=N). Other protons are designated as follows: 4-H, 8·15d (8·5); 5-H, 7·12t (9·0); 6-H, 8·30d (8·5); 8-H, 7·43d (8·0); 9, 10-H, 7·20m and 11-H, 7·00d (8·0) ppm (d = doublet; t = triplet, m = multiplet, the coupling constant (J, Hz) is given in parentheses). The d(COOH) does not appear and may be due to proton exchange with very small amounts of moisture in DMSO-d_6.

The complexes (**1–7**) exhibit broad medium bands centred at 3440 cm^{-1} corresponding to coordinated water. Complex **1** exhibits medium intense bands at 1590

and 1360 cm^{-1} corresponding to $\boldsymbol{n}_{as}$(COO) and $\boldsymbol{n}_s$(COO). There is substantial change in the position of $\boldsymbol{n}_{as}$(COO) in other complexes; it is shifted to lower energies by 15–40 cm^{-1} from that of **1**, which is a diagnostic feature for the formation of dinuclear complexes[23]. Differences in anti-symmetric and symmetric –COO^{-1} vibrations ($\Delta\boldsymbol{n}$) are > 200 cm^{-1} in the complexes, indicating monodentate binding of the –COO function[23]. The $\boldsymbol{n}$(C=N) in the complexes appears at 1615–1620 cm^{-1} (table 2) and is red-shifted by 5–10 cm^{-1} from that of the free ligand value. This supports N-coordination to the metal centre[15,16]. The $\boldsymbol{n}$(C–S) mode of the ligand is shifted to higher energies by 30–50 cm^{-1} in the complexes indicating M-S linkage[15,19]. The $\boldsymbol{n}$(C–O) (phenolic) occur at 1540–1545 cm^{-1} in **1–3** and appear at higher frequencies compared to the free ligand value by 30–35 cm^{-1}. This is in agreement with the phenolato-O single-bonded to the metal ion. In the complexes **4–9**, the $\boldsymbol{n}$(C–O) (phenolic) appears at 1560–1580 cm^{-1} and is blue-shifted by 50–70 cm^{-1} from that of H$_4$L. On comparing with the literature report[24], we assume that the greater shifting of the infrared frequency of the $\boldsymbol{n}$(C–O) (phenolic), may be due to the phenolato-O bridging the two metal centres. These observations support the structure of the complexes as given in scheme 1. Uranyl complexes (**5, 7–9**) display a very strong band at 910–930 cm^{-1} corresponding to $\boldsymbol{n}$(O=U=O) modes. The force constant (f_{U-O}) for the U=O bond has been calculated according to the published method[25] and the values obtained (7·00–7·45 mdynes/Å) agree well with those of similar uranyl complexes[22]. The f_{U-O} value in each case was used to calculate the U=O bond length using Jones' formula[25] and the values obtained (1·72–1·73 Å) are in the expected range (1·69–1·92 Å)[22]. (UO$_2$)$_2$L·H$_2$O shows stretching at the highest frequency of 930 cm^{-1}, which may be due to the decreased tendency to transfer charge from the bridging oxygen to the uranium on co-ordination to the second metal ion[1–3]. In [Cu·DMSO](UO$_2$)L (**8**), $\boldsymbol{n}$(S=O) appears at 980 cm^{-1} supporting >S=O → UO$_2$ coordination[26].

Because of the sparing solubility of H$_4$L in common organic solvents, the solution electronic spectrum was taken in DMF solution. [Cu·H$_2$O]Na$_2$L·H$_2$O (**1**) is sufficiently soluble in DMF while other complexes remain sufficiently insoluble to measure solution electronic spectra and their diffused reflectance spectra were taken. The spectral data are

Table 2. Infrared^a, magnetic moment and ESR data.

Compound	IR data (cm^{-1})								ESR data	
	$\boldsymbol{n}$(H$_2$O)	$\boldsymbol{n}_{as}$(COO)	$\boldsymbol{n}$(C=N)	$\boldsymbol{n}$(C–S)	$\boldsymbol{n}$(C–O) (phenolic)	$\boldsymbol{n}$(UO$_2$)	$\boldsymbol{n}$(M-S)	$\boldsymbol{m}$(BM)	$g_{\parallel}$	$g_{\perp}$
H$_4$L^a	3200^b	1705	1630	760	1510					
1	3450	1590	1620	790	1545		325	1·84	2·26	2·10
2	3420	1575	1620	795	1540		320	1·85	2·24	2·08
3	3400	1575	1618	795	1540		325	1·86	2·22	2·10
4	3420	1568	1617	810	1570		325	1·75	2·20	2·08
5	3450	1555	1620	800	1565	920	330	1·80	2·20	2·10
6	3430	1550	1615	800	1580		335	0·80	e	e
7	3400	1555	1625	800	1565	930	330			
8	–	1560	1620	800	1570	910	325	1·72	2·19	2·08
9	–	1560	1620	800	1570	910	325	1·74	2·18	2·09

^{a} KBr disk; ^{b} $\boldsymbol{n}$(O–H); ^{c} polycrystalline state at 77 K; ^{d} $\boldsymbol{n}$(S=O), 980 cm^{-1}; ^{e} six-line ESR spectrum

collected in table 1. The solution of H_4L shows two successive transitions at 353 and 339 nm and refer to intraligand charge transfer transitions. Bluish-brown solution of **1** in DMF shows a broad band centred at 685 nm and a shoulder at 620 nm along with a weak band at 425 nm. The reflectance spectra of (**2–6**) exhibit broad absorption bands in the range 665-675 nm and weak bands at 470–490 nm. The former are assigned to *d–d* transitions and the latter to $S \rightarrow Cu(II)$ charge transitions[27]. All the complexes show strong transitions in the range 375–390 nm assigned to intraligand charge transitions.

3.3 *Magnetic studies*

Magnetic susceptibility measurements at 300 K exhibit 1e paramagnetic moment of mono-copper(II) derivatives **1–5**, **8**, **9**. The magnetic moments (1·7–1·8 BM) deviated slightly from the spin only values. The homo-dinuclear copper(II) complex, $Cu_2L \cdot H_2O$ (**6**) shows very low magnetic moment, 0·80 BM per copper centre. The subnormal magnetic moment indicates that the copper centres are strongly anti-ferromagnetically coupled[1–3,8–10,28–30]. This is not present in monocopper derivatives (**1–5**, **8**, **9**) and is obviously due to the absence of unpaired spin in the second metal ions of the complexes. The origin of high anti-ferromagnetic interaction in $Cu_2L \cdot H_2O$ (**6**) may be due to the presence of sulphur coordination[29]. $(UO_2)_2L \cdot H_2O$ (**7**) is diamagnetic as expected.

The ESR spectra of the complexes (except **7**) in polycrystalline state exhibit broad signals which are attributable to dipolar broadening and enhanced spin-lattice
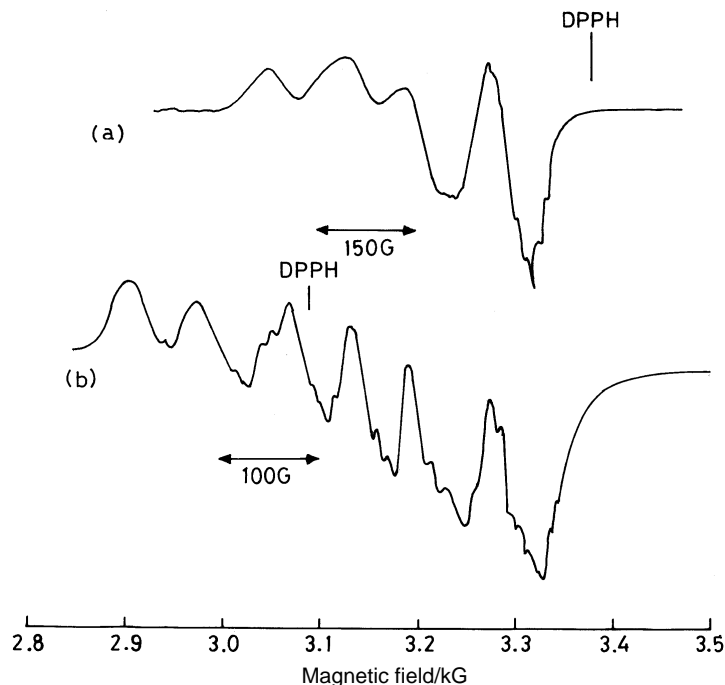

Figure 1. Solid-state ESR spectra of (**a**) [Cu]Na$_2$L·2H$_2$O, and (**b**) Cu$_2$L·H$_2$O at 77 K.

relaxation[31]. The anisotropic spectra are recorded for these complexes at liquid nitrogen temperature and the representative spectra are given in figure 1a. The spectra are anisotropic at high field and the three peaks of low intensity in the weaker field region are taken as originating from $g_\parallel$. $g_\parallel$ and $g_\perp$ are computed from the spectra using DPPH free radicals as g markers and these data are collected in table 2. The data reveal that $g_\parallel > g_\perp > 2 \cdot 0$ and $A_\parallel = 120 \times 10^{-4}$ cm^{-1}. This observation suggests a distorted octahedral geometry around Cu(II) centre[32]. The distortion may originate largely due to the thioether binding to the copper centre. This is supported by the strong preference of thioether to the copper ion when it is part of the ligand to form a five-membered chelate ring in which the other donors are N or O[33]. $Cu_2L \cdot 2H_2O$ (**6**) shows six-line X-band ESR spectrum at liquid nitrogen temperature in the polycrystalline state. The spectrum is shown in figure 1b. In principle, a seven-line $(2 \times (3/2) \times 2 + 1)$ hyperfine ESR spectrum is observable in an ideal dicopper system with one half $A_\parallel$ of the mononuclear species. This is also reflected from the observed data. $A_\parallel$ estimated from the spectrum is 75×10^{-4} cm^{-1}. Two copper centres in the complex appear in two different symmetry environments. The inner core copper centre appears in a distorted octahedral environment, $CuN_2SO_2(OH_2)$ and the outer core copper centre is in a square planar arrangement. It is difficult to assign the spectral region to a particular copper centre. We are able to detect additional weak ESR absorptions at ~ 1500 G near $g = 4$ for a spin coupled Cu(II)-dimer in **6** which is not observed in the case of monocopper derivatives. Superhyperfine structures are seen at higher fields. These fine structure transitions arise from the interaction of the nuclear spins of the nitrogen ligands ($I = 1$) of the C=N with the unpaired electron density on Cu(II). Five $(2 \times 2 \times 1 + 1)$ super-hyperfine transitions are observed as usual.

3.4 *Thermal studies*

A thermal study was carried out in air under non-isothermal conditions. The mass loss starts at 110°C, continues up to 150°C and corresponds to two moles of co-ordinated water in complexes **1–4** supporting our formulation, while complexes **5–7** exhibit the loss of one mole of H_2O. In the uranyl complexes $[Cu \cdot S](UO_2)L$ (S = Py, DMSO), (**8**, **9**), mass loss starts at high temperatures (200–260°C). All the complexes finally produce their oxides as residue on heating at 500–800°C, but their compositions have not been determined.

3.5 *Electrochemical studies*

Redox properties of monocopper(II) complexes were examined by cyclic voltammetry in DMF solution using glassy carbon milli-electrodes. The potentials are expressed with reference to SCE. Complexes exhibit $Cu^{II} \rightarrow Cu^{III}$ oxidation[34] and $Cu^{II} \rightarrow Cu^{I}$ reduction[34]. The potentials (V) are as follows: **1**, 0·20 (140), **2**, 0·23 (160), **3**, 0·27 (160), **4**, 0·33 (140), **5**, 0·49 (145), and the respective reduction potentials are: –0·612 (160), –0·803 (150), –0·854 (180), –0·868 (170) and –0·893 (170) (values in parentheses represent peak-to-peak separation, $\Delta E_p = E_{pa} - E_{pc}$). Thus, the redox processes are quasireversible in nature. Because of the insolubility of the dicopper complexes electrochemical activities could not be determined.

4. Conclusions

Condensation of 3-formylsalicylic acid and *bis*-(2-aminophenyl)disulphide has yielded a new type of septadentate compartmental Schiff base. It forms oxo-bridged binuclear complexes of inner N_2SO_2 and outer O_2O_2 coordination type. Hetero-dinuclear complexes with copper(II) at the inner compartment and calcium(II), barium(II), zinc(II), dioxouranium(VI) at the outer compartment are synthesised and characterized by IR, electronic/reflectance spectroscopy, ESR and magnetic moment measurements. These complexes exhibit $Cu^{II} \rightarrow Cu^{III}$ oxidation and $Cu^{II} \rightarrow Cu^{I}$ reduction reaction at cyclic voltammetric time scale. Homo-dinuclear complexes of copper(II) and dioxouranium(VI) are also synthesised and characterised by spectral and magnetic studies. The dicopper(II) complex shows antiferromagnetic coupling.

Acknowledgements

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