Higher Oxidation State Iron and Cobalt Phthalocyanine Derivatives. Phthalocyanine Radical Cation Complexes

By G. W. RAYNER CANHAM, J. MYERS, and A. B. P. LEVER*
(*Department of Chemistry, York University, Downsview, Ontario* M3J 1P3, *Canada*)

Summary Reaction of cobalt(II) phthalocyanine (CoPc) with thionyl chloride and with bromine leads to the formation of $CoPcCl_2$ and $CoPcBr_2$, respectively; magnetic i.r., oxidative titration, and e.s.r. data indicate these complexes to contain a phthalocyanine radical species, characterised in the solid state for the first time.

HIGHER oxidation states of iron and cobalt are of interest with regard to their role in the catalytic function of enzymes. Thus, iron in the oxidised form of horseradish peroxidase and Japanese radish peroxidase, once formulated as iron(V), has recently been reformulated, on the basis of Mössbauer studies,[1,2] to contain iron(IV), a very rare oxidation state for iron. One oxidising equivalent is assumed to reside on the ligand, rather than on the metal ion.[1,2] The existence of similar Co^{IV} compounds has not been established, although a Co^{IV} intermediate has been suggested in a model system for vitamin B_{12} to explain the oxidative cleavage of a cobalt–carbon bond.[3]

Recently there was a report of halide complexes derived from cobalt(II) phthalocyanine formulated[4] as $CoPcX_2$. Such complexes were obtained by reaction of $Co^{II}Pc$ with thionyl chloride, bromine, or thionyl bromide. We have re-prepared these complexes and have observed that reaction of $Fe^{II}Pc$ with thionyl chloride yields the complex $FePcCl_2$.

The complexes $CoPcCl_2$, $CoPcBr_2$, and $FePcCl_2$ gave satisfactory elemental analyses and are characterised as six-co-ordinate derivatives involving halogen co-ordinated to the metal on either side of the macrocyclic ring on the basis of the following data. (i) Reaction with alcoholic potassium hydroxide released the full amount of halogen in an ionic form, thereby excluding the possibility of ring halogenation. (ii) The far i.r. spectra contain absorption bands readily assignable to metal halogen stretching vibrations [ν(M–X) for $CoPcCl_2$, $CoPcBr_2$, and $FePcCl_2$ are 330, 253, and 332 cm^{-1}, respectively]. (iii) The magnetic data are fully compatible with a six-co-ordinate structure but are difficult to reconcile with structures of co-ordination numbers four or five (μ_{eff} at 298° for $CoPcCl_2$, $CoPcBr_2$, and $FePcCl_2$ are 1·75, 1·90, and 3·10 B.M., respectively).

Oxidative titrations using potassium dichromate under nitrogen[5] show unequivocally that the $MPcCl_2$ complexes are at an oxidation level of plus two in excess of the MPc starting materials. Since the starting materials undoubtedly contain M^{II} and the Pc^{2-} species, these oxidative titrations infer the presence either of an $M^{IV}Pc$ derivative or of an M^{III} derivative containing an oxidised phthalocyanine radical. Considering the nature of the metal ions concerned the possibility that the complexes contain M^{II} and doubly oxidised phthalocyanine seems remote. The $MPcX_2$ complexes have i.r. spectra, in the conventional region, similar to each other but different from the spectra of metal phthalocyanines in general. It has been noted[6] that the i.r. spectra of the metal phthalocyanines are very similar showing comparatively little dependence upon the nature of the metal ion. The marked variation observed with the $MPcX_2$ species, greater than the changes generally associated with polymorphism,[6] provides evidence for a strong perturbation of the phthalocyanine ligand.

The cobalt complexes exhibit a magnetic moment indicative of one unpaired electron, which would be consistent either with a low-spin six-co-ordinate Co^{IV} d^5 configuration or a low-spin six-co-ordinate, diamagnetic, Co^{III} d^6 configuration with one unpaired electron on the phthalocyanine ring. Since the complex $CoPcCl_2$ exhibits a strong e.s.r. signal at $g = 2{\cdot}0$ with a band width of only 6 G, a radical species seems assured. Such a sharp absorption would not be expected if the unpaired electron resided on the metal ion. No hyperfine interactions were observed either at room temperature or at liquid nitrogen temperature. Whilst there is abundant evidence[7-9] for the generation of radical species by oxidation of metal phthalocyanines in solution, solid derivatives do not appear to have been previously characterised; recent electrochemical studies[10] suggest that such complexes should be stable. We conclude, therefore, that the $CoPcX_2$ complexes contain Co^{III} and an oxidised phthalocyanine radical species.

The magnetic moment of the iron complex $FePcCl_2$ suggests two unpaired electrons, consistent with either a low-spin six-co-ordinate iron(IV) d^4 configuration, or a low-spin six-co-ordinate iron(III) d^5 configuration (one unpaired spin) with a further unpaired spin residing on the phthalocyanine ligand. We were unable to detect an e.s.r. resonance either at room temperature or at −196°, although the i.r. spectrum is consistent with an Fe^{III} radical cation formulation. The isomer shift in the Mössbauer spectrum, relative to sodium nitroprusside, of 0·35 mms^{-1} ($\Delta E_g = 2{\cdot}15$) is markedly lower than that observed for FePc[11] and is indicative of iron in an oxidation state higher than Fe^{II}. The various $MPcX_2$ species show broad multiple absorption in the visible region. Their brown colour is atypical for the phthalocyanine series.

In agreement with the previous electrochemical data,[10] nickel(II) phthalocyanine is resistant to oxidation under the conditions discussed.

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