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Reversible Formation of a High-spin Cobalt(II) Complex of the Neutral Dioxygen Ligand

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Summary The high-spin cobalt(II) complex $[\text{Co}(\text{pfp})_2(\text{H}_2\text{O})_2]^{2-}$ (pfp = perfluoropinacolato dianion) reacts reversibly with oxygen to give the ion $[\text{Co}(\text{pfp})(\text{Hpfp})\text{O}_2]^-$, isolated as a stable tetraalkylammonium salt; no oxidation of the cobalt atom appears to have occurred, and it is thought that the oxygen is attached to the metal by π -bonding.

Of the many adducts formed between cobalt and molecular oxygen, the great majority are derived from low-spin cobalt(II) complexes and are formulated as peroxide or superoxide complexes of cobalt(III) on the basis of e.s.r. studies,¹ and a recent direct synthesis² of a compound of this type by reaction between a superoxide ion and a cobalt(III) complex. It has been suggested³ that initial formation of an oxygen adduct and electron transfer can be regarded as two separate, successive steps, with the ability of the complex to function as an efficient oxygen carrier dependent on the relative ease of the steps, but it is difficult to find a complex in which it can be unambiguously shown that complexation of dioxygen to cobalt has occurred without electron transfer. We now report such a case.

Previous work⁴ has shown that perfluoropinacol, $(\text{CF}_3)_2\text{C}(\text{OH})\text{C}(\text{OH})(\text{CF}_3)_2$, (H_2pfp), is sufficiently acidic to form stable alkoxides in water or EtOH by chelation of the dianion, pfp^{2-} , to metal ions, and derivatives of VO^{3+} , CrO^{3+} , Mn^{3+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} have been prepared. We now find that interaction of H_2pfp with Co^{2+} in ethanol

at pH 7–8 gives the stable complex ion $[\text{Co}(\text{pfp})_2(\text{H}_2\text{O})_2]^{2-}$, isolated as, e.g., the violet crystalline Me_4N^+ salt.[†] This compound had $\mu_{\text{eff}} = 4.71$ B.M. measured over the range 90–295 K ($\theta = -9$ K) and the visible spectrum (MeOH) showed absorptions at $18,500\text{ cm}^{-1}$ (ϵ 16) and $22,200\text{ cm}^{-1}$ (15), typical of octahedral cobalt(II).

When an EtOH solution of this complex was acidified with H_2pfp and exposed to air or oxygen, a strong absorption peak at $24,600\text{ cm}^{-1}$ developed in a few minutes at 25° . Passage of nitrogen through the solution, or outgassing *in vacuo*, restored the original colour, and the oxygenation cycle could be repeated many times. Slow evaporation yielded the original violet compound, but when a larger cation (tetrabutylammonium) was employed and oxygen passed for 48 h at 25° , deep orange crystals separated which analysed as $[\text{Bu}_4\text{N}][\text{Co}(\text{pfp})(\text{Hpfp})\text{O}_2]\cdot\text{EtOH}$. The solid was photosensitive, but otherwise stable in air or vacuum to 100° . On redissolving the orange crystals in EtOH and passing nitrogen, the purple colour of the solution was restored. The presence of oxygen in a 1:1 ratio to cobalt was demonstrated by its liberation in 85–90% yield on treatment with sulphuric acid. The anion must contain an additional proton, as compared with the unoxygenated complex, in order to account for its single negative charge; consistent with this, it formed only in acidic solution and decomposed immediately in such basic solvents as pyridine or dimethylformamide. This proton is tentatively placed on one of the pfp^{2-} ligands (*i.e.* one H_2pfp chelate is singly

[†] Satisfactory analytical data have been obtained for new compounds reported.

ionized, the other doubly ionized), but the possibility that the oxygen molecule is protonated cannot be dismissed.

The complex had intense absorption bands in acetone at $24,600\text{ cm}^{-1}$ ($\epsilon\ 3,400$) and in CH_2Cl_2 at $24,700$ ($3,000$) and $36,000\text{ cm}^{-1}$ ($12,800$), typical of the charge-transfer bands commonly found in oxygen adducts of cobalt.⁵ However, magnetic susceptibility measurements over the range $90\text{--}295\text{ K}$ gave a linear Curie-Weiss plot with $\mu_{\text{eff}} = 3.64 \pm 0.04\text{ B.M.}$ and $\theta = -6\text{ K}$, whereas other oxygen adducts have magnetic moments in the range $1.5\text{--}2.2\text{ B.M.}$ ¹ Conclusive evidence that this complex contained high-spin cobalt(II) came from e.s.r. measurements (in conjunction with Dr. J. R. Bolton), which showed a typical high-spin d^7 signal at a temperature of 4 K with $g = 4.3$ (frozen acetone solution), disappearing when the temperature rose to 20 K . The unoxxygenated cobalt(II) perfluoropinacol complex showed a similar spectrum ($g = 4.5$) at 4 K .

We therefore conclude that this oxygen adduct contains a neutral dioxygen ligand co-ordinated to high-spin cobalt(II). The presence of the intense charge-transfer band shows that the oxygen is directly linked to the metal, but the i.r. spectrum, often indicative of oxygen's mode of attachment, could not be unambiguously interpreted because

of the presence of absorption bands associated with the pfp groups. However, the absence of any formal oxidation of cobalt strongly suggests that the bonding is similar to that in the complex $\text{IrO}_2\text{Cl}(\text{CO})\text{P}(\text{PPh}_3)_2$,⁶ which has two oxygen atoms 1.30 \AA apart symmetrically bonded to iridium⁷ and shows the diamagnetism expected for iridium(I) (the paramagnetism of the oxygen being lost when the degeneracy of the π^* orbitals is removed on coordination to the metal). Griffiths,⁸ discussing the attachment of oxygen to haemoglobin, described a model for systems of this type in terms of metal-ligand π -bonding, and this has been extended to cover iridium complexes of oxygen and of olefins.⁹

The remarkable thermal stability and ease of preparation of this oxygen adduct suggest that cobalt(II) complexed with perfluoropinacol may form a valuable model system for the study of oxygen transfer mechanisms, and also for the interaction of cobalt with other olefinic systems.

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