Mixed Ligand Complexes of Dioxouranium (VI) with Neocupferron

P. C. KUNDU* & A. K. BERA
Department of Pure Chemistry, University College of Science, Calcutta 700 009

Received 22 August 1978; revised and accepted 18 December 1978

Uranium (VI) forms 1 : 2 complex with neocupferron of the type [UO₃L₂(H₂O)₂], where L is union of neocupferron. Some of its derivatives having the compositions M₂[UO₃L₂X₂ₙ] · nH₂O (where X = F, Cl, Br, I, NO₃, SO₄, and M is univalent cation) and [UO₃L₂ phen]H₂O have also been isolated, and characterised on the basis of TG data, conductance values, and electronic and IR spectral data. U-O bond lengths and the force constants have been calculated from asymmetric stretching frequency of O-U-O group.

In a previous communication, we reported that uranyl ion forms 1 : 3 complex (ammonium salt of α-nitrosouaphthylhydroxylamine) with neocupferron. Recently, we have found that uranyl ion also forms a 1 : 2 complex with neocupferron. Using the metathesis reaction between 1 : 2 complex and other ligands like CO₃, SO₄, F, Cl, Br, I, NO₃, and 1,10-phenanthroline, different mixed ligand complexes both electrolytic and non-electrolytic in nature have been isolated. The preparation and characterization of these complexes are reported in this paper. The chelating behavior of the ligands with uranyl ion has also been studied on the basis of electronic and IR spectroscopy.

Materials and Methods
All the chemicals used were of AR grade. Neocupferron was prepared and purified by the method of Baudish. Nitrogen was analysed by Dumas method. Uranium was estimated either by Jones reductor technique using standard K₂Cr₂O₇ solution or as U₃O₈. Fluorine was estimated by the literature method but other halogens as silver halides. Sulphur was estimated as barium sulphate. Conductance measurements were carried out in 10⁻⁴M solution of DMF and acetonitrile at 30°C using a Philips conductivity bridge model GM 4249 and a dip-type cell. Electronic spectra of the complexes were recorded on a Hilger UVISPEK spectrophotometer using DMF and acetone as solvents. The IR spectra in cm⁻¹ of the complexes were recorded on a Perkin-Elmer 577 spectrophotometer using CsI pellets. Thermogravimetric analyses were carried out in a manual recording thermobalance at a heating rate of 7°C/min.

Diaquo-bis(neocupferronato)dioxouranium (VI) — Freshly prepared neocupferron (5g) was dissolved in water (100 ml), filtered and acidified by adding dil. HCl drop by drop until the precipitation of neocupferron acid was complete. The precipitate was filtered immediately and washed with water to remove ammonium chloride. The free acid was dissolved in 4% caustic soda solution and the pH of the solution maintained between 5.5 and 6.0 and filtered. To uranyl nitrate hexahydrate solution (9%, 100 ml) was added the above filtrate dropwise with constant stirring. An orange yellow crystalline precipitate separated out. It was allowed to stand for 1 hr. filtered and washed with water till free from uranyl nitrate. It was finally washed with ether and dried over conc. H₂SO₄ in a vacuum desiccator. Colour of the product changed to greenish yellow upon drying; yield 76%.

Ammonium carbonato-bis(neocupferron) dioxouranium (VI) — To an aqueous ammonium carbonate (6%, 10 ml), methanol (40 ml) was added. To this methanolic solution of diaquo-bis (neocupferron) dioxouranium (VI) (0.8 g) was added in small lots with constant stirring. When almost the whole amount of the diaquo salt was dissolved, it was filtered to remove the undissolved diaquo salt. To the filtrate, water (50 ml) was added and pH of the solution brought to 7.0 by adding dil. HCl. Immediately an orange red crystalline precipitate separated out. After 1 hr, it was filtered, washed with water and dried over conc. H₂SO₄; yield 66%

1,10-Phenanthroline-bis(neocupferron) dioxouranium (VI) — 1,10-Phenanthroline (1.6g) was dissolved in methanol (25 ml) and to this was added diaquo-bis (neocupferron) dioxouranium (VI) (1g) gradually with constant stirring during ½ hr when a yellowish coloured salt separated out. It was filtered, washed with ethanol and dried over conc. H₂SO₄; yield 70%.

Sulphato, nitrato and halo-complexes — These were prepared by the metathesis reaction between diaquo-bis (neocupferron)dioxouranium (VI) and corresponding ammonium or sodium salts in methanol-water solvent. In each case aqueous solutions of the respective salts (20 ml, 10%) were prepared and to these solutions, diaquo salt (0.5—0.6 g) was added in small lots during 1/2 hr with constant stirring. Methanol (50 ml) was added and stirred for another 10 min. After filtering, water was added to the filtrates with stirring till the crystalline precipitates of the corresponding salts separated out. These were allowed to settle for ½ hr, filtered, washed first with water and then with ether and dried over conc. H₂SO₄; yield 65-70%.

*Author to whom all correspondence should be made.
Results and Discussion

All the complexes are coloured, insoluble in water but soluble in methanol, dimethylformamide and dimethyl sulphoxide. Except the diaquo salt, all other salts are appreciably soluble in acetone and acetonitrile. The characterization data of the complexes, including electronic spectral data are recorded in Table 1.

Molar conductance values of the complexes in DMF and acetonitrile, given in Table 1, show that except the diaquo and 1,10-phenanthroline complexes, other behave as electrolytes, with conductance values lower than those for 2 : 1 electrolytes. These low values explain the incomplete dissociation of the salts in organic solvents. The diaquo and 1,10-phenanthroline complexes behave as non-electrolytes, as expected.

TG studies of the complexes show that except the diaquo complex, all other complexes contain water of crystallisation. The elimination of lattice water takes place between 70° and 90°C and the salts become anhydrous ~ 120°C but the sulphato complex decomposes at 100°C before dehydration. From the decomposition temperatures shown in Table 1, it is found that the order of stability of the complexes is diaquo > fluoro > chloro > nitrato > carbonato = bromo > 1,10-phen. > iodo > sulphato. Between 480°C and 680°C the residues attain constant weight with the composition UsO2. The water molecules in the diaquo complex are not lost upto 150°C and thereafter the compound begins to lose mass slowly and this continues upto 200°C. At this point, the compound decomposes abruptly due to necocupferron units. From 540°C, the weight becomes constant due to the formation of UO2. The presence of water molecules in the diaquo complex is also supported by the appearance of ν-OH at 3460 in the IR spectrum. Though it is not possible to distinguish between lattice water and coordinated water by νO—H, the bands at 905 and 510 provide evidence for coordinated water. It is well established that uranyl ion possesses planar hexagonal structure with two oxygen atoms in the axial position. In the present complex, two necocupferron units and two water molecules remain in the equatorial plane. It is also suggested that the two water molecules remain in the cis-position as they are replaced by bidentate ligands like CO3, SO4 and 1,10-phenanthroline.

Electronic spectral data have been recorded in the region 27,770 to 18,180 cm⁻¹ using DMF and acetone solvents. The peak positions are almost same in each solvent suggesting the absence of any solvent effect. The characteristic peaks of the present compounds reveal that the equatorial ligation have some influence on the spectrum of the uranyl ion. The low intensity bands in the region 21,010 cm⁻¹ suggest that transition has occurred between 5f orbitals and it may be assigned to 2Σg⁻→4T₂ transition which is somehow at lower region than that of free UO2⁺ ion. The bands in the region 27,000 cm⁻¹ are due to charge transfer from ligand to uranium and the bands in the region 21,830 and 20,410 cm⁻¹ are due to vibration of the uranyl entity.

Table 1 — Decomposition Temperature, Analytical Conductance and Electronic Spectral Data of the Mixed Ligand Complexes with Necocupferron

<table>
<thead>
<tr>
<th>Compound</th>
<th>Decomposition temp. (°C)</th>
<th>Colour</th>
<th>Molar conductance, (Ω⁻¹ cm² mol⁻¹)</th>
<th>ν(OH) (cm⁻¹)</th>
<th>ν(CO3) (cm⁻¹)</th>
<th>ν(SO4) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂UO₂CO₃.H₂O</td>
<td>110</td>
<td>Brown</td>
<td>3920</td>
<td>1420</td>
<td>1420</td>
<td></td>
</tr>
<tr>
<td>Na₂UO₂SO₄.H₂O</td>
<td>110</td>
<td>Yellow</td>
<td>3920</td>
<td>1420</td>
<td>1420</td>
<td></td>
</tr>
<tr>
<td>Na₂UO₂CL·H₂O</td>
<td>110</td>
<td>Yellow</td>
<td>3920</td>
<td>1420</td>
<td>1420</td>
<td></td>
</tr>
<tr>
<td>Na₂UO₂NIT·H₂O</td>
<td>110</td>
<td>Yellow</td>
<td>3920</td>
<td>1420</td>
<td>1420</td>
<td></td>
</tr>
</tbody>
</table>

In acetone
Among the three fundamental modes of vibrations of the UO$_2^+$ ion, $v_4$ (asymmetric stretching frequency) and $v_2$ (bending vibration) are IR active in the present complexes which explain the linearity of the uranyl anity. The bands in the region 3500 and 1630 are assigned to OH and 80–H but the bands around 3160 and 1615 are due to N–H and E–H respectively. The $v$–O of neocupferron appears as a triplet at 1220, 1200, 1180 and are shifted to lower region by 10–15 cm$^{-1}$ on complex formation. This indicates that chelation takes place through oxygen of neocupferron. Further, a band is found in the region 380–400 which is assigned to U–O bond of the complexes. In phenanthroline complex, the band at 300 is attributed to equatorial U–N bond. The analytical data and the metal ligand bands of the different ligands suggest that coordination of these ligands with uranium has no effect on neocupferron units.

Carbonato complex — In the carbonato complex, all the fundamental modes of vibrations are present. $v_4$ which is generally IR forbidden in the free carbonate ion ($D_{3d}$) is found at 1565 and 1535 and this indicates the presence of coordinated carbonate group. The splitting difference between $v_4$ and $v_3$ of this complex tentatively suggests the bidentate nature of the carbonate group with $C_{3v}$ symmetry. The band at 465 assigned to $v_7$ supports the above view for carbonate group.

Sulphato complex — All the four fundamentals are IR active in the present complex. $v_4$ (symmetric stretch) and $v_2$ (symmetric bend) which are IR, forbidden for uncoordinated sulphate group of $D_{6h}$ symmetry are found in the complex at 995 and 490 respectively. $v_3$ (asymmetric stretch) is splitted into triplet and their positions are found at 1180, 1140 and 1015. The bands at 640, 620 and 605 are due to $v_2$ (asymmetric bend) splitting. The splitting of $v_2$ and $v_4$ into triplets suggests that the sulphate group with $C_{3v}$ symmetry remains as bicoordinated ligand.

Nitrato complex — The free nitrate ion ($D_{3d}$) has four fundamental vibrations, three of which are IR active. In the present scomplex, six modes of vibrations are found, suggesting that the nitrate ion is coordinated with uranium and the symmetry is lowered to $C_{3v}$. The bands at 705 and 735 may be assigned to $v_4$ (asymmetric bend) and $v_3$ (symmetric bend) of the two N–O bonds respectively. The strong and sharp band at 810 can not be assigned definitely to $v_4$ of the nitrato group because a similar band is also found in neocupferron. The bands at 1540, 1325 and 990 are attributed to $v_4$ (asymmetric stretch), $v_1$ (symmetric stretch) and $v_2$ respectively. The splitting difference between $v_4$ and $v_3$ is close to that of a unidentate nitrato group found in the literature.

Halo complexes — The halo complexes show almost similar type of bands. The investigation of the halo complexes shows that the bands found in the region 300–285 cm$^{-1}$ are tentatively assigned to U–X where X = F, Cl, Br and I.

### Table 2 — Force Constants and U–O Bond Lengths of the Mixed Uranyl Complexes with Neocupferron

<table>
<thead>
<tr>
<th>Compound</th>
<th>$(v_0 - u - o)$ cm$^{-1}$</th>
<th>$F_{u-o}$ (mdyn/Å)</th>
<th>$R_{u-o}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO$_4$F$_4$]-</td>
<td>920</td>
<td>7.04</td>
<td>1.73</td>
</tr>
<tr>
<td>[UO$_4$Cl$_4$]-</td>
<td>890</td>
<td>6.59</td>
<td>1.75</td>
</tr>
<tr>
<td>[UO$_4$Br$_4$]-</td>
<td>890</td>
<td>6.59</td>
<td>1.75</td>
</tr>
<tr>
<td>[UO$_4$I$_4$]-</td>
<td>890</td>
<td>6.59</td>
<td>1.75</td>
</tr>
<tr>
<td>$L = C_{14}H_{24}N_{14}O_{16}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References
