Synthesis and characterisation of silver(I) complexes of some dithiocarbamates and thiosemicarbazones

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Silver(I) complexes of dithiocarbamates derived from morpholine (MorphDtc), piperidine (PipDtc), 1,2,3,4-tetrahydroisoquinoline (ThiqDtc), N-methylpiperazine (N-MePizDtc) and pyrrolidine (PyrrolDtc) and thiosemicarbazones of salicylaldehyde (SALTSC), 2-hydroxyacetophenone (HAPTSC), benzaldehyde (BALTSC) and piperonaldehyde (PIPTSC) have been synthesized and characterised. The complexes have the composition \([\text{Ag}(L)]^+\) where \(L\) = monoanionic dithiocarbamato or thiosemicarbazonato group. All the complexes are diamagnetic and behave as non-electrolytes in nitrobenzene solutions. IR spectra of the complexes indicate monovalent bidentate coordination of dithiocarbamates. The IR spectra also show that enolic form of thiosemicarbazones coordinates to the metal through sulphur. The dithiocarbamate complexes are stable up to 220°C while thiosemicarbazone complexes start decomposing at much lower temperatures (140°C).

Metal complexes of dithiocarbamates and thiosemicarbazones have aroused considerable interest in view of their industrial and biological importance. It has been observed that introduction of metal ions considerably modifies the properties of dithiocarbamates and thiosemicarbazones. This has led to an increased interest in the chemistry of the complexes of these molecules. The dithiocarbamato group, \(R_2\text{NCS}^-\), usually coordinates in a monovalent bidentate manner while thiosemicarbazones can coordinate through sulphur and hydrazinic nitrogen. Except for the pioneering synthetic studies by Akerstrom, Hesse and Nilson, and Cras, little work has been done on silver dithiocarbamates. Transition metal complexes of a few thiosemicarbazones have been reported. However, only one complex of silver(I) with thiosemicarbazone seems to have been prepared so far.

In this note, we report the preparation and characterisation of silver(I) complexes of dithiocarbamates derived from morpholine (MorphDtc), piperidine (PipDtc), 1,2,3,4-tetrahydroisoquinoline (ThiqDtc), N-methylpiperazine (N-MePizDtc) and pyrrolidine (PyrrolDtc) and of thiosemicarbazones of salicylaldehyde (SALTSC), 2-hydroxyacetophenone (HAPTSC), benzaldehyde (BALTSC) and piperonaldehyde (PIPTSC).

**Experimental**

Silver nitrate (AR, BDH), pyrrolidine and piperonaldehyde (Ridel AG) were used as such. Morpholine, piperidine, salicylaldehyde, benzaldehyde, 2-hydroxyacetophenone, 1,2,3,4-tetrahydroisoquinoline, N-methylpiperazine and thiosemicarbazide (Koch-Light) were used without further purification.

Dithiocarbamates were prepared using a method reported in literature.

For the preparation of thiosemicarbazones, an ethanolic solution of the respective carbonyl compound was added slowly to a hot ethanolic solution of recrystallised thiosemicarbazide until the mol ratio 1:1 was attained. The solution was refluxed for 2 hr and filtered while hot. The crystals separated on cooling were filtered and recrystallised from ethanol.

The purity of the compounds was checked by elemental analysis and TLC.

Silver was estimated volumetrically after decomposing the complexes with cone, HNO₃ using the ir-
Table 1—Colour and analytical data of silver(I) dithiocarbamates & thiosemicarbazones

<table>
<thead>
<tr>
<th>Complex (colour)</th>
<th>Found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag(MorphDtc)]</td>
<td>Silver</td>
</tr>
<tr>
<td>Greenish yellow</td>
<td>38.61 / 38.04</td>
</tr>
<tr>
<td>[Ag(PipDtc)]</td>
<td></td>
</tr>
<tr>
<td>Greenish yellow</td>
<td>39.62 / 38.04</td>
</tr>
<tr>
<td>[Ag(ThiqDtc)]</td>
<td></td>
</tr>
<tr>
<td>Pale yellow</td>
<td>33.83 / 38.04</td>
</tr>
<tr>
<td>[Ag(N-MePizDtc)]</td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>39.23 / 38.04</td>
</tr>
<tr>
<td>[Ag(PyrrolDtc)]</td>
<td></td>
</tr>
<tr>
<td>Pale yellow</td>
<td>34.15 / 34.04</td>
</tr>
<tr>
<td>[Ag(SALTSC)]</td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>36.37 / 36.04</td>
</tr>
<tr>
<td>[Ag(HAPTSC)]</td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>36.10 / 36.04</td>
</tr>
<tr>
<td>[Ag(BALTSCH)]</td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>36.10 / 36.04</td>
</tr>
<tr>
<td>[Ag(PIPLTSC)]</td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>32.92 / 36.04</td>
</tr>
</tbody>
</table>

on alum indicator. Sulphur was estimated gravimetrically as BaSO$_4$.

Molar conductance measurements were done on an Elico conductivity bridge CM 82T using a diprotype cell (CC-03). Magnetic measurements were made at room temperature on a Gouy balance, using Hg[Co(NCS)$_4$] as the calibrant. IR spectra were recorded in KBr and nujol mull on a Shimadzu IR-435 or Perkin-Elmer 397 spectrophotometer. Thermogravimetric measurements were made on a Perkin-Elmer TGS-1 thermobalance fitted with a Cahn Electrobalance under the conditions: heating rate, 10°C min; crucible, Pt: atmosphere, static air.

Results and discussion

The analytical data (Table 1) show that the complexes have the molecular formula [M(L)] where L= monoanionic dithiocarbamato or thiosemicarbazonato group.

All the complexes behaved as non-electrolytes. The $\Lambda_M$ values for dithiocarbamato complexes were found to be below 2 mho cm$^2$ mol$^{-1}$ in nitrobenzene while those for the thiosemicarbazone complexes were below 8 mho cm$^2$ mol$^{-1}$ in acetonitrile. In other solvents like MeOH, MeNO$_2$, DMF and (CH$_3$)$_2$CO the complexes were only sparingly soluble.

The complexes were found to be diamagnetic as expected for a d$^0$ system.

Strong bands present in the IR spectra of sodium dithiocarbamates around 3350 and 1620 cm$^{-1}$ can be assigned to νOH and δOH modes respectively of water of crystallization. In the spectra of the complexes these bands were not present showing the absence of lattice-held or coordinated water in the complexes.

The band observed in the region 1470-1450 cm$^{-1}$ in the IR spectra of dithiocarbamates is attributed to νC = N of thioureide group. The magnitude of C = N stretch depends on the ability of the substituent on the nitrogen atom to donate electrons. The C = N stretch in dialkyldithiocarbamates occurs at 1500 cm$^{-1}$. The red shift in the present case indicates a lowering of double bond character of C = N in dithiocarbamates derived from heterocyclic secondary amines. The tendency of heterocyclic ring systems to release electrons to the N – C bond is less than that of the alky groups. For the complex [Ag(ThiqDtc)], νC = N is observed at 1410 cm$^{-1}$. For all the other complexes νC = N occurs around 1460 cm$^{-1}$.

The band in the region 1030-940 cm$^{-1}$ can be assigned to asymmetric stretch of CSS moiety. The symmetric stretch of CSS appears around 890 cm$^{-1}$. The energy of the νCSS mode gives a rough estimate of the stability of the complexes. The complex with the lowest νCSS can be expected to be the most stable as it indicates a stronger bond between the metal and sulphur. In the present complexes, the presence of a single unsplit band in the region 1000-940 cm$^{-1}$ suggests occurrence of disulphur chelation. The νCSS in the present complexes is observed at a higher frequency than that in the dialkyldithiocarbamates which shows that the M – S bond in dialkyldithiocarbamates is, in general, stronger than the M – S bond in the dithiocarbamates derived from heterocyclic secondary amines. The N-MePizDtc complex shows νCSS at 1000 cm$^{-1}$. The lowest value of νCSS is exhibited by pyrrolDtc complex (940 cm$^{-1}$). On the basis of magnitude of νCSS, the stability order of the present complexes is found to be: pyrrolDtc > PipDtc > ThiqDtc > MorphDtc > N-MePizDtc.

All the four thiosemicarbazonates showed a band in the range 3450-3250 cm$^{-1}$ assignable to the stretching mode of NH$^{13,15}$. The band due to deformation modes of NH$_2$ and OH occurred as a strong band at 1640 ± 10 cm$^{-1}$. The strong band present at 3160 ± 10 cm$^{-1}$ in SALTSC and HAPTSC may be assigned to hydrogen-bonded νOH mode. The bands attributable to OH and NH$_2$ appeared more or less in the same regions in the spectra of the ligands and the complexes, indicating the non-participation of these groups in coordination.

Absence of bands in the region 2800-2650 cm$^{-1}$ clearly indicates that the ligands are not present in
the thiol form. Strong bands at 1600 ± 10 and 1550 ± 10 cm⁻¹ are assignable to coupled modes of C – N and N – H groups respectively. The band at 1600 ± 10 cm⁻¹ remained unaffected in complexes, but the band at 1550 ± 10 shifted to higher frequencies. This may be due to the coordination of the N – H nitrogen to metal.

A strong band present in the region ~ 1370 cm⁻¹ in the ligands can be assigned to the coupled modes of vC – N + vNH₂ + vC – S. In the metal complexes, this band occurred at 1380 cm⁻¹, a slightly higher energy. It is probable that the contribution of vC – N is more important in this case. The strong band at 1280 ± 10 cm⁻¹ in the spectra of the ligands is attributed to vCN + vCS. This band was lowered by 10 cm⁻¹ in all the complexes. The bands observed in the region 1220-1110 cm⁻¹ are deformation and rocking modes of NH. They were also slightly shifted to lower frequency region on complex formation. A strong band around 1060 cm⁻¹ in the spectra of the free ligands is assigned to N – N stretch.

The above observations suggest that the HN – C = S group in the ligands reacts with metal in the enol form coordinating through the deprotonated thiol sulfur. A weak band appearing at 450 ± 10 cm⁻¹ in the spectra of the metal complexes can be tentatively assigned to M – S stretching mode.

Complexes of ThiqDtc and PyrrolDtc were found to be stable from ambient temperature to 220°C. Thermally the most stable complex was the MorPhDtc complex which started decomposing only at 280°C. The PipDtc and N – Me PizDtc complexes were stable from ambient to 240 and 260°C respectively. All the complexes decomposed in a single stage leaving behind metallic silver as residue. Independent pyrolytic experiments were carried out which also showed the residue to be metallic silver.

The TG studies on thiosemicarbazone complexes showed that the complexes of SALTSC and BALTSC decompose in three stages. It has not been possible to correlate the mass loss observed in each stage with any specific change taking place in the complexes. The total mass loss observed after the complete decomposition of the complexes agreed well with the value calculated for their conversion to metallic silver. Independent pyrolytic studies also showed the final residue to be metallic silver.

The analytic, conductance and spectral data suggest that the dithiocarbamato complexes are likely to have a polymeric tricordinate structure as in the case of dialkyldithiocarbamate complexes. A linear polymeric structure can be assigned to thiosemicarbazone complexes.

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References