Alkali metal and ammonium oxoperoxomolybdenum(VI) complexes derived from salicylaldehyde isonicotinoylhydrazone.

R A Lal*, M L Pal, J Chakraborty & A Kumar
Department of Chemistry, Tripura University, Agartala 799004, Tripura, India
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The alkali metal and ammonium oxodiperoxomolybdenum(VI) complexes M[MoO(02h)(H5sih)].H2O (M = K(1), Na(2), and NH4(3)) and dioxoperoxomolybdenum(VI) complexes M[MoO2(O2)(Hsih) (C2H5OH)].H2O (M = K(4) and Na (5)) derived from salicylaldehyde isonicotinoylhydrazone (H5sih) have been synthesized in aqueous-ethanol media. The structural assignment of the complexes has been carried out on the basis of molar conductance, magnetic moment, EPR data and IR spectroscopic studies. H5sih coordinates to the metal centre in keto form as a monobasic bidentate ligand through phenolate oxygen atom and azomethine nitrogen atom. Peroxide is coordinated to the metal centre in a bidentate chelating fashion. All the complexes are proposed to have seven coordinate polyhedra around the molybdenum centre.

A survey of literature indicates that although metal complexes of hydrazides and hydrazones have been studied to a considerable extent1-6 reports on complexes involving peroxo as co-ligand are meagre7. In view of this, it was thought of interest to synthesize and characterize the oxo-peroxo molybdenum(VI) complexes involving coordinated salicylaldehyde isonicotinoylhydrazone (1).

![Salicylaldehyde isonicotinoylhydrazone (H5sih)](image)

Experimental
Molybdic acid, isonicotinoylhydrazone and salicylaldehyde were E. Merck reagents. Salicylaldehyde isonicotinoylhydrazone was prepared by the method of Sacconi8.

Molybdenum was determined gravimetrically by using 8-hydroxyquinoline (oxine) as the reagent7. The peroxide content was determined iodometrically in the presence of boric acid using a standard solution of sodium thiosulphate. Carbon, hydrogen and nitrogen were determined microanalytically. Water and ethanol contents were determined by heating the samples in an electric oven in the temperature range 80-250°C and determining the weight loss and passing the vapours through a trap containing anhydrous copper sulphate and through a solution of NaOH and iodine in a test tube. The molar conductance values of the complexes of 10-2 molar solutions in water were measured using a direct reading conductivity meter with a dip type conductivity cell. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer in the 4000-180 cm⁻¹ region. The pH of the reaction solutions was measured with pH indicator (BDH) paper.

Preparation of M[MoO(O2h)(Hsih)].H2O (M = K(1), Na(2) and NH4(3))
A typical procedure for the preparation of these complexes is given below. In order to prepare K[MoO(O2h)(Hsih)]. H2O (1), MoO3(0.5 g. 173.6 mmol) was suspended in 20 mL ethanol and stirred for about 15 min. To the suspension was added 10 mL, 30% H2O2 accompanied by stirring for about 30-45 min, at 60-65°C. Any undissolved material was removed by filtration. H5sih (0.83 g, 34.4 mmol) was dissolved in 100 mL ethanol by boiling for about 10 min. To MoO3 solution in 20 mL ethanol, H5sih solution was added slowly at 70°C accompanied by slow stirring in a period of 10-15 min. This gave an orange solution which was heated at 70-75°C for about 1 h accompanied by stirring. This followed addition of 4 mL of 10% KOH solution in water at 75°C accompanied by stirring. The reaction mixture was gently stirred for 5 min. This precipitated a yellow compound which was washed with ethanol and dried by pressing between the folds of filter paper and then under vacuum. The complex was stored in a polythene bag.
The compounds Na[MoO\(_2\)(Hsih)]\(\cdot\)H\(_2\)O (2) and NH\(_4\)[MoO\(_2\)(Hsih)]\(\cdot\)H\(_2\)O (3) were prepared by essentially the above procedure by using NaOH and NH\(_4\)OH, respectively, instead of KOH.

**Preparation of M[MoO\(_2\)\(_2\)\(\cdot\)\(\cdot\)H\(_2\)O] (M = K(4) and Na(5))**

A typical procedure for the preparation of these complexes is presented below.

In order to prepare the compound K[MoO\(_2\)\(_2\)\(\cdot\)H\(_2\)O] \(\cdot\)H\(_2\)O (4), MoO\(_3\) (0.5 g, 173.6 mmol) was suspended in 20 mL ethanol and stirred for about half an hour. To it, a hot solution of KOH (34.4 mmol) of H\(_2\)sih dissolved in 100 mL ethanol was added and stirred for half an hour. The solution was cooled to room temperature and then 10 mL, 30% H\(_2\)O\(_2\) was added. The mixture was stirred for about 2 h at 70°C accompanied by reduction of the volume to 50 mL which precipitated an orange coloured compound. The volume of the reaction mixture was further reduced to about 15 to 20 mL by evaporating the reaction mixture gently until a wet mass remained. The reaction mixture was brought to room temperature. To this mixture was added slowly accompanied by stirring at room temperature over a period of 5 min and then left overnight at room temperature accompanied by stirring. This gave a yellow coloured precipitate. The pH of the supernatant liquid was found to be 6.0. The precipitate was filtered, washed with ethanol, ether and dried at ambient temperature and stored in a polythene bag.

Na[MoO\(_2\)\(_2\)\(\cdot\)H\(_2\)O] \(\cdot\)H\(_2\)O (5) was also prepared by essentially the above procedure using NaOH instead of KOH.

**Results and discussion**

When the reaction of a solution of MoO\(_3\) in ethanolic H\(_2\)O \(\cdot\) with H\(_2\)sih was carried out at pH 6.0 (by addition of alkali metal hydroxide and ammonium hydroxide), the monooxo-diperoxo complexes M[MoO\(_2\)(Hsih)]\(\cdot\)2H\(_2\)O \(\cdot\)M = K(1), Na(2) and NH\(_4\)(3) were obtained. On the other hand, when the reaction of a mixture of hot ethanolic solution of MoO\(_3\) and H\(_2\)sih with H\(_2\)O\(_2\) was carried out at pH 6.5, another series of dioxomonoperoxomolybdenum(VI) complexes of the composition M[MoO\(_2\)(Hsih)(C\(_2\)H\(_5\)OH)]\(\cdot\)H\(_2\)O \(\cdot\)M = K(4), Na(5) were obtained.

When the reaction of a solution of MoO\(_3\) in ethanolic H\(_2\)O with H\(_2\)sih was carried out at pH 6.5, another series of dioxomonoperoxomolybdenum(VI) complexes of the composition M[MoO\(_2\)(Hsih)(C\(_2\)H\(_5\)OH)]\(\cdot\)H\(_2\)O \(\cdot\)M = K(4), Na(5) were obtained. These compounds are insoluble in ethanol, methanol, acetone and other common organic solvents and are soluble in water, DMF and DMSO. Heating of these complexes at 100°C was accompanied by the loss of active oxygen which precluded their genuine dehydration. These complexes are stable in a freezer for about a month. Their stability can be ascertained by chemical estimation of active oxygen contents and recording of IR spectra periodically. The peroxide estimation was accomplished iodometrically by redox titration involving standard solution of Na\(_2\)S\(_2\)O\(_3\). Boric acid was used to avoid any loss of active oxygen. The results of replicate determinations of the peroxide as well as Mo contents indicated the ratio of Mo:O\(_2\) as 1:2 in M[MoO\(_2\)(Hsih)]\(\cdot\)H\(_2\)O complexes and as 1:1 in M[MoO\(_2\)(Hsih)(C\(_2\)H\(_5\)OH)]\(\cdot\)H\(_2\)O complexes, respectively, lending credence to the suggested structure.

The molar conductance values of these compounds lie in the region 140.2-109.7 ohm\(^{-1}\) cm\(^{2}\) mol\(^{-1}\). This value is higher than that expected for 1:1 electrolyte. This indicates that the complexes are highly dissociated in aqueous medium.

The most important features of the IR spectra of the complexes are strong bands in the 965-930 and 911-711 cm\(^{-1}\) regions. The single band appearing in the region 964-959 cm\(^{-1}\) in the complexes (1) to (3) is assigned to \(\nu\)(Mo=O) arising form terminally bonded Mo=O group. On the other hand, the two bands appearing at 950 and 930 cm\(^{-1}\) in the complex (5) and four bands appearing at 965, 951, 938 and 931 cm\(^{-1}\) in the complex (4) are assigned to the symmetric and asymmetric stretching vibrations of the cis-MoO\(_2\)\(^{2+}\) group.

The appearance of four bands in the complex (4) may be attributed to coupling between oxo-oxygens and peroxy group in this complex. The strong bands
appearing in the region 911-771 cm\(^{-1}\) have been assigned to \(v(O-O)\) mode of coordinated peroxide.\(^{15}\) The stretching mode of coordinated peroxy group in complex (4) also shows four bands at 911, 871, 851, and 771 cm\(^{-1}\) due to reason cited above. The complementary \(v_3(Mo-O_2)\) and \(v_3(Mo-O_2)\) modes appear in the regions 688-684 and 590-552 cm\(^{-1}\), respectively. These observations are rather typical of the (O\(_2^2\)) ligand, bonded to the metal centre in a triangular bidentate (C\(_2v\)) manner.

The amide I band shifts to higher frequency by 3-5 cm\(^{-1}\) in all the complexes except the ammonium complex (3) and appears as a strong band in the region 1680-1678 cm\(^{-1}\) (at ca 1675 cm\(^{-1}\) in H\(_2\)sih). This rules out the possibility of coordination of carbonyl oxygen atom to the metal. In the complex (3), the amide I band shifts to lower frequency by 25 cm\(^{-1}\) and appears at 1650 cm\(^{-1}\). However, this cannot be related to coordination of >C=O group to the metal centre; instead, it may be attributed to hydrogen bonding between carbonyl oxygen and ammonium ion. The band due to bending C-O vibration at 1288 cm\(^{-1}\) splits into two components showing shifts to higher as well as lower frequency indicating coordination through phenolate oxygen atom.\(^{16}\) The pyridyl ring breathing vibration appearing at 1001 cm\(^{-1}\) as a weak band in free hydrazone remains almost unshifted in position ruling out the possibility of involvement of pyridyl ring nitrogen atom in coordination.\(^{17}\)

The \(v(C=N)\) band appearing at 1606 cm\(^{-1}\) in free hydrazone splits up into two components indicating coordination of azomethine nitrogen atom to the metal centre. The average position of this band remains either almost unchanged [in complexes (1) and (2)] or is shifted to higher frequency by about 2-10 cm\(^{-1}\) [in complexes (3) to (5)]. Such a feature associated with the \(vC=N\) band may be attributed to the shift of phenyl ring electron density to the metal centre through the >C=N group.

The IR spectra of all K and Na complexes show bands in the regions 3438-3416 and 3205-3182 cm\(^{-1}\), respectively. The band in the region 3438-3416 cm\(^{-1}\) resembles in its shape and position those commonly observed for water or ethanol and has been accordingly assigned to \(v(OH)\) mode. Pyrolysis studies show that these complexes begin to lose weight at 90\(^\circ\)C, and between 90 and 120\(^\circ\)C; almost all the peroxide and all water molecules are lost. However, the complexes (4) and (5) lose one ethanol molecule each beyond 160\(^\circ\)C suggesting that they are coordinated to the metal centre. The complexes (4) and (5) show a rather intense band at 1035 cm\(^{-1}\) assignable to \(\beta(OH)\) mode of ethanol molecule suggesting that it is coordinated to the metal centre.\(^{18}\) None of the complexes shows any band in the 750-650 cm\(^{-1}\) region assignable to \(\rho\) mode of coordinated water molecules.\(^{19}\) The loss of weight in combination with the absence of band in the region 750-650 cm\(^{-1}\) in these complexes suggests that water molecules are lattice-held. The band observed in the region 3220-3182 cm\(^{-1}\) is assigned to \(vNH\) vibration of secondary NH group of coordinated hydrazone.

In the ammonium compound (5), however, an additional sharp band appears at 1410 cm\(^{-1}\) which is clearly due to N-H deformation mode of NH\(^+_2\). The \(vNH\) modes arising from NH\(^+_2\) ion could not be identified clearly owing to their overlap with the \(vOH\)
Structure for complexes M[MoO(O_2)_{2}(Hsih)].H_2O, \{M = K(1), Na(2) and NH_4(3)\}

Structure for complexes M[MoO_2(O_2)(Hsih)(C_2H_5OH)].H_2O \{M = K(4) and Na(5)\}

mode originating from the lattice water and vNH mode originating from the secondary NH group of coordinated hydrazone.

On the basis of various physico-chemical and spectral data presented and discussed above, the complexes may be represented by seven coordinated polyhedron as shown in Structures II and III, respectively.

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Reference