

TABLE 1 — RATE CONSTANTS (k_{obs}) AT DIFFERENT [AMIDE] AND TEMPERATURES IN THE HYDROLYSIS OF ACETAMIDE

[Amide] M		(HCl conc. = 0.1 M)	
	$10^4 k_{\text{obs}}$ sec ⁻¹	[Amide] M	$10^4 k_{\text{obs}}$ sec ⁻¹
TEMP. 55°		TEMP. 60°	
1.0	1.73	3.0	5.18
2.0	2.69	4.0	6.14
4.0	3.84	6.0	6.90
5.00	4.61		
TEMP. 60°		TEMP. 65°	
0.80	2.23	1.0	4.42
1.0	2.57	2.0	7.96
1.5	3.46	3.0	9.60
2.0	4.22	4.0	11.5
2.5	4.99	5.0	12.3

agreement with the values cited² for lower $[H^+]$. The rate law (3) thus provides a strong kinetic evidence for the rapid protonation pre-equilibrium in the hydrolysis of acetamide.

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Nitration of Some Mixed Ligand Cu(II) Complexes of Acetylacetone, Benzoylacetone, Dibenzoylmethane & Schiff Bases

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Nitration of the coordinated ligands in the complexes of the type $[CuLL']$ where L = salicylaldehyde or 2-hydroxyacetophenone or 2-hydroxy-3-methylacetophenone and L' = acetylacetone or benzoylacetone or dibenzoylmethane have been carried out. Trinitro compounds have been obtained in all the cases, except in the case of 3-methyl derivative of acetophenone where a dinitro compound is obtained. The substitution products have been characterized by elemental analysis, magnetic moments, conductance measurements and IR spectral studies.

THE β -diketonates of metal ions are reported¹⁻⁹ to undergo electrophilic substitution reactions. Tetra-substituted compounds have been obtained with divalent metal complexes of salicylaldehyde under electrophilic substitution reaction condition¹⁰. We have earlier reported¹¹ the nitration of mixed ligand imine complexes $[CuLL']$ where L'H = salicylaldehyde, L'H = 2-hydroxyacetophenone or 2-hydroxy-3-methylacetophenone.

In the present study nitration reactions have been carried out on Cu(II) mixed ligand imine complexes of the type $[CuLL']$ where LH = salicylaldehyde or 2-hydroxyacetophenone or 2-hydroxy-3-methylacetophenone and L'H = acetylacetone (acac) or benzoylacetone (bzac) or dibenzoylmethane (dbm).

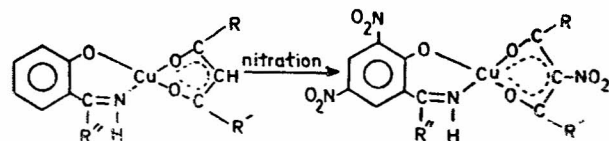
The reagent used were of AR grade. The mixed ligand imine complexes were prepared as described in a previous publication¹².

Nitration of imine complexes — Mixed ligand imine complex (0.0016 mole) and acetic anhydride (10 ml) were taken and cooled, and to this was added powdered $Cu(NO_3)_2 \cdot 3H_2O$ (0.0024 mole) in small portions with stirring during 30 min under ice-bath cooling. The ice-bath was removed after 5-6 hr. In the cases of bzac, dbm and 2-hydroxy-3-methylacetophenone mixed complexes, a longer time period was allowed for stirring at $\sim 0^\circ$. The resulting green-coloured slurry was decomposed by pouring into ice-cold water (100 ml) containing sufficient amount of sodium acetate and stirring for 1 hr. The precipitate obtained was filtered under suction, washed with water and finally with ethanol. The compounds were analysed for metal and nitrogen contents. The characterization data² of the mixed ligand complexes are given in Table 1.

As the complexes under study are unstable in the presence of nitric acid, a mild nitrating agent, acetyl nitrate¹⁰ prepared *in situ* was employed. Nitronium ions produced from this reagent act as electrophile to form the resonance stabilized σ -complex intermediates.

In the present mixed ligand complexes (I) the substitution of a nitro group leads to a trinitro compound (II).

In the β -diketone moiety only one group can enter as the hydrogen atom on the γ -carbon atom is labile and susceptible to electrophilic substitutions. On the other hand the nitrosubstitution can take place at 3- and 5-positions on the salicylideneimine moiety. Positions 4 and 6 in the benzene ring of aldehyde or acetophenone are not attacked by the electrophile as that would tend to place a positive charge at a carbon adjacent to an atom already carrying a positive charge in the σ -complex intermediate creating an energetically unfavourable situation.



(i) $R = CH_3$ (ii) $R = CH_3$; $R' = C_6H_5$ (iii) $R = R' = C_6H_5$ (iv) $R'' = H$ or CH_3

TABLE 1 — ANALYTICAL DATA AND MAGNETIC MOMENTS OF NITRATED MIXED IMINE SCHIFF BASE COMPLEXES OF Cu(II)

Complex	Calc. (%)		Found (%)*		μ_{eff} B.M.
	Cu	N	Cu	N	
(3,5-Dinitrosalicylaldimino-3-nitroacetylacetonato)Cu(II)	15.23	13.42	15.01	13.44	1.86
(3,5-Dinitrosalicylaldimino-3-nitrobenzoylacetonato)Cu(II)	13.25	11.68	13.43	11.74	1.82
(3,5-Dinitrosalicylaldimino-3-nitrodibenzoylmethanato)Cu(II)	11.73	10.34	11.53	10.68	1.89
[(2-Hydroxy-3,5-dinitroacetophenonimino-3-nitroacetylacetonato)Cu(II)]	14.72	12.98	14.92	12.88	1.93
[(2-Hydroxy-5-nitroacetophenonimino-3-nitroacetylacetonato)Cu(II)]	15.95	7.03	15.73	7.24	1.91

*Satisfactory C, H analyses have been obtained for all the compounds.

In the mixed complexes containing bzac and dbm, the electrophilic substitution in the phenyl ring is not favoured⁸. In general the nitration reaction on acac is faster than on bzac or dbm⁸. Though there is an increase in electron density at reaction site in the phenyl ring due to $-M$ effect, the steric effects of coplanar phenyl rings at *ortho* position to reaction site retards the rate of reaction.

TLC analysis shows the compounds to be pure. The chloroform solutions of the compounds are non-conducting indicating non-electrolytic nature. The complexes are paramagnetic having magnetic moment corresponding to one unpaired electron.

In the IR spectra of the compounds bands in the region $\sim 3400 \text{ cm}^{-1}$ are absent showing that water is absent in these compounds. The nitrated compounds show a band at $\sim 1510 \text{ cm}^{-1}$ corresponding to asymmetric νNO_2 , while that at $\sim 1330 \text{ cm}^{-1}$ corresponds to symmetric νNO_2 . The disappearance of the C-H in-plane bending vibrations at $\sim 1340 \text{ cm}^{-1}$ and appearance of NO_2 stretching vibration bands at $\sim 1550 \text{ cm}^{-1}$ at the same time provides strong evidence for the NO_2 group entering each chelate ring.

The solubility of the nitrated compounds is very low in all the solvents and hence absorption spectra could not be obtained.

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Ligating Properties of Tertiary Phosphine/Arsine Sulphides or Selenides: Part III—Complexes of Ditertiary Phosphine Disulphides & Diselenides with Mercury(II) Halides

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Mercury(II) halide adducts of ditertiary phosphine disulphide and diselenide of the types $\text{HgX}_2(\text{L-L})$, $\text{Hg}_2\text{X}_4(\text{L-L})$, $\text{Hg}_2\text{X}_6(\text{L-L})_2$ and $\text{Hg}_4\text{X}_8(\text{L-L})_3$ [where $\text{X}=\text{Cl, Br or I}$ and $\text{L-L}=1,2\text{-ethylenebis(diphenylphosphine sulphide or selenide)}$ (EDPS or EDPSe); $1,3\text{-propylenebis(diphenylphosphine sulphide or selenide)}$ (PDPS or PDPSe); $1,4\text{-butylenebis(diphenylphosphine sulphide or selenide)}$ (BDPS or BDPSe) and $1,6\text{-hexamethylenebis(diphenylphosphine sulphide)}$ (HDPS)] have been prepared. The adducts have been characterized on the basis of elemental analyses, infrared spectra and molar conductance data.

DONOR properties of a few tertiary phosphine sulphides and selenides towards mercury(II) halides have been reported in literature¹⁻⁹. In the present note, the preparation and characterization of adducts of some ditertiary phosphine disulphides and diselenides with mercury(II) halides are being reported. The adducts have 1:1, 2:1, 3:2 and 4:3 (metal-ligand) stoichiometries.

The ligands, 1,2-ethylenebis(diphenylphosphine sulphide or selenide) (EDPS or EDPSe), 1,3-propylenebis(diphenylphosphine sulphide or selenide) (PDPS or PDPSe), 1,4-butylenebis(diphenylphosphine sulphide or selenide) (BDPS or BDPSe) and 1,6-hexamethylenebis(diphenylphosphine sulphide) (HDPS), were prepared by the methods reported in literature^{7,10}. The analytical data have already been reported¹¹.

The adducts of mercury(II) halides were prepared by adding a solution of the ligand in a suitable solvent to a solution or suspension of the mercury(II) halide in methanol, ethanol or benzene. The white solids obtained either on mixing or refluxing of the mixture were filtered and washed well with suitable solvents and dried *in vacuo*.