The νCO at 1660 and 1650 cm⁻¹ in the IR spectra of urea and tetramethylurea respectively appear at 1630 and 1552 ± 3 cm⁻¹ in their respective complexes. A shift in νCO by 30 cm⁻¹ in the case of urea adducts and by 100 cm⁻¹ in the case of TMU adducts indicates coordination of the ligands to tin through the oxygen atom.

The νCN of urea at 1455 and 1499 cm⁻¹ in urea and TMU respectively. These are shifted to higher frequency in the adducts: 1478 ± 3 cm⁻¹ for urea and TMU respectively. These are shifted to higher frequency in the adducts: 1478 ± 3 cm⁻¹ for urea and TMU respectively. These are shifted to higher frequency in the adducts: 1478 ± 3 cm⁻¹ for urea and TMU respectively.

The νC=O in the IR spectra of TMU adducts indicates coordination of the ligands to the nitrogen atom of the Lewis base in coordination. The δC=O of urea and TMU also undergoes a distinct negative shift and is split (~770, 740 cm⁻¹) in the spectra of TMU adducts, which may be taken as an evidence for the presence of the coordinated base.

The relative magnitude of the lowering of νCO and δC=O indicates that TMU is a better donor compared to urea. The electron releasing methyl groups in TMU are likely to increase the electron density at the oxygen atom of the carboxyl group in TMU.

Since urea adducts are insoluble in common organic solvents, PMR and dipole moment studies have been restricted to TMU adducts. The PMR data of Ph₂SnCl₂-TMU and Ph₂SnCl₂-2TMU exhibit two groups of signals: a multiplet due to the phenyl protons attached to tin atom and a singlet due to protons of two N(CH₃)₂ groups. The and their integration are consistent with the proposed stoichiometry of the compounds. The absence of splitting in the protons due to N(CH₃)₂ groups is attributed to the free rotation about the C–N bond, which makes the two alkyl groups magnetically equivalent.

The electrical dipole moments of Ph₂SnCl₂-TMU and Ph₂SnCl₂-2TMU were determined in benzene following the concentration dependence of dielectric constants and the refractive indices. Calculations are based on the Guggenheim method. The dipole moment values, 5.94 and 7.20 respectively, are significantly higher than those reported for neutral complexes of biochemically important metal ions. The EXCESSIVE studies have been carried out on the complexes of diaceetamide, biuret (H₂NCONH₂), its mono and di-thio analogues and diacacetamide (H₂CONHCONH₂). These ligands many times reveal unusual type of coordination. For example, the ligands may sometimes behave as monodentate as opposed to their more common bidentate behaviour. The ligands in the complexes usually have cis-trans conformation when acting as monodentate, and trans-trans conformation when acting as bidentate. In a recent communication, we investigated the, ambidentate nature of monothio-biuret (H₂NCONHCONH₂), its mono and di-thio analogues and diacacetamide (H₂CONHCONH₂). These ligands many times reveal unusual type of coordination. For example, the ligands may sometimes behave as monodentate as opposed to their more common bidentate behaviour. The ligands in the complexes usually have cis-trans conformation when acting as monodentate and trans-trans conformation when acting as bidentate.

Monothiodiacetamide Complexes with Ni(II), Zn(II), Cd(II) and Hg(II) Chlorides

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Complexes of monothiodiacetamide (H₂CONHCSCH₃) with Ni(II), Zn(II), Cd(II) and Hg(II) chlorides have been prepared and characterized. The ligand shows both monodentate as well as bidentate coordination behaviour depending on the metal ion.

REFERENCES

performed microanalytically at the Bhabha Atomic Research Centre, Bombay. The analytical data are given in Table 1.

Attempts to prepare MTDA complexes of CoCl₂ and CuCl₂ yielded a green and yellow complexes respectively, which decomposed to their sulphides in 20-30 min.

The infrared spectra (4000-200 cm⁻¹) were recorded in nujol and KBr on a Beckmann IR 12 spectrophotometer. The electronic spectra were recorded on a Unicam SP 700 A spectrophotometer. The molar conductances were determined using a Siemens conductivity bridge.

The Ni(II) and Cd(II) complexes of MTDA are stable and nonhygroscopic whereas the Zn(II) complex is very hygroscopic and the Hg(II) complex decomposes slowly on keeping for several days. The molar conductances at room temperature of Ni(II) and Cd(II) complexes were recorded in nitrobenzene and those of Zn(II) and Hg(II) complexes in acetonitrile at 0.001M concentrations. The molar conductivities were nearly zero suggesting the complexes to be non-electrolytes having coordinated chloride ions.

The assignment of the infrared bands of the present ligand and complexes is based on an approximate normal coordinate analysis⁷ of MTDA with a trans-cis -CONHCS- conformation. The infrared spectra of Ni(II) and Zn(II) complexes show one pattern of change from the ligand spectrum and those of Cd(II) and Hg(II) complexes another pattern as detailed below.

The C=O stretching band at 1720 cm⁻¹ in the ligand is not changed in Ni(II) and Zn(II) complexes. This behaviour is comparable to the complexes of diacetamide, where also the C=O stretching frequency is not lowered on coordination⁸. In the Cd(II) and Hg(II) complexes, the band due to C=O stretching is observed as a doublet at slightly lower frequencies. The NH in-plane bending at 1520 cm⁻¹ in the ligand occurs at slightly lower frequencies in the Ni(II) and Zn(II) complexes but with reduced intensity in Cd(II) and Hg(II) complexes. An unambiguous assignment of the NH out-of-plane bending (at 830 cm⁻¹ in the ligand) is difficult for Cd(II) and Hg(II) complexes because of the presence of weak bands in region 700-900 cm⁻¹.

The 1260 cm⁻¹ band of MTDA remains almost unaffected with respect to its position and intensity in Ni(II) and Zn(II) complexes, but in the other two complexes it occurs at lower wave numbers with reduced intensity.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Found (calc., %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal</td>
<td>C</td>
</tr>
<tr>
<td>Ni(MTDA)Cl₂</td>
<td>Greyish-brown</td>
<td>24.01</td>
</tr>
<tr>
<td>Zn(MTDA)Cl₂</td>
<td>Yellow</td>
<td>(23.80)</td>
</tr>
<tr>
<td>Cd(MTDA)Cl₂H₂O</td>
<td>Yellow</td>
<td>25.92</td>
</tr>
<tr>
<td>Hg(MTDA)Cl₂</td>
<td>Pale-yellow</td>
<td>(25.80)</td>
</tr>
</tbody>
</table>

The C=S bending mode observed as a doublet at 458, 450 cm⁻¹ is slightly raised, to 460 and 475 cm⁻¹ in Hg(II) and Cd(II) complexes, respectively. In Ni(II) and Zn(II) complexes, this band is found at lower frequencies (~430 cm⁻¹). An increase in the C=S bending frequency is to be expected when coordination occurs through sulphur.

The in-plane C=O bending at 613 cm⁻¹ in MTDA increases by 10 to 14 cm⁻¹ in Ni(II) and Zn(II) complexes while the C=O out-of-plane bending at 595 cm⁻¹ decreases by 10 to 14 cm⁻¹. On the other hand, both in-plane and out-of-plane C=O bendings are found at lower frequencies in Cd(II) and Hg(II) complexes.

The above differences in the spectra of Ni(II) and Zn(II) complexes from those of the complexes of Cd(II) and Hg(II) may be interpreted as indicating bidentate coordination through sulphur and oxygen in Ni(II) and Zn(II) complexes and unidentate, bonding through sulphur in Cd(II) and Hg(II) complexes. A similar coordination behaviour was noted for monothiobiuret⁹. Because of the mixed nature of the vibrations, definite conclusions about the bonding sites of the ligand cannot be drawn based on infrared spectra alone. On the basis of more common tetrahedral coordination of Hg(II) also, unidentate behaviour of MTDA is expected. It may be noted that Cd(MTDA)Cl₂H₂O, is similar to the DA complex⁸, Cd(2DA)Cl₂H₂O where DA is in a Fa-interaction with unidentate coordination with the metal.

The metal-chloride vibrations in the complexes occur in the range 210-330 cm⁻¹. These are assigned according to Ferraro⁹. Reliable assignment of the metal-ligand vibrations is difficult because of the presence of the ligand bands in this region.

The electronic spectrum of MTDA was recorded in n-heptane. It exhibits three absorptions at 218, 282 and 420 nm. The bands at 218 (ε ~216 m²mole⁻¹) and 282 nm (ε ~1632 m²mole⁻¹) are attributed to π-π transitions of the C=S and C=S groups, respectively. The weak absorption at 420 nm (ε ~4 m²mole⁻¹) is due to n-π* absorption of the C=S group.

The electronic spectra of the complexes were recorded in ethanol solution. The π-π* absorption of the C=S group at 282 is shifted to lower wavelengths, 259, 262, 264 and 270 nm in Hg(II), Cd(II), Zn(II) and Ni(II) complexes, respectively. Blue shifts for π-π* absorption of the C=S group is expected on coordination of sulphur to a metal ion. The solid state electronic spectrum of the Ni(II)
complex gives a shoulder at 450 nm in the visible region suggestive of a square-planer geometry around the metal.\(^{21,22}\)

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Spectral & Magnetic Studies on Nickel(II) Complexes with p-Diethylaminoanil of Phenylglyoxal

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Ni(II) complexes of p-diethylaminoanil of phenylglyoxal of the type [Ni(C\(_6\)H\(_5\),N\(_2\),O\(_2\)Cl\(_2\)] (where X = Cl, CN, SCN) and [Ni(C\(_4\)H\(_4\),N\(_2\),O\(_2\)Cl\(_2\)] have been prepared and characterized on the basis of various physicochemical studies. Magnetic moments of the complexes (3-00-3-14 B.M.) reveal the octahedral stereochemistry. Electronic spectral data have been analysed using Konig's approach. The IR data indicate (M-O), (M-N) and (M-Cl) stretching frequencies in the ranges 580-570, 510-500 and 350 cm\(^{-1}\), respectively.

Recent Konig\(^{2,4}\) has discussed the phenomenon of nephelauxetism and showed its importance in evaluating the covalency factor. In the present note, magnetic moment, electronic and IR spectral data of some Ni(II) complexes with p-diethylaminoanil of phenylglyoxal are being reported. Various ligand field parameters have been evaluated using Konig's approach.

The ligand, p-diethylaminoanil of phenylglyoxal (DEAPG), was prepared by condensation of equimolar quantities of phenylglyoxal and p-diethylaminoaniline in an ethanolic medium. The ligand was recrystallized from pet. ether and it gave satisfactory C, H and N analyses.

\[\text{Ni(DEAPG)}_2\text{Cl}_2\] — Nickel(II) chloride hexahydrate (2-377 g, 10 m mole) in 25 ml ethanol was mixed with DEAPG (5-60 g, 20 m mole). A bluish-violet solution was obtained. The solution was concentrated by evaporation at room temperature. The bright-violet crystals obtained, were thoroughly rinsed with acetone-ethanol mixture (there was little tendency of dissolution) and dried in an oven at \(\sim 80^\circ\). Yield, \(\sim 70\%\), [Found: C, 62-20; H, 5-48; N, 7-64; Cl, 10-24; Ni, 8-48. Calc. for Ni(DEAPG)_2Cl_2: C, 62-63; H, 5-79; N, 8-11; Cl, 10-29; Ni, 8-50%].

\[\text{Ni(DEAPG)}_2\text{NH}_3\text{Cl}_2\] [Ni(DEAPG)_2(CN)_2] and [Ni(DEAPG)_2(SCN)_2] — Above procedure was repeated to obtain [Ni(DEAPG)_2Cl_2]. The ammino, cyano and thiocyanato complexes were prepared by adding dil.aq. solutions of ammonia, KCN and KSCN respectively. Orange to red coloured substances were obtained, which were filtered off, washed with ethanol-acetone mixture and dried in vacuo. Yield, 60-75%.

Analyses: [Found: C, 59-50; H, 6-12; N, 25-10; Cl, 9-78; Ni, 8-00. Calc. for Ni(DEAPG)_2(NH_3)_2Cl_2: C, 59-69; H, 6-35; N, 25-42; Cl, 9-81; Ni, 8-10%]. [Found: C, 67-41; H, 5-43; N, 12-12; Ni, 8-62. Calc. for Ni(DEAPG)_2(CN)_2: C, 67-98; H, 5-96; N, 12-52; Ni, 8-75%]. [Found: C, 61-81; H, 5-41; N, 11-24; S, 8-54; Ni, 7-92. Calc. for Ni(DEAPG)_2(SCN)_2: C, 62-06; H, 5-44; N, 11-43; S, 8-71; Ni, 8-02%].

The molar conductance measurements of 10M\(^{-3}\) solutions of the complexes in DMF reveal that the complexes Ni(DEAPG)_2Cl_2, Ni(DEAPG)_2(CN)_2 and Ni(DEAPG)_2(SCN)_2 are non-electrolytes, while the complex Ni(DEAPG)_2(NH_3)_2Cl_2 is uni-divalent electrolyte.

The electronic spectra of the complexes were recorded on a Hilger Uvispeck spectrophotometer in nitromethane. Three spin-allowed transitions, \(A_{2g}(F) \rightarrow \delta T_{2g}(F) (\nu_1)\), \(A_{2g}(F) \rightarrow \delta T_{1g}(F) (\nu_2)\) and \(A_{2g}(F) \rightarrow \delta T_{1g}(F) (\nu_3)\) are expected for Ni(II) in an octahedral field. In the case of weak ligand field

\[\nu_1 = 10Dq\]
and \(\nu_2 \nu_3 = \frac{1}{2}(15B' + 30Dq) \pm \frac{1}{2}(15B' - 10Dq)^2\) + 12B' \(10Dq\)^3...

The value of B may then be calculated using Eqs. (3-6).

\[B = (2v^2 + v_2 - 3v_3)(15v_3 - 27v_1)\]...
\[B = (2v^2 + v_2 - 3v_3)(15v_2 - 27v_1)\]...
\[B = (v_2 + v_3 - 3v_4)/15\]...
\[B = 1/75[3v_4 \pm (25v_4 - v_2)^2 - 16v_4]^1/2]...}

Analytical data show 1:2 (metal to ligand) stoichiometry for the complexes. The magnetic

NOTES