Complexes of Zn(II), Cd(II), Hg(II), Pb(II), Tl(I) & Ag(I) with 1,2,4-Triazole-3(5)-thiol

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Zn(II), Cd(II), Hg(II), Pb(II), Tl(I) & Ag(I) complexes of 1,2,4-triazole-3(5)-thiol have been prepared and characterized on the basis of analytical and IR data. Hg(II), Cd(II), Zn(II) and Pb(II) complexes are tentatively assigned tetrahedral structures with polymeric intermolecular linkages through S and N atoms while Ag(I) and Tl(I) complexes are suggested to have polymeric linear structures.

TABLE 1 - ANALYTICAL DATA OF THE COMPLEXES

<table>
<thead>
<tr>
<th>Formula</th>
<th>Calc. (Found), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, H, N, S</td>
<td>N</td>
</tr>
<tr>
<td>Zn(C$_2$H$_3$N$_3$S)$_2$</td>
<td>25.40 (25.07)</td>
</tr>
<tr>
<td>Cd(C$_2$H$_3$N$_3$S)$_2$</td>
<td>26.88 (26.43)</td>
</tr>
<tr>
<td>Hg(C$_2$H$_3$N$_3$S)$_2$</td>
<td>21.00 (20.49)</td>
</tr>
<tr>
<td>Pb(C$_2$H$_3$N$_3$S)$_2$</td>
<td>13.60 (13.92)</td>
</tr>
<tr>
<td>Tl(C$_2$H$_3$N$_3$S)$_2$</td>
<td>13.80 (13.55)</td>
</tr>
<tr>
<td>Ag(C$_2$H$_3$N$_3$S)$_2$</td>
<td>20.20 (20.01)</td>
</tr>
</tbody>
</table>

C and H elemental analyses were within ± 3%.

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like NMR, mol. wt., molecular conductivity measurements could not be used for their structural studies.

The ligand in solution can exist either in thiol or thione form and behaves as a weak dibasic acid. It has four bonding sites (three nitrogen atoms and one thiocarbonyl sulphur). Therefore, it can behave as a mono-, bi-, tri- or tetra-dentate ligand.

**IR spectrum of the ligand** — The ligand spectrum showed a very broad band (half-width ~500 cm\(^{-1}\)) from 4000-2000 cm\(^{-1}\). Besides the breadth, like NMR, mol. wt., molecular conductivity measurements could not be used for their structural studies.

The ligand spectrum showed a very broad band (half-width ~500 cm\(^{-1}\)). This band is less broader as compared to that of 3050 cm\(^{-1}\). The band at 680 cm\(^{-1}\) is assigned mainly due to \(\nu\)N-H (thioamide band-IV). The presence of shoulders and broad nature of the band indicates that extensive inter- and intra-molecular hydrogen bonding may be present in the ligand and there may be cooperative proton transfer. Besides the band at 3050 cm\(^{-1}\), one should also expect in this region bands due to \(\nu\)C-H and \(\nu\)S-H (in case the ligand exists in the thiol form). The band at 3050 cm\(^{-1}\) shifts to 2250 cm\(^{-1}\) which confirms our assignment. In the spectrum of the deuterated ligand the bands due to \(\nu\)N-H and \(\nu\)S-H possibly are masked by the broad band due to \(\nu\)N-H.

In the spectrum of the deuterated ligand the bands at 3050 cm\(^{-1}\) were shifted to 2250 cm\(^{-1}\) which confirms our assignment. Another band besides the one at 2250 cm\(^{-1}\) also appeared at 2180 cm\(^{-1}\), this may be due to the interaction of two vic-N-H groups whereby one should expect bands due to \(\nu\)N-NH and \(\nu\)NH. This band is less broader as compared to that of 3050 cm\(^{-1}\) possibly because of reduced extent of proton transfer arising from the increased mass. There is no band present around 2600 cm\(^{-1}\) due to \(\nu\)S-H suggesting the absence of S-H group.

In the fingerprint region of the spectrum, the ligand should show bands due to \(\nu\)N-C-S, \(\nu\)N=C\(\equiv\)N, and \(\nu\)N-S\(\equiv\)S groups. Since it contains more than one HNC\(\equiv\)S and N=C groups, the IR bands should either be split or broad ones. Also, on deuteration, the positions of all the bands arising due to normal coordinates having contribution from the motion of the N-H bond will be shifted.

The bands at 1560(s) and 1255 cm\(^{-1}\) have been respectively assigned to thioamide band-I and -II. Since these bands have major contribution from \(\delta\)NH and \(\nu\)CN, the positions of these bands, on deuteration, were shifted to 1160 and 965 cm\(^{-1}\) respectively and there appeared a split band (weak to medium intensity) at 1550 (1530) cm\(^{-1}\) and 1255 cm\(^{-1}\).

The split in the band at 1550 cm\(^{-1}\) may be due to interaction of two CN bonds. The position of broad band at 1460 cm\(^{-1}\) in the spectrum of the ligand was shifted to 1470 cm\(^{-1}\) in that of deuterated ligand. This band is assigned to mixed mode of vibrations having contributions from \(\nu\)C-N, \(\nu\)N-N, \(\delta\)N-H and \(\delta\)C-H. The small shift in the position of this band signifies that it does not have any appreciable contribution from \(\delta\)N-H.

The band at 1200 cm\(^{-1}\) has been assigned to \(\delta\)CH. It may also have small contributions from other modes of vibrations. The assignment was confirmed by the fact that the positions of this band remained practically constant (±5 cm\(^{-1}\)) in the spectra of the deuterated ligand and the complexes.

The bands at 1065, 945 and 855 cm\(^{-1}\) arise from normal coordinates having major contributions from \(\nu\)C-N and \(\nu\)C=S. Since the band at 1065 cm\(^{-1}\) did not shift on deuteration, it should have major contribution from \(\nu\)C-N and \(\nu\)C=S. The bands at 945 and 855 cm\(^{-1}\) appeared as split bands in the spectra of the deuterated ligand. The split may mainly be due to the interaction of \(\delta\)N-D with \(\nu\)C-N and \(\nu\)C=S.

The band at 680 cm\(^{-1}\) is assigned mainly due to \(\nu\)C=S (thioamide band-IV). The position of this band as expected was not shifted on deuteration. A band at 700 cm\(^{-1}\) is assigned to \(\gamma\)NH, which shifts to 520 cm\(^{-1}\) on deuteration confirming the assignment.

**Spectra of the complexes** — The study of the IR spectra of present complexes can be classified into the following two broad classes: (A) Zn(II) and Pb(II) complexes where both the N-H groups of the ligand are deprotonated; (B) Ag(I), Tl(I), Hg(II) and Cd(II) complexes where one of the two N-H groups of the ligand is deprotonated.

**Complexes of Zn(II) and Pb(II)** — The bands due to \(\nu\)N-H and \(\nu\)N-H disappear indicating complete deprotonation of the complexes. The band due to \(\delta\)N-H at 1560 cm\(^{-1}\) shifts to 1510 cm\(^{-1}\) and the intensity of the band reduces considerably. The bands at 1065 and 945 cm\(^{-1}\) shift (±10 cm\(^{-1}\)) towards lower wave numbers indicating the bonding through thiocarbonyl sulphur.

**Complexes of Ag(I), Tl(I), Cd(II) and Hg(II)** — The intensities of the bands due to \(\nu\)NH and \(\gamma\)NH are reduced considerably. This indicates that one of the two N-H groups is deprotonated. This is also further substantiated by the fact that the intensities of the bands at 1560 and 1255 cm\(^{-1}\) are reduced. The position of the band at 1255 cm\(^{-1}\) shifts (±15 cm\(^{-1}\)) towards lower wave numbers indicating the bond order of CN to be slightly decreased. In the case of Hg(II) and Cd(II) complexes the bands split but in those of others these bands are broad showing the unsymmetrical nature of the complex.

The positions of the bands at 1065, 945 and 680 cm\(^{-1}\) shift towards lower wave numbers (±20 cm\(^{-1}\)) indicating the interaction of the metal ion through thiocarbonyl sulphur.

The position of the band at 1465 cm\(^{-1}\) remained practically constant indicating that the bond order of C≡N remains constant in the complexes. But this band becomes broad or splits in the spectra of the Cd(II) and Hg(II) complexes. This further indicates the unsymmetrical nature of the bonding in these complexes.
In the light of the IR results we propose for all the complexes reported in this paper polymeric structures with ligand links to metal ions through nitrogen and sulphur atoms. The insolubility of these complexes in water and other solvents points towards polymeric intermolecular linkages.

If the preferential stereochemistries of the metal ions are taken into account, Hg(II), Cd(II), Zn(II) and Pb(II) are expected to have tetrahedral geometries with linkages through S and N atoms. Ag(I), Ti(IV) complexes are expected to be linear with linkages through N and S.

References

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