

TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES*

Complex	Colour	Analysis (%), Found (calc.)		log k_1	log k_2	log K	$\mu_{eff.}$ (BM)
		Metal	N				
[Cu(C ₄ H ₄ O ₂ N) ₂ (H ₂ O) ₂]	Blue	21.25 (21.49)	9.29 (9.47)	3.68	2.76	6.44	1.81
[Ni(C ₄ H ₄ O ₂ N)(OH)(H ₂ O) ₄]	Green	24.00 (23.89)	5.52 (5.69)	3.00	—	3.30	3.10
[Co(C ₄ H ₄ O ₂ N) ₂ (H ₂ O) ₂]	Blue	20.10 (20.25)	9.53 (9.62)	3.17	3.11	6.28	4.30
[Fe(C ₄ H ₄ O ₂ N)(OH)(H ₂ O) ₄]	Pale green	23.10 (22.99)	5.58 (5.76)	3.10	—	5.60	5.20
[Hg(C ₄ H ₄ O ₂ N)(OH)]	White	63.99 (63.56)	4.29 (4.43)	6.88	—	6.88	—

*Satisfactory C and H analyses were obtained.

ethanol and dried *in vacuo*. The ferrous complex slowly changed to the ferric complex in air. Hence the preparation was carried out under N₂ atmosphere. The Fe(II) complex is stable for 4 hr after drying. Analysis for the metal, C, H and N are given in Table 1.

Stability constants (Table 1) were determined by Bjerrum's³ *pH*-metric method. Solutions of succinimide (40 ml, 0.0125M) with and without metal ion (5.0 ml, 0.01M) were titrated against KOH (0.075M) at 20° ± 1°. The ionic strength (μ) was maintained constant at 0.1M with KCl, KNO₃, K₂SO₄ and NaClO₄ in the case of Cu(II), Co(II), Fe(II), Ni(II) and Hg(II) complexes respectively. The accuracy of log K values (concentration constants) reported is ± 0.02.

The data in Table 1 indicate that Ni(II), Hg(II) and Fe(II) form 1:1 complexes while Cu(II) and Co(II) form 1:2 complexes. The presence of polynuclear species can be neglected since the formation curves (\bar{n} vs *pA*), determined from the ligand-metal ratio of 5:1 and 6:1 are identical. For Fe(II)-succinimide complex, \bar{n} values beyond 0.5 could not be obtained due to the onset of hydrolysis⁴. The titrations were carried out in nitrogen atmosphere using freshly prepared FeSO₄·7H₂O solution. The error in log K value was of the order of ± 0.1 log units.

The compositions of the complexes were further confirmed by conductometric titration and chemical analysis. *pK* values as determined by potentiometric titration of 40 ml succinimide (0.025M) against 0.084M KOH were found to be 9.45, 9.70, 9.55 and 9.30 in KCl, KNO₃, K₂SO₄ and NaClO₄ medium ($\mu=0.1M$) respectively.

Chemical analysis of the solid complexes is in accordance with the formulae assigned to them. Their magnetic moment values are given in Table 1. While Hg(II) complex is diamagnetic, Cu(II), Ni(II), Co(II) and Fe(II) complexes are shown to contain 1, 2, 3 and 4 unpaired electrons respectively. The complexes are nonelectrolytes in nitrobenzene. Apart from other bands, their IR spectra show bands at 1030 and 600 cm⁻¹ which may be assigned to coordinated hydroxo groups.

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Reaction of Bis- β -diketonates of Zn(II) with Thiourea

B. PRADHAN & D. V. RAMANA RAO

Department of Chemistry, Regional Engineering College Rourkela 8

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The mixed ligand complexes of Zn(II) of the type Zn(β -dik)₂L (where L = thiourea and β -dik = acetylacetonate, benzoylacetonate or dibenzoylmethane) have been prepared as examples of 5-coordinated complexes of Zn(II) with a sulphur donor ligand. The compounds have been characterized on the basis of magnetic, conductance and spectral data.

THE best examples of 5-coordination for Zn²⁺, which has a completely filled 3*d* non-bonding shell and which usually forms four coordinated tetrahedral compounds, are found among the β -diketonate complexes having the formula Zn(β -dik)₂H₂O. A wide variety of base adducts of the type Zn(β -dik)₂L have been reported where L is a nitrogen donor ligand¹⁻⁴. In this note, some penta-coordinated mixed ligand complexes of Zn(II) containing β -diketonates and a sulphur donor ligand like thiourea are reported.

All the chemicals used were of Analar grade. Bis-acetylacetonato, benzoylacetonato and dibenzoylmethanato Zinc(II) compounds are prepared by the literature methods. Ethanolic solution of these compounds and thiourea in stoichiometric ratio of 1:1 were refluxed for 3-4 hr. On cooling, white micro-crystalline compounds which separated out were filtered, washed with absolute ethanol followed by ether and dried *in vacuo*.

Zn(II) in the mixed complexes was estimated as ZnNH₄PO₄ and sulphur as BaSO₄ after oxidizing⁵ with bromine in carbon tetrachloride solution. The conductance measurements were carried out in M/1000 nitrobenzene solutions using a Toshniwal conductivity bridge. Magnetic susceptibilities of solid samples were determined at room temperature using the Guoy method. Characterization data of the complexes are given in Table 1.

The complexes have the composition [Zn(β -dik)₂L] and are soluble in nitrobenzene and have low values of molar conductances (<1.0 mhos) indicating the nonelectrolytic nature of the complexes. These are diamagnetic as expected for Zn(II) ion with a completely filled 3*d* shell.

TABLE 1 — CHARACTERIZATION DATA OF Zn(II) COMPLEXES

Complex	Colour	m.p. (°C)	Zn (%)		S (%)	
			Found	Reqd	Found	Reqd
Zn(acac) ₂ L	White	170	19.20	19.24	9.61	9.43
Zn(bzac) ₂ L	Grey	198	14.41	14.09	7.04	6.91
Zn(bzbz) ₂ L	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 $\nu(\text{O-H})$ band $\sim 3490 \text{ cm}^{-1}$ 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 $\nu(\text{O-H})$ band disappeared and a band due to $\nu(\text{C-S})$ appeared $\sim 710 \text{ cm}^{-1}$. In thiourea the $\nu(\text{C-S})$ appears⁶ 740 cm^{-1} . In the mixed complexes, this band is shifted to lower frequency ($\sim 710 \text{ cm}^{-1}$) 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 $\nu(\text{C-C})$ and $\nu(\text{C-O})$ after thiourea has been introduced. The $\nu(\text{C-C})$ 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

A. N. SUNDER RAM & C. P. PRABHAKARAN
Department of Chemistry, University of Kerala
Trivandrum 695001

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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, NiL_2Py_2 has also been isolated. The pyridine adduct is paramagnetic and octahedral.

N-(SALICYLIDENE)PHENYLHYDRAZINE (LH) has been recommended as a gravimetric reagent for transition metals¹. 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 methods².

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 CuL_2 and NiL_2 while the pyridine adduct has the composition NiL_2Py_2 .

The molar conductance values of less than unity for $10^{-3}M$ 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 assigned to $\nu\text{N-H}$. 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 $-\text{OH}$ 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 $\nu\text{C=N}$ of a conjugated ring system³ 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 $-\text{OH}$ group and nitrogen of the azomethine group in coordination.