Five- and Six-co-ordinate Isocyanidecobalt(II) Complexes

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THE low-spin cobalt(II) complex formulated as $Co(PhNC)_5(ClO_4)_2$ was prepared by Sacco[1] in 1954 as a blue–green solid. He suggested that this complex was five-co-ordinate and it has been quoted as such in subsequent Reviews. Because of the current interest in five-co-ordination (see the Reviews by Nyholm and Tobe[2] and Muetterties and Schunn[3]) we report our observations on this complex.

Using Sacco's method we obtained a blue, rather than blue–green, compound. The solid, however, turns yellow on drying *in vacuo* over P_2O_5 at room temperature, irrespective of whether the atmosphere is initially air, nitrogen, or argon; on admitting moist air it is immediately reconverted into the blue form. The infrared, e.s.r., and visible spectra show that the change is reversible. All attempts to prepare the yellow form in solution have so far failed. Elemental analysis of the blue form agrees with the basic formula $Co(PhNC)_5(ClO_4)_2,1{\cdot}5\ H_2O$; Sacco apparently failed to notice the presence of water. The infrared spectrum shows the presence of water (bands at ~3500 and 1620 cm.$^{-1}$) in the blue form and their absence in the yellow. The change is therefore simply the reversible removal of water. The question remains as to the configuration of the two complexes.

Because of experimental difficulties it has only been possible to study the yellow form by e.s.r. (powders at 77°K) and infrared spectroscopy (a Nujol mull of the blue form can be slowly dried to give the yellow form and the reverse uptake of moisture is sufficiently slow to enable the spectrum to be taken). Both forms gave e.s.r. signals, showing, first, that the yellow form is not a diamagnetic dimer like the analogous methyl isocyanide complex[4] and suggesting, secondly, that both have an A ground term (*i.e.*, probably have C_{4v} and not D_{3h} symmetry). The similarity of the two g-values (blue 2·12; yellow 2·14) shows that the yellow as well as the blue form is a low-spin complex. The ν_3 band of the perchlorate ion shows a single peak at 1090 cm.$^{-1}$ in the yellow form (*i.e.*, not co-ordinated) but is split in the blue form; since ClO_4^- is not co-ordinated even in the absence of water this splitting is obviously due to hydrogen-bonding with the water. There are no bands in the 1600—2000 cm.$^{-1}$ region where a bridging isocyanide might absorb.[5] Both forms show great similarities in the C≡N stretching region (blue

2220 cm.$^{-1}$ strong, 2195 medium; yellow 2220 strong, 2180 shoulder) though the bands of the latter are broader due, probably, to destruction of the lattice on dehydration. Although two bands are expected for D_{3h} symmetry and three for C_{4v}, anomalies are often observed[6] with other triple-bonded ligands such as CO and CN^-, so that the number of observed bands cannot be used diagnostically. The great similarity does however suggest the presence of the same symmetry in both cases. From these results we conclude that the blue complex is the six-co-ordinate $[Co(PhNC)_5H_2O]$ and the yellow the five-co-ordinate and probably square pyramidal $[Co(PhNC)_5]$. The analytical data and the splitting of the perchlorate band can be explained if the co-ordinated H_2O forms hydrogen bonds to both attendant ClO_4^- ions and the additional water molecule forms hydrogen bonds to the co-ordinated H_2O of two separate complexes.

The above results show, therefore, that a five-co-ordinate complex does exist, but that it is not the blue compound reported by Sacco. In addition to being one of the relatively few known five-co-ordinate transition-metal complexes with identical unidentate ligands this is the first case where a simple equilibrium with other configurations can be observed. As a group the pentakisisocyanide-cobalt(II) complexes have an interesting stereochemistry: blue, octahedral $[CoL_5H_2O]$ (in solution L = PhNC and MeNC, in solid L = PhNC only; all show similar visible spectra); red, diamagnetic and dimeric $[L_5Co{-}CoL_5]$ (L = MeNC in solid only[4]); yellow, five-co-ordinate $[CoL_5]$ (L = PhNC in solid only; the phenyl groups obviously prevent dimerisation).

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