

TABLE 1 — pK_{BH^+} OF MESOIONIC THIONES IN 50% *v/v* AQ. METHANOL AT 25°

Compd	λ_{max} (nm)	$10^6 k_{obs}$ sec ⁻¹	$10^6 k'_2$ mole ⁻¹ sec ⁻¹	pK_{BH^+}
I	390	4.336	5.868	-2.02
II (R=Me)	355	7.997	10.820	-1.70
II (R= <i>n</i> -Pr)	355	10.660	14.420	-1.52
II (R= <i>n</i> -Bu)	355	9.594	12.980	(-1.58)†
III	375	4.498	6.087	-2.00
IV	340	15.350	20.770	(-1.92)†
V (R=Me)	300	1322	1789	-1.15
V (R= <i>p</i> -MePh)	310	1322	1789	-1.15
VI†	390	45.06	609.8	0.60

†Values obtained by direct determination as per ref. 1.

The pK_{BH^+} values of mesoionic thiones, viz. 1,3,4-thiadiazolo[3,2-*a*]quinolinium-5-thione³ (I), 1-alkyl-1,3,4-triazolo[3,2-*a*]quinolinium-5-thione³ (II, alkyl = Me, *n*-Pr and *n*-Bu), 1,3,4-thiadiazolo[2,3-*a*]isoquinolinium-5-thione³ (III), 1-*n*-Bu-1,3,4-triazolo[2,3-*a*]isoquinolinium-5-thione³ (IV) and 1-substituted 3-methyl-2,4-diphenylimidazolium-5-thione⁴ (V, R = Me and *p*-Me Ph) presented in Table 1 lead to the following conclusions:

(i) Calculated rate constants (k'_2) cover a significantly wide range as expected² for compounds of diverse structural type, and this difference is also adequately reflected in the estimated pK_{BH^+} values from Eq. 1. This is also in accord with observed slope (= 0.7745), and confirms the usefulness of our findings.

(ii) Tricyclic systems (I, II, III and IV), as anticipated, are weaker bases than the monocyclic imidazoles (V) indicating appreciable intranuclear conjugation in I to IV. Stronger basicity of imidazole derivatives is a well-known fact.

(iii) Compounds I and III are isomeric, but the effect of position of sulphur (*endo*) on their pK_{BH^+} values is only marginal. The insertion of =NR fragment *in lieu* of the *endo*-S generally raises the pK_{BH^+} values, and the difference is conspicuous in the case of II. Similar trend in other mesoionic systems has been recorded earlier by us².

(iv) In support of our estimated pK_{BH^+} values derived from Eq. 1, these were directly determined for II (R=*n*-Pr) and III on account of better stabilities of the tricyclic systems under the experimental condition. Agreement between the two sets (Table 1) is indeed quite satisfactory, and the observed difference falls within the estimated standard deviation (± 0.108) justifying the utility of Eq. 1.

The mesoionic compounds (I-V) used were prepared by the literature method^{3,4}.

The dried samples were stored in the desiccator prior to their use. Imidazoles (V) tend to decompose slowly on storage at room temperature and freshly made samples were used for our work. Other reagents, viz. methanol, KCl, chloroacetic acid, H₂SO₄, NaOH, etc., were of AR grade. All spectrophotometric measurements were made with either Hilger UVspec or recording spectrophotometer in 1 cm quartz cells. *pH* measurements were made on a Philips *pH* meter, model PR9405L.

Kinetic runs — Rate measurements were carried out spectrophotometrically under *pseudo* first order conditions at appropriate wavelength (Table 1) determined previously by separate experiments in aq. methanol (50% *v/v*). In all cases the rate constants (k_{obs}) were obtained from duplicate runs in methanol-buffer (chloroacetate) mixtures (at *pH* = 3.40, temp. = 30° and μ = 0.1M) where the [chloroacetic acid] varied from 10² to 10³ moles litre⁻¹ over the [substrate]. Values of k'_2 were derived by dividing k_{obs} with the total molar concentration of the buffer in the reaction medium. Other experimental details and calculations were the same as before¹.

Determination of pK_{BH^+} — Experimental details for pK_{BH^+} determination have been reported earlier². pK_{BH^+} (25°C) values obtained for the two stable systems in 50% *v/v* aq. methanol determined at 355 nm (II, R = *n*-Pr, isosbestic point, 325 ± 2 nm) and at 375 nm (III, isosbestic point 340 ± 2 nm) are also recorded in Table 1.

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Succinimide Complexes of Cu(II), Ni(II), Co(II), Fe(II) & Hg(II)

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Stability constants of succinimide complexes of Fe(II), Co(II), Ni(II), Cu(II) and Hg(II) have been determined and are found to be 3.10, 6.28, 3.30, 6.44 and 6.88 respectively. The solid complexes are non-electrolytes in nitrobenzene and show IR bands due to coordinated hydroxo groups.

METAL-LIGAND stability constants of Cu(II), Ni(II), Co(II), Fe(II) and Hg(II) complexes with succinimide have been determined in aqueous medium using Bjerrum's *pH* titration technique.

Succinimide (BDH) was recrystallized from ethanol. CuCl₂·2H₂O; NiSO₄·6H₂O; Co(NO₃)₂·6H₂O; FeSO₄·7H₂O and HgCl₂ were of AR grade. Carbonate-free KOH was prepared by the method of Davies and Nancollas¹. All the solutions were prepared in doubly distilled water. Physical measurements were carried out as described earlier².

The solid 1:1 and 1:2 metal complexes were prepared by mixing the reactants containing a little excess of succinimide over the calculated amount and adjusting the *pH* to 8.5, 5.8, 7.0, 9.0 and 8.5 in the case of Ni(II), Hg(II), Fe(II), Cu(II) and Co(II) complexes respectively by the addition of KOH. The resulting solutions were heated to ≈ 40° and ethanol added until the precipitates were formed. The precipitates were filtered, washed with 50%

TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES*

Complex	Colour	Analysis (%), Found (calc.)		log k_1	log k_2	log K	μ_{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 hydrolysis.⁴ 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

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The mixed ligand complexes of Zn(II) of the type Zn(β -dik)₂L (where L = thiourea and β -dik = acetylacetonone, benzoylacetone 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 3d 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 -diketones and a sulphur donor ligand like thiourea are reported.

All the chemicals used were of Analar grade. Bis-acetylacetonato, benzoylacetone 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 3d shell.