The e.m.f. values recorded at different temperatures are given in Table 2.

The reaction taking place in the cell is

\[ \text{Ni} + \text{CuD}_2 \rightleftharpoons \text{NiD}_2 + \text{Cu} \]

where D stands for laurate, myristate, palmitate or stearate ion.

Both the electrodes involved in the cell under consideration are reversible with respect to the detergent anion. The e.m.f. of the cells should be independent of the concentration of potassium soap and should be equal to algebraic difference of standard reduction or oxidation potential of electrodes. The concentration ranges of potassium soaps investigated were from \( 1 \times 10^{-2} \) to \( 5 \times 10^{-2} \), \( 5 \times 10^{3} \) to \( 1 \times 10^{-3} \), \( 2.5 \times 10^{-3} \) to \( 1 \times 10^{-3} \), \( 8 \times 10^{-4} \) to \( 5 \times 10^{-4} \) for potassium laurate, myristate, palmitate and stearate respectively. These concentrations of potassium soaps are just below the critical micelle concentration (cmc) values. It is evident from Table 2 that the e.m.f. of the cells are independent of the concentration of potassium soap solution.

The following equations have been used for calculating \( \Delta G \), \( \Delta H \) and \( \Delta S \) at 303°K:

\[
\Delta G = -nFE
\]

\[
\Delta S = nF \left( \frac{\Delta E}{\Delta T} \right)_p
\]

\[
\Delta H = -nFE + nF \left( \frac{\Delta E}{\Delta T} \right)_p
\]

The values of the e.m.f. of the cells at 303°K, the temperature coefficient of e.m.f. and the values of \( \Delta G \), \( \Delta H \) and \( \Delta S \) for the cell reactions are given in Table 1.

References

Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) & UO_2(II) Chelates of Schiff Bases Derived from o-Aminobenzenesulphonic Acid & 2-Aminoethanesulphonic Acid & 2-Hydroxy-1-naphthaldehyde

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N - (2-Hydroxy - 1 - naphthaldehyde) orthanilic acid (H_2NO) and N-(2-hydroxy-1-naphthaldehyde)taurine (H_2NT), the two structurally similar Schiff bases, form solid chelates with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and UO_2(II). Elemental analyses, molecular weight, magnetic moment values and electronic spectral data indicate nearly octahedral stereochemistry for Mn(II), Fe(II), Co(II), Ni(II) and UO_2(II) chelates, whereas Cu(II) chelates display a tetragonal configuration. Zn(II) and Cd(II) chelates are tetrahedral in structure and the Pd(II) chelate possesses square-planar geometry.

A PERUSAL of the literature reveals that no systematic studies have been carried out on Schiff bases derived from o-aminobenzenesulphonic acid & 2-a...
The two Schiff bases, which are structurally similar, are expected to behave as bidentate ligands.

Metal salts (BDH) were of AR grade. Orthoanilic acid (LR) and 2-aminoethanesulphonic acid (taurine) and 2-hydroxy-1-naphthaldehyde (AR) supplied by Fluka were used.

Gallenkamp semimicro ebulliometer was used to determine the molecular weights of the solid chelates using dioxane as the solvent. Magnetic susceptibility measurements were made on Gouy apparatus using mercury(II) tetrahydroxocyanocobaltatalate as the reference. The electronic absorption spectra of the compounds were determined on a VEB Carl Zeiss, Jena, VSU-2P spectrophotometer at room temperature.

**Preparation of ligands and their metal chelates** — H$_2$NO and H$_2$NT were synthesized by the method of Pfeiffer et al. These gave satisfactory elemental analyses. Their metal chelates with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and UO$_2$(II) were prepared by the method of Yamada et a/.

**Elemental analyses and magnetic moment data of the chelates are given in Table 1.**

In general, the metal chelates display 1:1 (metal-ligand) stoichiometry. The molecular weight data suggest that Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) chelates have the composition (MLX$_3$)$_2$ where M = metal ion; X = H$_2$O or Py and LH$_2$ = H$_2$NO [C$_7$H$_7$NSO$_4$] or H$_2$NT [C$_7$H$_7$NSO$_4$]. Their magnetic moments indicate the presence of 5, 4, 3, 2 and 1 unpaired electron in the Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) chelates respectively.

A little lower value (5.81 and 5.83) of the magnetic moment of Mn(II) chelates than the normal value of 5.92 BM for octahedral or tetrahedral Mn(II) complexes may be due to spin-exchange in the solid state or due to the presence of a little Mn(III) species which may have been formed due to aerial oxidation. The high magnetic moments of Co(II) chelates may be due to spin-orbit coupling. The Cu(II) chelates exhibit magnetic moments of 1.92 and 1.94 BM at 298°K. The magnetic moment of planar chelates are generally lower (1.8-1.9 BM) than those of octahedral complexes (1.9-2.0 BM). As the planar stereochemistry may be considered as the limiting case of tetragonally distorted octahedral stereochemistry, the separation of the interaction terms (i.e. between ground term $^2B$ and the components of $^2T$) is larger in square-planar chelates than that in the octahedral chelates which possibly explains the lower magnetic moments of square-planar chelates. The magnetic moments of perfect tetrahedral chelates are higher than those for square-planar or octahedral chelates due to spin-orbit coupling and are temperature dependant.

The observed bands in the electronic spectra of the chelates correspond to the transitions $^4A_1g$→$^4E_1g$ and $^4A_1g$→$^4T_2g$ for the Fe(II) chelates, $^3T_2g$→$^3E_g$ for the Co(II) chelates, $^4T_2g$→$^4E_g$ for the Cu(II) chelates, $^4T_2g$→$^4T_2g$ and $^4T_2g$→$^4T_2g$ for the Ni(II) chelates, and $^2E$→$^2T_2g$ for the Cu(II) chelates. These data supported by the magnetic moment data confirm nearly octahedral structure.

### Table 1 — Elemental Analyses and Magnetic Moment Data of the Metal Chelates of N-(2-Hydroxy-1-naphthalenedione)orthanilic Acid and N-(2-Hydroxy-1-naphthalaldehyde)taurine

<table>
<thead>
<tr>
<th>Metal chelate</th>
<th>Hydrated chelate</th>
<th>Pyridine adducts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μmag (BM)</td>
<td>N (%)</td>
</tr>
<tr>
<td></td>
<td>at 298°K</td>
<td>Found (Calc.)</td>
</tr>
<tr>
<td><strong>CHELATES OF N-(2-HYDROXY-1-NAPHTHALIDINE)ORTHANILIC ACID</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>5.81</td>
<td>3.19 (3.22)</td>
</tr>
<tr>
<td>Fe(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>5.45</td>
<td>3.18 (3.21)</td>
</tr>
<tr>
<td>Co(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>5.16</td>
<td>3.09 (3.19)</td>
</tr>
<tr>
<td>Ni(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>3.08</td>
<td>3.10 (3.19)</td>
</tr>
<tr>
<td>Cu(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>1.92</td>
<td>3.08 (3.16)</td>
</tr>
<tr>
<td>Cd(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td></td>
<td>3.05 (3.11)</td>
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<tr>
<td>Zn(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td></td>
<td>2.98 (3.07)</td>
</tr>
<tr>
<td>UO$_2$(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td></td>
<td>3.31 (3.42)</td>
</tr>
<tr>
<td><strong>CHELATES OF N-(2-HYDROXY-1-NAPHTHALIDINE)TAURINE</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>5.83</td>
<td>3.58 (3.62)</td>
</tr>
<tr>
<td>Fe(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>5.44</td>
<td>3.59 (3.61)</td>
</tr>
<tr>
<td>Co(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>5.10</td>
<td>3.45 (3.59)</td>
</tr>
<tr>
<td>Ni(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>3.10</td>
<td>3.46 (3.59)</td>
</tr>
<tr>
<td>Cu(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td>1.94</td>
<td>3.47 (3.54)</td>
</tr>
<tr>
<td>Pd(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td></td>
<td>3.32 (3.49)</td>
</tr>
<tr>
<td>Cd(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td></td>
<td>3.32 (3.43)</td>
</tr>
<tr>
<td>Zn(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td></td>
<td>3.76 (3.88)</td>
</tr>
<tr>
<td>UO$_2$(C$_7$H$_7$NSO$_4$)X$_3$</td>
<td></td>
<td>2.42 (2.47)</td>
</tr>
</tbody>
</table>

*X = H$_2$O or pyridine; satisfactory metal analyses were obtained.

†Estimation of water molecules gave satisfactory results.
for Mn(II), Fe(II), Co(II) and Ni(II) chelates and tetragonal configuration for the Cu(II) chelates. The tetragonal structure of Cu(II) chelates is also confirmed by infrared analysis of the metal chelates in the region of 3·1 to 4·0 \(\text{cm}^{-1}\). These results indicate three absorption bands at 22200, 26500 and 30600 \(\text{cm}^{-1}\) which can be assigned to the transitions \(A_1 \rightarrow B_1\), \(A_1 \rightarrow B_2\) and \(A_1 \rightarrow A_2\) respectively. Thus the Pd(II) chelates exhibit a square-planar configuration.

The Zn(II), Cd(II), Pd(II) and UO\(_2\)(II) chelates show 1:1 (metal-ligand) stoichiometry (Table 1). The complexes may be represented by the formula \([\text{MLX}]\), where \(M =\) metal ion, \(\text{LH}_2 =\) H\(_2\)NO \([\text{C}_8\text{H}_8\text{NSO}_4]\) or H\(_2\)NT \([\text{C}_6\text{H}_5\text{NSO}_4]\) and \(X = H_2O\) or Py. All the hydrated chelates and their pyridine adducts have been found to be diamagnetic, as expected. These results can be best explained by assigning a tetrahedral structure for Zn(II) and Cd(II) chelates. UO\(_2\)(II) chelates possess an octahedral structure in conformity with the usual behaviour of UO\(_2\)(II) ion.

References


Chlorotellurium Compounds of Aryl Ethers

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Conductance studies and molecular weight measurements on ethoxytelluriumtrichloride and bis(methoxyphenyl)tellurium dichloride suggest their presence in molecular form in organic solvents. IR and NMR studies show the presence of TeCl\(_3\) group in the para position to ethoxy or methoxy group in the ring, in both the compounds.

In the present note, structural aspects of \(p\)-ethoxyphenylltellurium trichloride\(^{12}\) (I) and bis\((p\)-methoxyphenyl)tellurium dichloride\(^3\) (II) are discussed. Recently, infrared and NMR studies of \(p\)-methoxyphenylltellurium trichloride have been reported\(^4\).

Compounds I (m.p. 180-82\(^\circ\)) and II (m.p. 190\(^\circ\)) were prepared by literature methods\(^2,3\) and crystallized from chloroform and methanol respectively.

Conductivities of these compounds at different concentrations have been measured in acetonitrile at 30\(^\circ\)\(\pm\)1\(^\circ\). The conductivity increases with dilution. However, the molar conductances are lower than the values expected\(^6\) for 1:1 electrolytes (120-160 ohm\(^{-1}\) cm\(^{-2}\) mole\(^{-1}\)) in the concentration range of 10\(^{-3}\)M. This suggests that the compounds are present in the solution mainly in the molecular form. Molecular weight determination in benzene by cryoscopic method further supports this contention.

The asymmetric and symmetric C-O-C stretchings in phenetole and anisole appear at 1240 and 1040 cm\(^{-1}\) whereas compound I exhibits these bands at 1260 and 1050 cm\(^{-1}\) and compound II at 1270 and 1045 cm\(^{-1}\). This shift to higher frequency side indicates \(p\)- or \(p\)-substitution of TeCl\(_3\) group in the ring. The appearance of a very intense band (1580 cm\(^{-1}\)) in both these compounds could be due to a change in the dipole moment because of the presence of \(para\)-substituted TeCl\(_3\) group in the ring. Further support for \(para\)-substitution is obtained from the overtone and combination bands which appear at 1880, 1780 and 1710 cm\(^{-1}\) as expected\(^3\). A medium intensity band at 455 cm\(^{-1}\) in compound I and at 480 cm\(^{-1}\) in compound II corresponds to the tellurium-carbon bond. The compounds I and II show bands at 320 and 290 cm\(^{-1}\) respectively assigned to Te-Cl bonds.

PMR spectra of I and II have been recorded in deuterio-acetonitrile. These spectra are of \(A_2X_2\) type and give a definite proof of the \(para\)-substitution of chlorotellurium group in the ring. Spectrum (8 chem.) of bis(methoxyphenyl)tellurium dichloride shows two quartets at 8·30 and 7·12 ppm. Their intensities show each of them to be due to a pair of protons in identical chemical environment. The \(J_{H_{ortho}}-H_{meta}\) is 9·0 \(\pm\) 0·3 Hz. The methoxy groups give rise to a singlet at 3·87 ppm.

The NMR spectrum of II shows even finer structural details. The protons \(ortho\) to OC\(_2\)H\(_5\) group (H\(_A\) and H\(_B\)) in II are chemically equivalent as are the protons \(ortho\) to TeCl\(_3\) group (H\(_X\) and H\(_Y\)). \(J_{AX}\) and \(J_{AY}\) should be the same (~7-10 Hz). The \(ortho\) and \(meta\) aromatic protons (with respect to TeCl\(_3\) group) show a multiplet at 8·27 and 7·80 ppm respectively. \(J_{AX}\) which is equal to \(J_{AY}\) is 9·3 \(\pm\) 0·3 Hz. The spectrum also shows coupling between H\(_A\) and H\(_A\) (as also between H\(_X\) and H\(_Y\)). \(J_{AX}\) is equal to \(J_{AY}\) and is 2·2 \(\pm\) 0·3 Hz. This spectrum can be better described as of the type AA'XX'. A quartet and a triplet appearing at 4·14 and 1·38 ppm respectively are due to the ethyl group (\(J_{CH_{2}CH_{2}} = 7·0 \pm 0·3\) Hz).

Authors wish to thank Mr J. W. Akitt of the University of Leeds, UK, for his help in recording and valuable comments on the NMR spectra.

References