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FLUORONITROSO COMPLEXES OF RHENIUM

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SUMMARY

The first stable series of fluoronitroso complexes have been prepared with rhenium. These include $M_2[Re(NO)F_5]$ (M = K, Cs), $Re(NO)LF_3$ (L = dipy, phen), $Re(H_2O)_2(NO)(OH)F_2$, $Re(H_2O)_2(NO)(OH)_2F$ and a cationic species $[Re(dipy)_2(NO)F]PtCl_6$. These are characterized by their analytical, magnetic, conductance and i.r. spectral data.

INTRODUCTION

Halonitrosyl complexes of transition elements are varied and well known, the chloro and bromo nitrosyls being particularly well characterized. Curiously enough, the fluoro derivatives of the metal-nitroso complexes are practically unknown with the lone exception of $Cu(NO)F_2$, which again is rather ill-defined and is known to exist only in solution [1]. The absence of fluoronitroso derivatives may, in part, be due to the absence of d-orbitals in fluoride ligands and the consequent inability of these ligands to remove electron density from the metal atoms which they usually acquire from the nitric oxide. We have, for the first time, been able to synthesize and characterize a series of really stable fluoronitroso derivatives of rhenium. This forms the subject matter of the present communication.

RESULTS AND DISCUSSION

The preparation and properties of $Re(NO)(OH)_3$ has been described earlier [2]. The most obvious route for the syntheses of fluoro complexes of rhenium is by reacting this hydroxide with hydrofluoric acid. The resulting solution contains $H_2Re(NO)F_5$ which, however, cannot be isolated as such either by precipitation or by drying. $Re(NO)F_3$ also cannot be obtained in the solid state but may exist in solution. $Re(H_2O)_2(NO)F_2(OH)$ is obtained as an insoluble powder by drying a mixture of hydrofluoric acid and $H_2Re(NO)F_5$ on the water bath. This difluoro compound, on pyrolysis, loses one molecule of hydrofluoric acid and after the absorption of one molecule of water from the atmosphere gives a monofluoro complex, $Re(H_2O)_2(NO)F(OH)_2$. From the solution of $Re(NO)(OH)_3$ in aqueous HF, the potassium and caesium salts of $H_2Re(NO)F_5$ are obtained by the addition of the corresponding alkali fluorides, showing the presence of the free acid in solution. On treatment of the solution with basic diimines like 2,2'-dipyridyl or 1,10-phenanthroline, non-electrolytic compounds viz., $Re(dipy)(NO)F_3$ and $Re(phen)(NO)F_3$ have been obtained as insoluble substances. A cationic species viz., $[Re(NO)(dipy)_2F]^{2+}$, which can be isolated as its chloroplatinate salt, is produced along with the non-electrolytic compound.

The potassium and caesium salts of $[Re(NO)F_5]^{2-}$ are moderately soluble in water to produce green solutions. Aqueous solutions are not stable in absence of free acid and, on standing, slowly decompose, the colour of the solution changing to brown. The free acid, $H_2Re(NO)F_5$, can be obtained in aqueous solution by passing a freshly prepared aqueous solution of $Cs_2Re(NO)F_5$ through a column of Amberlite IR 120 cation exchanger in its H^+ form packed in a polythene tube. This is a strong acid but gradually hydrolyses in water. Potentiometric titration of the acid in an air free environment using a quinhydrone electrode shows a sharp change of pH on the addition of five equivalents of the base with two ill-defined breaks at 2 and 4 equivalents of added alkali.

After the addition of five equivalents of base the green colour of the solution disappears with precipitation of $Re(NO)(OH)_3$. The absence of any precipitate in the intermediate stages of titration proved that hydrolysed products like $Re(H_2O)_2(NO)(OH)F_2$ or $Re(H_2O)_2(NO)(OH)_2F$ were not generated by the reaction with alkali.

These fluoronitroso complexes are completely analogous to the corresponding chloro and bromo nitroso derivatives of rhenium [2,4,5,6]. The fluoro series is remarkable for the absence of a solid nitrosotrifluoride - the parent compound. It is known [7] that $Re(NO)Cl_3$, the parent chloro complex, exists in solution in the form of $Re(NO)(OH)Cl_2$.aq but, on evaporation of the solution in presence of hydrochloric acid, reformation of the trichloro species takes place provided that the heating is not continued in absence of free HCl. The same is true for the bromo compound. In the case of the fluoro compound, the monohydroxo species is insoluble in water and is only attacked by hydrofluoric acid on prolonged digestion with direct formation of $H_2Re(NO)F_5$. Such a situation explains our inability to isolate the trifluoro compound and points to a polymeric structure of the hydroxofluoro complex, $Re(H_2O)_2(NO)(OH)F_2$ which may involve fluorine bridges.

The total oxidation number of the 'Re(NO)' unit has been determined [2] to be +3 as in the cases of the chloro and bromo [6] compounds. Due to the uncertainty [2] in the charge state of 'NO', the oxidation state of rhenium in these complexes remain uncertain and is not, therefore, mentioned in the formulae.

The non-electrolytic nature of the nitrosotrifluoro dipyridyl and phenanthroline derivatives have been confirmed from their conductance measurements in dimethylsulphoxide. The molar conductivity for the dipyridyl complex was 3.61 $ohm^{-1}cm^2$ and for the phenanthroline complex was 4.51 $ohm^{-1}cm^2$ at 30°. The magnetic moment values of these complexes are given in Table 1. For the alkali metal salts of the ion $[Re(NO)F_5]^{2-}$, the values indicate the presence of one unpaired electron. The absolute values are lower than the

TABLE 1

Infrared bands (in KBr) and Magnetic moments (at 30°)

Compound μ (eff) in B.M.	i.r. bands (in cm^{-1})
$Cs_2[Re(NO)F_5]$ 1.09	1720(s,sh), 1660(s,sh),1530(w,br), 1260(w,sh), 1135(w,br),1045(w,br), 740(m,sh), 635(m,sh),500(s), 480(s,sh)
$K_2[Re(NO)F_5]$ 1.26	1740(s,sh),1670(s,sh),1530(w,br), 1230(w,br),1120(s,sh),1050(w,br), 915(s,sh),745(s,sh),620(m,sh), 585(w),510(s),485(s,sh),365(w,sh)
$Re(H_2O)_2(NO)(OH)F_2$ 0.64	3400(m,br),1760-1690(m,br), 1080-980(w,br),900(w,br),725-600 (s,br).
$Re(H_2O)_2(NO)(OH)_2F$ 0.71	3400-3000(m,br),1760-1690(s,br), 1060-970(m,br),900(s,sh), 750-600(s,br).
$Re(phen)(NO)F_3$ 1.26	3400(m,br),1750(s),1685(s,br), 1510(w,sh),1425(m,sh),1335(w,sh), 1300(w,sh),1200(m,br),1130(m,sh), 1100(m,sh),1020(m,sh),840(s,sh), 710(s,sh),610(w,br),490(s),740(s,sh).
$Re(dipy)(NO)F_3$ 0.41	3420(s,br),1750(s),1700(s), 1600(s,sh),1470(w,sh),1445(m,sh), 1315(w,sh),1280(w,br),1240(w,br), 1160(w,sh),1110(w,br),1040(w,sh), 770(s,sh),600(w,sh),500(s),480(s,sh).
$[Re(dipy)_2(NO)F]PtCl_6$	3400(s,br),1700(s,sh),1600(s,sh), 1460(w,sh),1435(s,sh),1305(w,sh), 1230(w,sh),1150(w,sh),1100(w,br), 1000(w,br),760(s,sh),720(w,sh), 600(w,br),500(m,br),420(w,br).

s = strong, m = medium, w = weak, sh = sharp, br = broad.

spin only values, due to orbital contribution and antiferromagnetic effects. For the non-electrolytic compounds, the difference in magnetic moments is significant. The value for the dipyridyl compound is abnormally low. This might be due to the steric influence of the ligand which is capable of forming bridges between two different rhenium atoms and the non-electrolyte is considered to be a polymer with bridging dipyridyl ligands. The lower μ(eff) values of the hydroxo derivatives are also attributable to their polymeric structures. Molecular weight determinations were not possible due to their insolubility in suitable solvents.

The infrared bands for these fluoronitroso derivatives have been listed in Table 1. The stretching mode for nitric oxide is exhibited in the region of 1720-1750 cm^{-1} in all the compounds. The weak band at 610 cm^{-1} can be assigned to the Re—N stretch. The 740 cm^{-1} and 480 cm^{-1} bands are due to the two Re—F vibrational modes.

EXPERIMENTAL

Johnson Matthey's 99.8% potassium perrhenate was the source of rhenium. Infrared spectra were recorded on a Beckmann IR 20 instrument in KBr pellets. Magnetic susceptibility measurements were made with a Gouy balance. Potentiometric measurements were done with an ECIL Expand pH meter of the Electronics Corporation of India using a quinhydrone-saturated calomel electrode assembly. Conductivity measurements were done with a Philips' RCL bridge. For the purpose of analysis, the compounds were decomposed either with hydrogen peroxide in solution or by fusion of the solid with sodium-potassium carbonate with free access of air in a platinum crucible. The cationic chloroplatinate was decomposed by heating in a current of hydrogen, the hydrogen fluoride being fixed by adding sodium carbonate. Platinum was determined in the residue in the boat by extracting the sodium fluoride and then igniting off the rhenium as Re_2O_7.

Potassium nitrosopentafluororhenate, $K_2 Re(NO)F_5$

200 mg of $Re(NO)(OH)_3$ was dissolved in a minimum volume of 40% hydrofluoric acid and the solution filtered. The clear filtrate was digested for one hour with 100 mg of potassium fluoride and then evaporated to dryness on a water bath. The residue was dissolved in the minimum volume of water and filtered again. Ethanol was added to the filtrate, when precipitation of potassium salt took place. In order to get a pure product (free from KHF_2) incomplete precipitation was performed. The process was repeated twice. The precipitate was finally centrifuged and washed with ethanolic hydrofluoric acid and then dried in vacuum. 150 mg of the product was obtained.

Caesium nitrosopentafluororhenate, $Cs_2 Re(NO)F_5$

200 mg of hydrated rhenium(IV) oxide (free from any adsorbed metal ion) was suspended in 50 ml of 4M aqueous hydrofluoric acid in a closed polythene flask. It was freed from air by a stream of carbon dioxide. A slow stream of pure nitric oxide was then passed through the suspension kept at 70-80° for 24 hours. The resulting solution was freed from nitric oxide by passing CO_2 and then digested on a water bath with 300 mg of caesium fluoride for 3 hours and finally evaporated to dryness. The deep green mass was extracted with the minimum volume of water and then precipitated fractionally by the addition of ethanol. Repeated extractions and precipitations were done to get a product free from caesium perrhenate [3] and caesium bifluoride. The solid was finally dried in vacuum. The yield was 250 mg.

The same product could also be obtained by dissolving nitrosotrihydroxorhenium in hydrofluoric acid and subsequent digesting with caesium fluoride, following a procedure exactly similar to that of the potassium salt.

These salts are highly soluble in water, producing deep green solutions. The aqueous solutions are considerably more stable to hydrolysis than the chloro and bromo compounds. The visible absorption spectrum of the freshly prepared aqueous solution showed maxima at 15.15 and 21.74 kK with log ϵ values of 2.58 and 2.09 respectively. The analytical data of the compounds are given in Table 2.

Diaquonitrosohydroxodifluororhenium, $Re(H_2O)_2(NO)(OH)F_2$

250 mg of nitrosotrihydroxorhenium was digested with 20 ml of 40% aqueous hydrofluoric acid for a prolonged period to make the dissolution as complete as possible. The deep green solution was filtered from insoluble solids and was evaporated just to dryness on a water bath. The deep green solid was thoroughly washed with cold dilute hydrofluoric acid and finally with ethanol. 200 mg of the air-dried product was obtained.

The compound is insoluble in all common organic solvents and could only be taken in solution by prolonged digestion with aqueous hydrofluoric acid. The analytical data of the compound are given in Table 2.

Diaquonitrosodihydroxomonofluororhenium, $Re(H_2O)_2(NO)(OH)_2F$

A weighed quantity (50 mg) of the difluoro compound was taken in a platinum boat and heated slowly to 100-105° in an atmosphere of carbon dioxide. There was no apparent change in colour but evolution of hydrofluoric acid took place. After about one hour the system was allowed to cool to room temperature. The residue in the boat was quickly weighed. The loss in weight was 11.9% which corresponded to the loss of one equivalent each of water and hydrofluoric acid (12.4%) from the difluoro compound. The residue in the boat was hygroscopic and, on allowing it to stand, gained weight corresponding to the absorption of two molecules of water from the atmosphere. This product is also insoluble in all organic solvents. Its analytical data are given in Table 2.

TABLE 2

Analytical data and colour of the compounds

Compound Colour	% Re	% F	% other metal	% N
$Cs_2Re(NO)F_5$	32.5	16.6	46.8	2.73
Dark green	(32.3)	(16.5)	(46.1)	(2.43)
$K_2Re(NO)F_5$	48.1	25.2	19.2	3.95
Dark green	(47.8)	(24.4)	(20.1)	(3.59)
$Re(H_2O)_2(NO)(OH)F_2$	61.1	12.5		4.44
Dark green	(60.6)	(12.4)		(4.56)
$Re(H_2O)_2(NO)(OH)_2F$	60.0	7.13		4.67
Dark green	(60.9)	(6.22)		(4.60)
$Re(phen)(NO)F_3$	40.6	11.6		9.90
Black	(41.1)	(12.5)		(9.26)
$Re(dipy)(NO)F_3$	43.4	14.1		9.31
Black	(43.4)	(13.3)		(9.78)
$[Re(dipy)_2(NO)F]PtCl_6$	24.3*	2.41	20.4	6.67
Brown	(25.1)	(1.99)	(20.4)	(7.32)

Figures in parentheses are the required percentages
*percentage of carbon

1,10-phenanthrolinenitrosotrifluororhenium, $Re(phen)(NO)F_3$

200 mg of $Re(NO)(OH)_3$ and 150 mg of 1,10-phenanthroline were allowed to react in aqueous hydrofluoric acid solution. After evaporation on a water bath the residue was washed with ethanolic hydrofluoric acid and finally with pure ethanol. The analytical data are given in Table 2. The visible absorption spectrum was recorded in DMSO and showed maxima at 14.49 and 20.00 kK with $\log\epsilon$ values of 2.70 and 2.82 respectively.

2,2'-dipyridylnitrosotrifluororhenium, $Re(dipy)(NO)F_3$

To a solution prepared from 300 mg of $Re(NO)(OH)_3$ in aqueous hydrofluoric acid, excess dipyridyl hydrofluoride was added and the mixture was evaporated to dryness on a water bath. The dry mass was extracted with ethanolic hydrofluoric acid when, unlike the phenanthroline derivative, a red brown solution was extracted out leaving a dark coloured residue. The residue was thoroughly washed with ethanolic hydrofluoric acid and finally with pure ethanol. 100 mg of the product was obtained. It was analysed (Table 2) and was also found to be a non-electrolytic species in DMSO. The visible absorption spectrum was recorded in DMSO and showed maxima at 14.71 and 22.22 kK with $\log\epsilon$ values of 3.14 and 3.24 respectively.

Bis 2,2'-dipyridylnitrosomonofluororhenic hexachloroplatinate, $[Re(dipy)_2(NO)F]PtCl_6$

The ethanolic hydrofluoric acid extract obtained from the preparation of dipyridylnitrosotrifluororhenium was evaporated to dryness and the residue was washed well with dry benzene to remove the excess dipyridyl hydrofluoride. The washed mass was then dissolved in a minimum volume of ethanol and an ethanolic solution of chloroplatinic acid was added. The brown coloured precipitate was filtered, washed with ethanol and then dried. 50 mg of the salt was obtained which was analysed (Table 2).

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