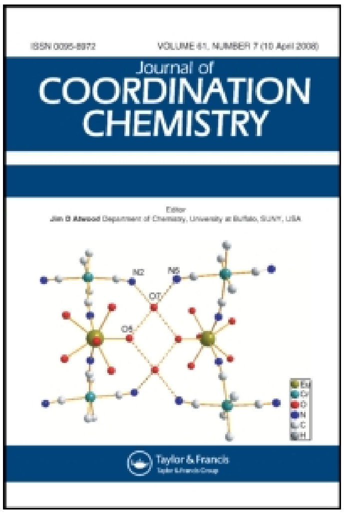

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SHORT COMMUNICATION
A Binuclear Ruthenium(III)-Dioxygen Complex

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A binuclear μ-peroxo ruthenium(III) complex of the composition $[Cl_2(AsPh_3)_3RuO_2Ru(AsPh_3)_3Cl_2]Cl_2$ is reported.

Dioxygen complexes of the platinum group metal ions Ru(O), Ir (I), Rh(I), Pt(O), and Pd(O) have been very thoroughly investigated.[1-4] A ruthenium(II) dioxygen complex with the composition $RuCl_2(AsPh_3)_3(O_2)$, **1**, was reported by Taqui Khan *et al.*[5] The compound was obtained by the oxygenation of a species obtained[6] by the reaction of $RuCl_3 \cdot xH_2O$ in acidic ethanol with a ten fold excess of triphenylarsine. The ruthenium arsine complex which was originally reported[5] as $RuCl_2(Asph_3)$ was found to be a mixture of $RuCl_3(AsPh_3)_3$, **2**, and $RuCl_3(AsPh_3)_2S$, **3**, (S = solvent). Compound **1** has been reformulated as $\{[RuCl_2(AsPh_3)_3]_2O_2\}Cl_2$, **4**, which is now obtained by a simple route.

Complex **4** was obtained by the oxygenation of **2** in benzene solution for three to four hours. The bulk of the solvent was removed under vacuum and the solution poured on a silica gel column in benzene and washed thoroughly with benzene or a mixture of benzene and petroleum ether (60–80) to remove any excess of arsine or arsine oxide. The complex was eluted with CH_2Cl_2 and $CHCl_3$ and precipitated with petroleun ether. The analysis of the compound corresponds to the composition shown in **4**. Conductivity measurement of **4** in DMA indicated that it is a 2 : 1 electrolyte.

The infrared spectrum of **4** exhibits a very strong band at 865 cm^{-1} due to the coordinated peroxo group. The paramagnetism of the compound corresponds to two unpaired electrons per ruthenium ion (μ_{eff} = 4.53 BM). Thus each ruthenium ion in the complex can be considered to be in a (+4) oxidation state with a $(t_2g)^4$ spin paired configuration corresponding to two unpaired electrons. Such a configuration has recently been suggested[7] to the Ru(IV)oxo-octoethylprophyrin complex $[Ru(OEP)(OH)]_2O$. Complex **4** can be thus formulated as Ru^{IV}–O_2^{2-}–Ru^{IV} moiety with each ruthenium housing two unpaired electrons and the peroxo group bound in an end on manner to the two ruthenium(IV) ions.

The electronic spectrum of **4** exhibits bands at 520 nm (ε = 1696) and 410 nm (ε = 4162). There is also an intense band observed at 380 nm (ε = 4810) which would be due to L → M charge transfer involving the peroxo group. An epr spectrum of the compound at liquid nitrogen temperature has not given any detectable signal probably due to the presence of as many as four unpaired electrons in the system. The infrared spectrum of **4** gave a band at 472 cm^{-1} split into shoulders at 485 cm^{-1} and 467 cm^{-1} attributed to the coordinated arsine. The M-Cl bands come at 323 and 355 cm^{-1} and may be assigned to *cis* chlorides. The photoelectron spectrum of the compound shows the presence of arsenic in the (+3) oxidation state. The signal (3d 5/2) due to the pentavalent arsenic in arsine oxide was completely absent, indicating that the coordinated arsine in the complex has not been oxidized and the observed ir band at 865 cm^{-1} is due to the peroxo group and not due to the As=O stretch. The dioxygen is irreversibly bound in the complex.

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