A Novel Five-co-ordinate Complex of Cobalt(II)

By Shoichiro Yamada and Hiroaki Nishikawa

(Received February 12, 1965)

Most cobalt(II) complexes are known to be four- or six-co-ordinate; very few five-co-ordinate complexes have so far been characterized.[1] The present communication deals with the successful preparation of a new cobalt(II) complex of a Schiff base, which is now believed to be five-co-ordinate.

The compound prepared (A) is a pyridine adduct of bis-(*N-o, o'*-xylidyl-salicylideneiminato)cobalt(II), which is abbreviated as Co-(Sal·N·*o,o'*-xyl)$_2$·Py. This pyridine adduct has been obtained as green crystals by cooling a hot solution of the red-coloured parent cobalt(II) complex in pyridine or in pyridine-petroleum ether. Elemental analysis agreed quite well with the above formula with one pyridine molecule, but not with the formula with two pyridine molecules.

The spectrum of compound A in the solid state is quite different from any of the typical spectra[2] of the tetrahedral, the square-planar and the octahedral cobalt(II) complexes, as well as from the spectrum of the parent complex in the solid state or in solution (Fig. 1).

All these findings indicate that the pyridine adduct A in the solid state is most likely to be a five-co-ordinate complex, one in which the pyridine molecule is bound with the cobalt(II) ion.

On the contrary, the use of a similar procedure with the *N*-monosubstituted phenyl complexes of cobalt(II) yielded adducts B, Co-(Sal·N·R)$_2$·2Py, which has been concluded, from electronic spectra and elemental analysis, to be six-co-ordinate. The difference in the structure of the pyridine adduct between the parent complexes of A and B is regarded as due to the much more marked steric hindrance in A, which prevents the complex from taking the otherwise favourable six-co-ordination.[3]

---

[1] G. A. Barclay and R. S. Nyholm, *Chem. & Ind.*, **1953**, 378; R. S. Nyholm and M. L. Tobe, "Essays in Coordination Chemistry," Ed. by W. Schneider, G. Anderegg and R. Gut, Birkhäuser Verlag, Basel (1964), p. 112.

[2] H. Nishikawa and S. Yamada, This Bulletin, **35**, 1430 (1962); ibid., **37**, 8 (1964); L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962); L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, ibid., **85**, 411 (1963), and references therein.

[3] Recently Sacconi and Ciampolini (private communication) studied the equilibrium between bis(salicylaldehyde)-*N*, *N*-disubstituted polymethylenediiminato-cobalt(II) complexes and their pyridine adducts in solution; they concluded the existence in solution of the adduct of the cobalt(II) complex with one pyridine molecule.

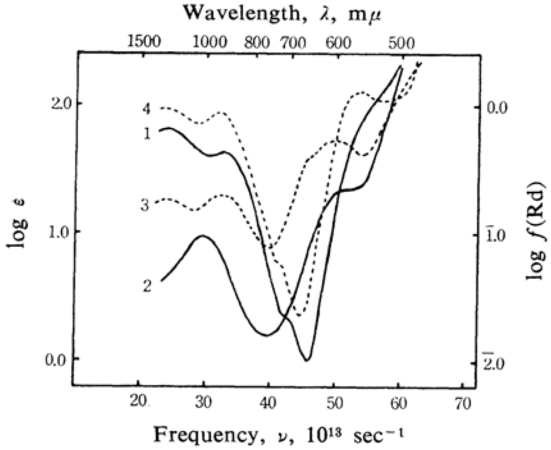

Fig. 1. Electronic spectra of: 1, [Co(Sal·N·*o,o'*-xylidyl)$_2$] in chloroform (tetrahedral); 2, [Co(Sal·N·*o*-tolyl)$_2$] in pyridine (octahedral); 3, [Co(Sal·N·*o,o'*-xylidyl)$_2$·Py] in the solid state by reflectance (five-co-ordinate); 4, [Co-(Sal·N·cyclohexyl)$_2$]·1Piperidine in the solid state by reflectance (tetrahedral).

The conclusion of the five-co-ordination in A is also supported by the magnetic moment of A (4.53 B.M.), which is definitely different from the moment of the parent complex (4.35 B. M.). Thus, A is of a high-spin type and differs from the previously-reported five-co-ordinate cobalt(II) complexes, which are of a low-spin type.[1] As has been discussed by Nyholm and others on the basis of the current theory of directed valence,[4] the magnetic moment indicates that, in compound A, $4s4p^34d$ hybridized orditals may most probably be used for bonding, a trigonal-bipyramidal configuration being predicted; a tetragonal pyramid on the basis of $4s4p^24d^2$ hybridization may not be completely eliminated.

It should be noted that the solid spectra of Co(Sal·N·cyclohexyl)$_2$·Py and Co(Sal·N·cyclohexyl)$_2$(Piperidine) are nearly identical with the spectrum of the parent cobalt(II) complex of a tetrahedral configuration.

Institute of Chemistry
College of General Education
Osaka University
Toyonaka, Osaka

---

[4] H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons, New York (1949), p. 231.