PEROXY COMPOUNDS OF Mo(VI) AND W(VI) WITH PYRIDINE

[Mo(O₂)₂(H₂O)₂(py)] (where M = Mo or W) have been isolated from the reaction of the corresponding MO₃ with H₂O₂ in presence of excess of organic ligand. The complexes on strong desiccation lose water to give complexes of the type [MO(O₂)₂py].

Unlike chromium, its higher cogeners are prone to give dimeric diperoxy complexes of the type, Mo₂O₄(H₂O)₂ (M=Mo or W). However, Lewis² has isolated some peroxy complexes of the unit, [Mo(O₂)₂O] using some phosphorus containing ligands, yet no complexes of molybdenum or tungsten have been reported so far where peroxy compounds of these elements can exist in hexacoordination as in the case of chromium complexes. In this communication we report the preparation and characterisation of [MoO(O₂)₂(H₂O)₂py] and [WO(O₂)₂H₂Opy] which on strong desiccation give hexacoordinated [MoO(O₂)₂py] and [WO(O₂)₂py] respectively.

Experimental

All the reagents used were of analytical grade. The complexes were prepared by treating freshly precipitated MoO₃ or WO₃ with excess of H₂O₂ (6%) followed by adding excess pyridine to the filtered solution and allowing it to crystallise. The yellow shining crystals were washed once with cold water and finally with acetone and air dried. On analysis they correspond to the formulae, [MoO(O₂)₂H₂Opy] and [WO(O₂)₂H₂Opy]. (Found: Mo, 36.23; O₂, 22.8; N, 5.0; W, 51.0; O₂, 17.2; N, 3.75%. Required for the above formulae: Mo, 35.17; O₂, 23.44; N, 5.13 and W, 50.94; O₂, 17.74; N, 3.88% respectively). The complexes are slightly soluble in water. In HCl they dissolve with the evolution of chlorine.

Results and Discussion

The molybdenum and tungsten complexes in 10⁻⁸M aqueous solution show the molar conductance of 15 and 23 Ohm⁻¹ Cm² respectively showing their non-electrolyte behaviour. Their electronic spectra show intense bands at 250, 272, 346 and at 250, 276, 337 nm respectively. We presume that the lowest energy band is responsible for charge transfer transition between the metal and peroxo ligand in each case by comparing these spectra with the reported spectra of other molybdenum (VI) complexes. Both the compounds are diamagnetic in nature at room temperature. By comparing the infrared spectra of these complexes with other reported spectra of oxoperoxo compounds, we assign the important i.r. bands for these as: ν(M⇔O), 950(vs); ν(O₂)²⁺, 875(vs); ν(M⇔O₂), 558(s), 492(s); ν(OH), 310 s, br, and ν(W⇔O), 940(vs); ν(O₂)²⁺, 866(vs); ν(WO₂), 575(s), 492(m); ν(OH), 3380(s, br). A few more bands appear at the same frequencies as the pyridine complexes investigated by Gill et al.⁶.

On strong desiccation over P₂O₅, one molecule of water is lost from these compounds to give the complexes [MoO(O₂)₂py] and [WO(O₂)₂py]. (Found: the loss of H₂O, 6.48 and 5.2% respectively. Required for the above formulae: 6.59 and 4.99% respectively). This is supported by the disappearance of ν(OH) in the i.r. spectra of the anhydrous complexes. The ν(M⇔O) and ν(W⇔O) are observed at 960(vs) for both. However on exposure to atmosphere they retake one molecule of water to give the original compounds. H₂O molecule is present trans to the M⇔O group. Thus we presume that these hydrated complexes are pentagonal bipyramidal in structure where the peroxy group and pyridine molecules are in equatorial positions and the oxo group is attached to the apical position. This structure is consistent with their chromium analogue⁷.

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Department of Chemistry, S. SARKAR∗.
T.D. College, R. C. MAURYA**.
Jaunpur 222 002 (U.P.), India, R. SABHARWAL.
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∗ Present address: Department of Chemistry, University of Dortmund, 4600 Dortmund, West Germany.
** To whom correspondence should be addressed.
2. Lewis, J., Ibid., 1966, A, 211.