Crystal Structures of Two Five-co-ordinated Cobalt(II) and Nickel(II) Complexes having the MN_2P_2Br Chromophore ($M=Co^{II}$ or Ni^{II})

By A. BIANCHI, C. A. GHILARDI, C. MEALLI, and L. SACCONI*
(*Istituto di Chimica Generale dell'Universitá di Firenze, Laboratorio del C.N.R.*, 41 *via Jacopo Nardi*, 50132 *Firenze, Italy*)

Summary X-Ray structural analysis on two five-co-ordinated complexes of cobalt(II) and nickel(II) having the MN_2P_2Br chromophore and the same ligands shows that axial elongation in square-pyramidal low-spin complexes is more favourable for nickel than cobalt.

NUMEROUS X-ray structural analyses on five-co-ordinated cobalt (II) and nickel(II) complexes show that many structures are strongly distorted.[1,2] In particular, an enhanced elongation of the axial bond is often found in the low-spin square-pyramidal complexes,[3,4] accompanied by a lowering of the metal atom towards the basal plane. Such a distortion seems to be larger and more frequent for nickel than for cobalt complexes.[1] Nevertheless no direct comparison has been made so far, because of the absence of X-ray structures of two cobalt and nickel complexes formed with the same ligands and having the same geometry.

With this in mind we have undertaken the X-ray analysis of two complexes $[M(pnnp)Br]^+$, where $M = Co^{II}$ and Ni^{II} and pnnp is the open-chain tetradentate ligand $PPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}N(Me){\cdot}CH_2{\cdot}CH_2{\cdot}N(Me){\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$. The two complexes $[Ni(pnnp)Br]Br, 0{\cdot}5\,BuOH$ and $[Co(pnnp)Br]PF_6$ respectively, are low-spin and their electronic spectra suggested a five-co-ordinated square-pyramidal structure

Crystal data. For the nickel complex: $C_{32}H_{38}Br_2N_2NiP_2$ $0{\cdot}5C_4H_{10}O$, $M = 768{\cdot}27$, monoclinic $a = 15{\cdot}910(2)$, $b = 15{\cdot}177(1)$, $c = 17{\cdot}035(3)$ Å, $\beta = 120°4(1)'$, $U = 3559{\cdot}6$ Å^3, $D_m = 1{\cdot}44$, $Z = 4$, $D_c = 1{\cdot}43$, space group $P2_1/c$. Multiple-film equi-inclination Weissenberg data were collected using Cu-K_α radiation and the intensities of 1510 reflections were measured. The structure was solved by the heavy atom method and refined by full-matrix least-squares to a final R 7·7%.

For the cobalt complex: $C_{32}H_{38}CoBrF_6N_2P_3$, $M = 796{\cdot}45$, monoclinic, $a = 17{\cdot}073(2)$, $b = 15{\cdot}262(1)$, $c = 17{\cdot}205(2)$ Å, $\beta = 127°1(1)'$, $U = 3579{\cdot}2$ Å^3, $D_m = 1{\cdot}51$, $Z = 4$, $D_c = 1{\cdot}49$, space group $P2_1/c$. An automatic four-circle diffractometer was used to collect 1238 independent reflections of intensity $>2{\cdot}5\,\sigma\,(I)$ with Mo-K_α radiation. The structure was solved by direct methods and refined by full-matrix least-squares to R 10·3%. Refinement is continuing.

Both the complexes show an elongated square-pyramidal co-ordination with the four donor atoms of the ligand in the basal plane and the bromine atom in the apical position (see Figure). The nickel and the cobalt atoms are respectively 0·20 and 0·22 Å out of the mean basal plane toward the bromine atom. The co-ordination geometry for the complexes is strictly the same, the only difference being in the amount of axial distortion.

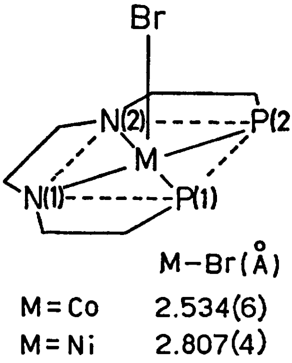

Figure.

The Ni–Br and Co–Br distances are 2·807(4) and 2·534(6) Å respectively, with a very significative difference of 0·27 Å. Other meaningful distances are: Co–P = 2·22(1) (av.), Ni–P = 2·21(1) (av.), Co–N = 2·03(3) (av.), Ni–N = 2·00(2) (av.). The Ni–Br bond length of 2·807 Å must be compared with the values of 2·79, 2·70, 2·69, and 2·37, 2·33 Å reported respectively for the apical and basal Ni–Br distances in other low-spin square pyramidal complexes.[3]

As far as we know, no low-spin square pyramidal cobalt(II) complex with a bromine as donor atom has been reported so far. Values of 2·54 and 2·33 Å for Co–Br bond distances in a distorted trigonal bipyramidal low-spin complex have been given.[5]

The larger apical distance in the nickel complex with respect to the cobalt complex can be accounted for by a simplified MO picture. The effect of elongation of the axial bond (z axis) is to decrease the antibonding character of the electrons in the molecular orbital, which is essentially d_{z^2}. As a result of this axial elongation, low-spin nickel(II) complexes, having two electrons in this orbital, gain more energy than cobalt(II) complexes, which has only one electron in the d_{z^2} orbital.

(*Received, 2nd March* 1972; *Com.* 357.)

---

[1] L. Sacconi, Proceedings XIII I.C.C.C., Poland 1970; *Pure Appl. Chem.*, 1971, **27**, 161.

[2] P. L. Orioli, *Co-ordination Chem. Rev.*, 1971, **6**, 285.

[3] E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, 1968, **7**, 2312; P. L. Orioli and C. A. Ghilardi, *J. Chem. Soc.* (*A*), 1970, 1511; G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 1960, 415.

[4] P. Dapporto, R. Morassi, and L. Sacconi, *J. Chem. Soc.* (*A*), 1970, 1298; A. Bianchi and C. A. Ghilardi, *ibid.*, 1971, 1096; D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1915; D. W. Allen, F. G. Mann, I. T. Millar, H. M. Powell, and D. Watkin, *Chem. Comm.*, 1969, 1004; M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, 1968, **90**, 4253; S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671; M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

[5] J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, 1966, **5**, 879.