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A CONVENIENT METHOD FOR THE PREPARATION OF α -ARYLAMINO PHENYL ACETIC ACIDS

McKENZIE and coworkers¹ prepared α -phenylamino phenyl acetic acid by condensing α -halophenyl acetic acid with aniline. We have prepared α -arylamino phenyl acetic acid of the type $C_6H_5 \cdot CH(R)COOH$ where R = phenylamino; *o*-, *m*- and *p*-tolylamino *o*- and *p*-anisylamino; *m*- and *p*-chlorophenyl amino; *p*-bromo and *p*-iodophenyl amino, etc. They have been prepared by hydrolysing α -arylamino phenyl acetonitriles, first by treating with concentrated H_2SO_4 as a result of which amide formation takes place which then gets hydrolysed by aqueous sodium hydroxide solution (10%) to the corresponding acids. This method is found to be convenient and the yield of the products is also very good.

Experimental

(a) Preparation of α -arylamino phenyl acetonitriles

They have been prepared by the method suggested by Sandhu and coworkers². The different substituents R, % yields and the m.p. in $^{\circ}C$ are as follows:

Aryl, 85, 90 $^{\circ}$; *o*-tolyl, 79, 75 $^{\circ}$; *m*-tolyl, 82, 95 $^{\circ}$; *p*-tolyl, 80, 110 $^{\circ}$; *o*-anisyl, 85, 68 $^{\circ}$; *p*-anisyl, 86, 80 $^{\circ}$; *m*-chloro phenyl, 80, 78 $^{\circ}$; *p*-chloro phenyl, 78, 70 $^{\circ}$; *p*-bromo phenyl, 76, 100 $^{\circ}$; *p*-iodophenyl, 60, 75 $^{\circ}$. All compounds gave correct N-analysis.

(b) Preparation of α -arylamino phenyl acetamide

α -Phenylamino phenyl acetonitrile (0.025 mole) was dissolved in concentrated sulphuric acid (10 ml)

below 10 $^{\circ}$ and kept for 48 hours at room temperature. Contents were then poured into ice-water and filtered. The filtrate was made alkaline by aqueous sodium hydroxide solution. The product obtained was crystallised from alcohol.

Different substituents R, % yield and the m.p. in $^{\circ}C$ are as follows:

Aryl, 75, 120 $^{\circ}$; *o*-tolyl 63, 110 $^{\circ}$; *m*-tolyl, 60, 100 $^{\circ}$; *p*-tolyl, 65, 129 $^{\circ}$; *o*-anisyl, 72, 165 $^{\circ}$; *p*-anisyl, 74, 105 $^{\circ}$; *m*-chloro phenyl, 62, 103 $^{\circ}$; *p*-chloro phenyl, 58, 146 $^{\circ}$; *p*-bromo phenyl, 70, 174 $^{\circ}$; *p*-iodophenyl, 74, 172 $^{\circ}$.

All compounds gave correct N-analysis.

(c) Preparation of arylamino phenyl acetic acid

α -Arylamino phenyl acetamide (0.025 mole) was mixed with aqueous sodium hydroxide solution (10%) and refluxed for 4 hours. It was diluted with ice-water and filtered. The filtrate was then acidified with concentrated hydrochloric acid. The product obtained was crystallised from alcohol.

Different substituents R, % yield and the m.p. in $^{\circ}C$ are as follows:

Aryl, 55, 179 $^{\circ}$ (Reported 175 $^{\circ}$); *o*-tolyl, 50, 149 $^{\circ}$; *m*-tolyl, 53, 145 $^{\circ}$; *p*-tolyl, 51, 164 $^{\circ}$; *o*-anisyl 49, 280 $^{\circ}$ (d); *p*-anisyl, 51, 173 $^{\circ}$; *m*-chloro phenyl, 48, 147 $^{\circ}$; *p*-chloro phenyl, 45, 175 $^{\circ}$; *p*-bromo phenyl, 46, 171 $^{\circ}$; *p*-iodophenyl, 42, 160 $^{\circ}$.

All compounds gave correct N-analysis.

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MIXED LIGAND COMPLEXES OF COBALT (III) CONTAINING N, N'-TETRAMETHYLENEBIS (SALICYLIDENEIMINE) AND BIDENTATE LIGANDS

IN recent years there has been considerable interest on the transition metal complexes of quadridentate Schiff bases I¹⁻⁴. As the number of the carbon atoms in the methylene bridge increases from $n = 2$ to $n = 3$ or 4 the stereochemistry of the metal (II) complexes [where M = Co (II) and Cu (II)] changes from square planar to tetrahedral⁵⁻⁷. We have recently reported the synthesis and characterisation of cobalt (III) complexes of salt⁸, where saltⁿ = N, N'-trimethylenebis (salicylideneimine). In this preliminary communication we report the syntheses of several new cobalt (III) mixed ligand complexes of saltⁿ and

bidentate ligands like acetylacetonate, acetoacetanilide, tropolone, *N*-benzoylphenylhydroxylamine and picolinic acid. The complexes have been characterised

mixture of chloroform and ethanol. The analytical and electronic spectral data of the complexes are given in Table I.

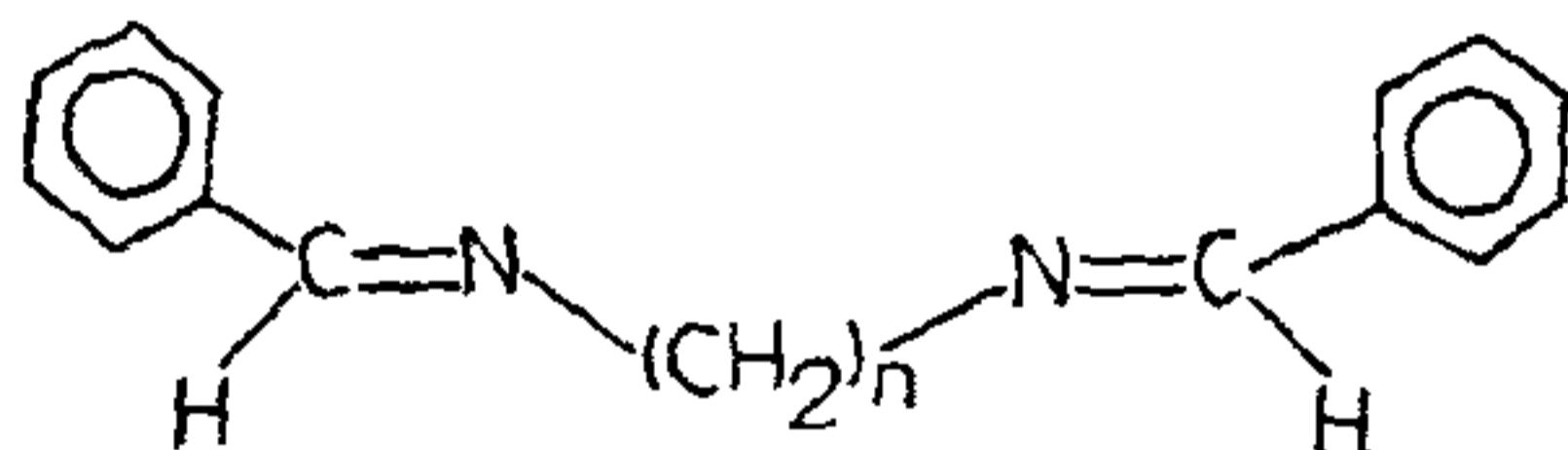
TABLE I
Analytical and electronic spectral data of mixed ligand cobalt (III) complexes^{a, b}

Complex	% Co	% N	Band I cm ⁻¹	Band II cm ⁻¹	Band III cm ⁻¹
[Co (acac) (salbn)] Co C ₂₃ H ₂₅ O ₄ N ₂	Found: 12.6 Reqd.: 13.05	6.3 6.19	16,840 (2.65)	25,640 (3.90)	38,830 (4.86)
[Co (acan) (salbn)] Co C ₂₈ H ₂₈ O ₄ N ₂	Found: 11.1 Reqd.: 11.15	7.7 7.94	16,670 (2.51)	25,840 (3.88)	39,220 (4.82)
[Co (tropolone) (salbn)] Co C ₂₃ H ₁₃ O ₄ N ₂	Found: 12.5 Reqd.: 12.45	5.8 5.91	16,840 (2.57)	25,970 (4.12)	39,530 (4.88)
[Co (BPHA) (salbn)] Co C ₃₁ H ₂₈ O ₄ N ₂	Found: 10.0 Reqd.: 10.44	7.6 7.43	17,030 (2.46)	25,910 (3.78)	38,760 (4.70)
[Co (pic) (salbn)] Co C ₂₃ H ₂₂ O ₄ N ₂	Found: 12.8 Reqd.: 12.42	9.2 8.84	17,010 (2.66)	25,840 (3.81)	38,020 (4.71)

^a Abbreviations: acac = deprotonated anion of acetylacetonate; acan = deprotonated anion of acetoacetanilide; BPHA = deprotonated anion of *N*-benzoylphenylhydroxylamine and pic = deprotonated anion of picolinic acid.

^b Figures in the parentheses indicate log ϵ .

by elemental analysis, electronic spectra, conductance and magnetic measurements.



- I. $n=2$, salen
 $n=3$, saltn
 $n=4$, salbn

Co (salbn), where salbn = N, N'-tetramethylenebis (salicylideneimine), was prepared according to the method of Hariharan and Urbach⁵. [Co (salbn)]₂O₂ was prepared by following a similar procedure as described⁹ for the synthesis of [Co (salen)]₂O₂, where salen, = N, N'-ethylenebis (salicylideneimine).

The mixed ligand complexes were prepared by reacting [Co (salbn)]₂O₂ (0.0014 mole) and the appropriate bidentate ligand (0.0028 mole) in boiling ethanol. The resulting green solution was filtered and the partial evaporation of the filtrate gave green precipitates of the complexes. These were purified by recrystallisation from 1:1

The magnetic susceptibility measurements (27° C) of the complexes by the Gouy method indicate that the complexes are diamagnetic suggesting octahedral structure for these cobalt (III) complexes. The low molar conductance values of the complexes ($\Lambda_M = \sim 5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) in methanol are indicative of the non-electrolytic nature of the complexes. The complexes exhibit two ligand field bands in chloroform solution at around 17000 and 26000 cm⁻¹ due to the probable transitions ${}^1A_g \rightarrow {}^1T_g$ and ${}^1A_g \rightarrow {}^1T_g$, respectively¹⁰. The high molar absorptivity of the band at $\sim 26000 \text{ cm}^{-1}$ indicates some contribution from the metal-ligand charge transfer transitions. The band at around 39000 cm⁻¹ is assigned to the charge transfer and intraligand transitions. In these mixed ligand complexes the quadridentate ligand salbn adopts an unusual non-planar twisted conformation and the bidentate ligand occupies two *cis* positions similar to that of *cis*- β -[Co (acac) (salen)]¹¹.

The synthesis of mixed ligand complexes using other bidentate OO, NO and NN donor ligands and also the synthesis of similar heterochelates with the ligands I ($n = 5$ and 6) are in progress, and the details will be reported in due course.

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PROTON-LIGAND FORMATION CONSTANTS AND FORMATION CONSTANTS OF Tl(I)-3:5-DINITRO SALICYLATES

ALTHOUGH the co-ordination chemistry of salicylic acid is well documented, the study of its derivative, the 3:5-Dinitro salicylic acid (DNSA), remained neglected until quite recently. Metal complexes of DNSA with Be (II)¹, Cu (II)^{2,3}, Ni (II)^{2,4,12}, Co (II)^{2,4,12}, Mn (II)², Zn (II)², UO₂ (II)^{5,6}, Fe (III)^{7,8,14}, V (IV)⁹, Mg (II)⁹, Al (III)¹¹, Ga (III)¹¹ and In (III)¹¹ are reported in the literature. No work seems to have been made to study the complexing tendency of DNSA with Tl(I). The present work deals with the same. The proton-ligand formation constants of DNSA and formation constants of its complexes with Tl(I) have been determined employing half-integral (HI), point-wise calculation (PC) and linear plot (LP) methods. Refined values of the formation constants have been obtained by the method of least-squares.

Experimental

All the chemicals used were of Analar grade. Polymetron model CL-41 pH-meter was used for pH-metric titrations conducted at 30 C. Measurements were made with an accuracy of ± 0.05 pH

units and the reproducibility of the readings was of the same order.

pH-metric titrations of solutions of (i) free HClO₄, (ii) free HClO₄ + DNSA and (iii) free HClO₄ + DNSA + Tl(I), were performed in 50% (v/v) aqueous ethanol medium against standard NaOH solution while maintaining the ionic strength at 0.1 M NaClO₄.

The experimental set up and method of calculation is the same as described earlier¹⁵⁻¹⁷.

TABLE I
Proton-ligand formation constants of DNSA

pH	\bar{n}_A	$\log \frac{\bar{n}_A - 1}{2 - \bar{n}_A}$	pH	\bar{n}_A	$\log \frac{\bar{n}_A}{1 - \bar{n}_A}$
2.1	1.47	-0.052	7.6	0.83	+0.688
2.2	1.36	-0.249	7.8	0.72	+0.412
2.4	1.23	-0.524	8.0	0.59	+0.158
2.8	1.10	-0.954	8.2	0.44	-0.092
3.0	1.08	-1.060	8.4	0.38	-0.212
3.2	1.05	-1.278	8.6	0.29	-0.380
3.4	1.05	-1.278	8.8	0.22	-0.720

Results and Discussion

The Irving-Rossotti expression¹⁸ was used for the calculation of \bar{n}_A , \bar{n} and $p(L)$. In the calculation of \bar{n}_A , \bar{n} and $p(L)$, the concentrations were corrected for the changes in volume as a result of addition of the alkali during the titrations. A series of values of \bar{n}_A , \bar{n} and $p(L)$ corresponding to different B-values (pH-meter readings) were calculated (Tables I-II) and the formation curves for the ligand and the complex were obtained by plotting \bar{n} vs. pH and \bar{n}_A vs. $p(L)$ respectively (Figs. 1-2). The values of $\log pK_1$, \log

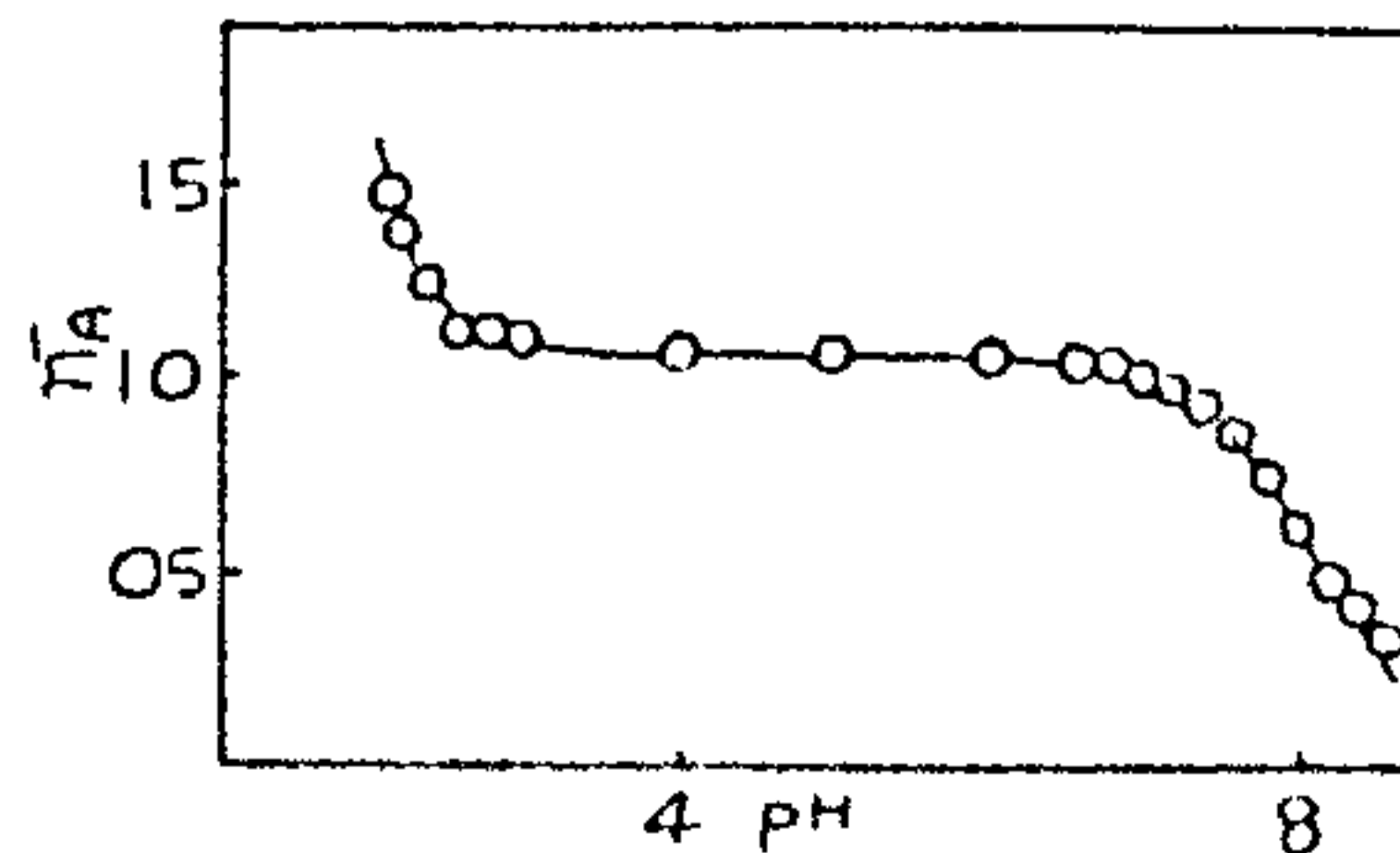


Fig. 1