Crystal Structure of $(\pi\text{-}C_5H_5Co)_2(NBu^t)_2CO$

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MANY polynuclear organometallic complexes have been found, which involve metal–metal bonds, and some of them contain nitrogen or sulphur atoms bridging between the metal atoms.[1] The bridge nitrogen or sulphur atom in those complexes may stabilise the metal–metal bonds. To determine the co-ordination around the metal atoms, the crystal structure analysis of $(\pi\text{-}C_5H_5Co)_2(NBu^t)_2CO$ has been undertaken by means of *X*-ray diffraction. The dark green crystals were prepared from $\pi\text{-}C_5H_5Co(CO)_2$ and $(Bu^tN)_2S$.[1]

The crystals of this substance are orthorhombic, with cell dimensions: $a = 9{\cdot}10$, $b = 17{\cdot}97$, and $c = 23{\cdot}61$ Å; $D_m = 1{\cdot}46$, $D_c = 1{\cdot}44$ g.cm.$^{-3}$ for $Z = 8$. The space group is *Fdd*2. The three-dimensional intensity data were collected by use of a G.E. XRD-5 diffractometer equipped with a single-crystal orienter using zirconium-filtered Mo-K_α radiation. 641 Independent reflexions were observed, of which 83 were too weak to be used.

Since the general position in *Fdd*2 is sixteen-fold, the carbonyl group must lie on a special position and the whole asymmetric unit must have C_2 symmetry. The structure was solved by the heavy atom method. The co-ordinates of the cobalt atom were found from the three-dimensional

Patterson function, and then other non-hydrogen atoms were obtained from the minimum function and from the Fourier synthesis based on the location of the cobalt atom. The positional and anisotropic thermal parameters of these atoms were refined by a block-diagonal least-squares method on the NEAC 2200 computer of this university. The R factor at the present stage is 0·064 for non-zero reflexions. The figure illustrates the molecular structure with the principal dimensions.

The Co–Co distance of 2·37 Å is shorter than that of 2·47 Å found in $(CO)_6Co_2(C_2Ph_2)$.[2] This suggests that the metal–metal bond in this complex may be stabilised by the bridge nitrogens. The Co-N distances are similar to or somewhat shorter than those found in a number of cobalt–ammine complexes.[3] The C(10) of the carbonyl group is bonded to N(1) and N(1′) to form a urea-like structure. The carbon atoms of each cyclopentadienyl ring lie almost exactly in one plane, maximum deviation being 0·006 Å. The cobalt atom is at a distance of 1·71 Å from the plane of each cyclopentadienyl ring. This structure provides an inert 18-electron shell for the metal atom, in accord with the observed diamagnetism of this compound.[1]

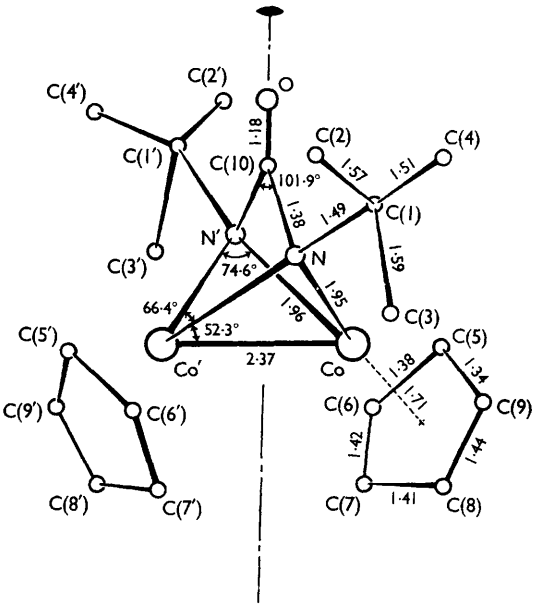

FIGURE. *Structure of* $(\pi\text{-}C_5H_5Co)_2(NBu^t)_2CO$.

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