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1. Swaminathan, K. and Irving, H. M. N. H., J.
29, 1937.
1970, 8 (II), 1023.
1972, 80 (2), 201.
103; C.A. 1971, 74, 6064 J.
6. Yamaguchi, A., Penland, R. B., Mizushima, S.,
Lane, T. J., Curran, C. and Quagliano, J. V.,

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A CONVENIENT METHOD FOR THE PREPARATION OF \( \alpha\)-ARYLAMINO PHENYL ACETIC ACIDS

McKENZIE and coworkers² prepared \( \alpha\)-phenylaminophenyl acetic acid by condensing \( \alpha\)-helophenyl acetic acid with aniline. We have prepared \( \alpha\)-arylamino phenyl acetic acid of the type \( \text{C}_6\text{H}_5\text{CH}(\text{R})\text{COOH} \) where \( \text{R} = \text{phenylamino}, \alpha-, m-, \) and \( \text{p-} \) tolylaminio \( \alpha- \) and \( \text{p-} \) anisylamino; \( \text{m-} \) and \( \text{p-} \) chlorophenyl amino; \( \text{p-} \) bromo and \( \text{p-} \) iodophenyl amino, etc. They have been prepared by hydrolysing \( \alpha\)-arylamino phenyl acetonitriles, first by treating with concentrated \( \text{H}_2\text{SO}_4 \) as a result of which amide formation takes place which then gets hydrolyzed 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 \( \alpha\)-arylamino phenyl acetonitriles

They have been prepared by the method suggested by Sandhu and coworkers³. The different substituents \( \text{R} \), % yields and the m.p. in °C are as follows:

- Aryl, 85, 90°; \( \alpha\)-tolyl, 79, 75°; \( \text{m-} \) tolyl, 82, 95°; \( \text{p-} \) tolyl, 80, 110°; \( \alpha\)-anisyl, 85, 68°; \( \text{p-} \) anisyl, 86, 80°; \( \text{m-} \) chlorophenyl, 80, 78°; \( \text{p-} \) chlorophenyl, 78, 70°; \( \text{p-} \) bromo phenyl, 76, 100°; \( \text{p-} \) iodophenyl, 60, 75°.

All compounds gave correct N-analysis.

(b) Preparation of \( \alpha\)-arylamino phenyl acetamide

\( \alpha\)-Phenylaminophenyl acetonitrile (0.025 mole) was dissolved in concentrated sulphuric acid (10 ml) below 10° 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 \( \text{R} \), % yield and the m.p. in °C are as follows:

- Aryl, 75, 120°; \( \alpha\)-tolyl, 63, 110°; \( \text{m-} \) tolyl, 60, 100°; \( \text{p-} \) tolyl, 65, 129°; \( \alpha\)-anisyl, 72, 165°; \( \text{p-} \) anisyl, 74, 105°; \( \text{m-} \) chlorophenyl, 62, 103°; \( \text{p-} \) chlorophenyl, 58, 146°; \( \text{p-} \) bromo phenyl, 70, 174°; \( \text{p-} \) iodophenyl, 74, 172°.

All compounds gave correct N-analysis.

(c) Preparation of arylaminophenyl acetic acid

\( \alpha\)-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 crystallized from alcohol.

Different substituents \( \text{R} \), % yield and the m.p. in °C are as follows:

- Aryl, 55, 179° (Reported 175°); \( \alpha\)-tolyl, 50, 149°; \( \text{m-} \) tolyl, 53, 145°; \( \text{p-} \) tolyl, 51, 164°; \( \alpha\)-anisyl 49, 280°(d); \( \text{p-} \) anisyl, 51, 173°; \( \text{m-} \) chlorophenyl, 48, 147°; \( \text{p-} \) chlorophenyl, 45, 175°; \( \text{p-} \) bromo phenyl, 46, 171°; \( \text{p-} \) iodophenyl, 42, 160°.

All compounds gave correct N-analysis.

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University Department of Chemistry, S. B. Bhatt,
Saurashtra University, A. R. Parikh,
Bhavnagar, September 29, 1975.

197, 1681.
2. Sandhu, J. S., Sethi, P. S. and Suresh Mohan,

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MIXED LIGAND COMPLEXES OF COBALT (II) CONTAINING N, N'-TETRAMETHYLENÉBIS
(SALICYLIDÉNÉIMINE) AND BIDENTATE LIGANDS

In recent years there has been considerable interest on the transition metal complexes of quadridentate Schiff bases 1³-4. 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 \( \text{M} = \text{Co (II)} \) and \( \text{Cu (II)} \)] changes from square planar to tetrahedral ²-7. We have recently reported the synthesis and characterisation of cobalt (III) complexes of saltna, where saltna = N,N'-trimethylethenebis (salicylideneimine). In this preliminary communication we report the syntheses of several new cobalt (III) mixed ligand complexes of saltna and
bidentate ligands like acetylacetone, acetoacetanilide, tropolone, N-benzoylphenylhydroxylamine and picolinic acid. The complexes have been characterised by elemental analysis, electronic spectra, conductance and magnetic measurements.

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 (\(\Lambda M = 5 \, \text{ohm}^{-1} \, \text{cm}^{2} \, \text{mole}^{-1}\)) 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 \(^{3}A_{g} \rightarrow ^{3}T_{g}\) and \(^{3}A_{g} \rightarrow ^{3}T_{g}\) respectively. The high molar absorptivity of the band at \(\approx 26000 \, \text{cm}^{-1}\) 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-\(\beta\)-[Co(acac)(acat)]\(^{2}\).

The synthesis of mixed ligand complexes using other bidentate O-O, N-O and N-N 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(II)-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)\textsuperscript{3}, Cu(II)\textsuperscript{2}, Ni(II)\textsuperscript{2,3}, Co(II)\textsuperscript{2,4,12}, Mn(II)\textsuperscript{2}, Zn(II)\textsuperscript{2}, UO\textsubscript{2}(II)\textsuperscript{9,10}, Fe(III)\textsuperscript{7,11}, V(IV)\textsuperscript{8}, Mg(II)\textsuperscript{2}, Al(III)\textsuperscript{3}, Ga(III)\textsuperscript{11} and In(III)\textsuperscript{21} are reported in the literature. No work seems to have been made to study the complexing tendency of DNSA with Tl(II). The present work deals with the same.

The proton-ligand formation constants of DNSA and formation constants of its complexes with Tl(II) 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 HClO\textsubscript{4}, (ii) free HClO\textsubscript{4} + DNSA and (iii) free HClO\textsubscript{4} + DNSA + Tl(II), were performed in 50% (v/v) aqueous ethanol medium against standard NaOH solution while maintaining the ionic strength at 0.1 M NaClO\textsubscript{4}.

The experimental set up and method of calculation is the same as described earlier\textsuperscript{15-17}.

**Table I**

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<th>pH</th>
<th>(\tilde{n}_A)</th>
<th>(\log \frac{\tilde{n}_A - 1}{2 - \tilde{n}_A})</th>
<th>pH</th>
<th>(\tilde{n}_A)</th>
<th>(\log \frac{\tilde{n}_A - 1}{1 - \tilde{n}_A})</th>
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<td>2.4</td>
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<td>0.59</td>
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<td>8.2</td>
<td>0.44</td>
<td>-0.092</td>
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<td>1.08</td>
<td>-1.060</td>
<td>8.4</td>
<td>0.38</td>
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<tr>
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<td>-1.278</td>
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<td>0.29</td>
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<tr>
<td>3.4</td>
<td>1.05</td>
<td>-1.278</td>
<td>8.8</td>
<td>0.22</td>
<td>-0.720</td>
</tr>
</tbody>
</table>

Results and Discussion

The Irving-Rossotti expression\textsuperscript{15} was used for the calculation of \(\tilde{n}_A\), \(\tilde{n}\) and \(p(L)\). In the calculation of \(\tilde{n}_A\), \(\tilde{n}\) 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 \(\tilde{n}_A\), \(\tilde{n}\) 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 \(\tilde{n}\) vs. pH and \(\tilde{n}_A\) vs. \(p(L)\) respectively (Figs. 1-2). The values of log \(pK_{1A}\), log