TABLE 1 — CHARACTERIZATION DATA OF Zn(II) COMPLEXES

Complex	Colour	m.p. (°C)	Zn (%)		S (%)	
			Found	Reqd	Found	Reqd
Zn(acac)₂L	White	170	19·20	19·24	9·61	9·43
Zn(bzac)₂L	Grey	198	14·41	14·09	7·04	6·91
Zn(bzbz)₂L	White	210	11·32	11·12	5·70	5·45

H.acac = acetyl acetone; H.bzac = benzoyl acetone; H.bzbz = dibenzoyl methane; L = thiourea.

The β-diketonates of Zn(II) exhibit ν(O—H) band ~3490 cm⁻¹ in the IR spectra (nujol) due to the presence of a coordinated water molecule. When the β-diketonates are reacted with thiourea, water molecule gets replaced by thiourea and this is shown in the IR spectra of the mixed complexes in which ν(O—H) band disappeared and a band due to ν(C—S) appeared ~710 cm⁻¹. In thiourea the ν(C—S) appears[6] 740 cm⁻¹. In the mixed complexes, this band is shifted to lower frequency (~710 cm⁻¹) indicating definite metal-sulphur bonding in the adducts. Further, the resonating ring system present in the β-diketonates gets disturbed by the introduction of thiourea ligand, in place of water molecule. This results in shifting of ν(C—C) and ν(C—O) after thiourea has been introduced. The ν(C—C) observed at 1600 cm⁻¹ in β-diketonates was shifted to a higher frequency (ranging between 1610 cm⁻¹ and 1620 cm⁻¹) in thiourea complexes. Hence, thiourea is definitely bonded to the zinc ion. The present complexes provide examples of penta-coordinated complexes of Zn(II) with sulphur as one of the donor atoms.

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Magnetic & Spectral Studies on Ni(II) & Cu(II) Complexes of N-(Salicylidene)phenylhydrazine

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Ni(II) and Cu(II) form 1:2 complexes with the Schiff base (LH) derived from salicylaldehyde and phenylhydrazine. The physico-chemical data indicate a square-planar stereochemistry for the Ni(II) complex and a tetrahedral stereochemistry for the Cu(II) complex. A pyridine adduct of the nickel complex, NiL₂Py₂ has also been isolated. The pyridine adduct is paramagnetic and octahedral.

N-(SALICYLIDENE)PHENYLHYDRAZINE (LH) has been recommended as a gravimetric reagent for transition metals[1]. However, complexes of this ligand have not been investigated so far. We report here the preparation of Ni(II) and Cu(II) complexes of SPH and their characterization on the basis of magnetic moment, conductance and electronic and IR spectral data. A pyridine adduct of the Ni(II) complex has also been prepared.

The chemicals employed were of reagent quality. The solvents were purified by standard methods[2].

Preparation of the complexes — The complexes were prepared by adding an aqueous solution of the metal chloride to an ethanolic solution of the Schiff base, LH, in an ammoniacal medium. The brown and the greenish-yellow precipitates obtained in the case of Cu(II) and Ni(II) respectively were filtered, washed with ethanol and ether and dried *in vacuo*.

The pyridine adduct of the Ni(II) complex was prepared by refluxing an ethanolic solution of the complex with pyridine. The orange-yellow crystals separated were washed with ether and dried *in vacuo*. The complexes were found to be insoluble in water, but soluble in almost all organic solvents.

Copper was estimated iodometrically after decomposing the complex with nitric acid, while nickel was estimated gravimetrically as dimethyl glyoximate.

The analytical data of the Cu(II) and Ni(II) complexes correspond to the compositions CuL₂ and NiL₂ while the pyridine adduct has the composition NiL₂Py₂.

The molar conductance values of less than unity for 10⁻³M solutions in nitrobenzene show the non-conducting nature of the complexes.

The IR spectrum (KBr) of the free ligand, which has three potential coordinating sites, exhibits a sharp medium intensity band at 3300 cm⁻¹ which can be assined to νN-H. In the spectra of the complexes, this band does not show any shift indicating that coordination does not occur through the N-H group. A broad medium-intensity band observed around 2900 cm⁻¹ in the ligand due to hydrogen bonded —OH disappears on complexation showing that hydrogen of the OH group is replaced by the metal ion. A medium intensity band at 1530 cm⁻¹ assigned to νC=N of a conjugated ring system[3] in the ligand is shifted to 1540 cm⁻¹ in its complexes showing that nitrogen of the C=N group is involved in complexation. Thus, the IR data indicate that the potentially tridentate ligand acts only as a monovalent bidentate ligand making use of the oxygen of the —OH group and nitrogen of the azomethine group in coordination.

The electronic spectrum of the Cu(II) complex (recorded in mull) in the solid state does not show any absorption in the range 600-700 nm which excludes the possibility of a square or distorted octahedral geometry for this complex[4]. Keeping in view the steric factors operating in the ligand, the complex is likely to have a tetrahedral geometry[5,6]. A band observed at 360 nm can be assigned to an electronic transition associated with the ligand. The Cu(II) complex shows a magnetic moment value of 1·74 B.M.

The electronic spectrum of the Ni(II) complex shows a band at 610 nm which is usually observed for square-planar Ni(II) complexes[7,8]. The spectrum shows another band at 440 nm which may also be assigned to one of the d-d transitions expected for square-planar Ni(II). The complex is diamagnetic which conforms to the square-planar geometry of the compound. The pyridine adduct, however, is paramagnetic and its effective magnetic moment (3·17 B.M.) is typical of an octahedral Ni(II) complex[9]. Attempts to prepare similar pyridine adduct with Cu(II) complex were unsuccessful.

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IN continuation of our earlier work[1-5] the polarographic behaviour of organo-sulphur compounds and their complexes with metals[1-5], in this note is reported the results of investigation on the behaviour of $UO_2(II)$ and Th(IV) ions in the presence of ethane-1, 2-dithiol for which there is no reference in the literature.

Ethane-1,2-dithiol (referred herein as EDT) and other chemicals used were of Analar (BDH) grade. A manual polarograph with scalamp galvanometer and SCE as reference electrode was used for recording the polarograms. The capillary had the following characteristics in 25% ethanol, $0·1M$ $NaClO_4$ at $-0·5$ V vs SCE with h_{Hg} value of 40 cm: $m=2·895$ mg/sec, $t=2·39$ sec.

The effects of change in Hg-pressure, temperature and concentration of metal ions on the waves due to UO_2^{2+} and Th^{4+} were investigated. The values of kinetic parameters were determined from the polarograms of the solutions containing 1·0 mM UO_2^{2+} or 0·1 mM $Th^{4+}+0·1M$ $NaClO_4+0·002\%$ Triton X-100 $+25\%$ ethanol+different amounts of EDT. The current was recorded at the end of the drop life instead of average current as the determination of kinetic parameters is based on Koutecky's method which are accurately reproduced by measuring the maximum current[6].

The conventional log plots of the reduction waves for UO_2^{2+} and Th^{4+} in ethane-1,2-dithiol were linear and their slope values indicated the irreversible nature of the waves for both the systems.

The constancy of $I_d/h_{eff}^{\frac{1}{2}}$ in each case and the values of temperature coefficients of 1·138% (for UO_2^{2+}-EDT) and 1·838% (for Th^{4+}-EDT) indicate the diffusion controlled nature of the waves. The plots of i_d vs temperature and $h_{eff}^{\frac{1}{2}}$ are shown in Fig. 1. The limiting current increases linearly with increase in [metal ion]. With increase in EDT the $E_{\frac{1}{2}}$ shifts towards more negative potential showing the complex formation between metal ions and ligand, whereas i_d increases for UO_2^{2+} and decreases for Th^{4+} indicating that the aquo-uranyl and aquo-thorium ions differ in size from their complexes of EDT.

Since the reduction of UO_2^{2+} and Th^{4+} ions in the presence of EDT is irreversible, it is considered expedient to determine the values of transfer coeffi-

Polarographic Behaviour of UO₂(II) & Th(IV) in Ethane-1,2-dithiol

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UO_2^{2+} and Th^{4+} ions in ethane-1,2-dithiol give irreversible and diffusion-controlled waves in the presence of $0·1M$ $NaClO_4$, $0·002\%$ Triton X-100 and 25% ethanolic media. The values of kinetic parameters, viz. transfer coefficient (α), formal rate constant ($K_{f,h}^0$) for the electrode reactions have been determined by Koutecky's method as extended by Meites and Israel. The values of ΔH, ΔG and ΔS have also been calculated.
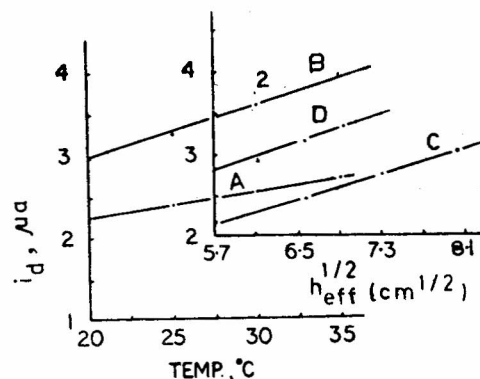
Fig. 1 — Plots of i_d versus temperature (curves A and B) and plots of i_d versus $h_{eff}^{1/2}$ (curves C and D) for the systems UO_2^{2+}-EDT (curves A and C) and Th^{4+}-EDT (curves B and D)