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The Crystal and Molecular Structure of π-Cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt, $Co(C_8H_{13})(C_8H_{12})$

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Summary The cobalt atom in the title compound has a planar configuration with the two π-bonds of the diene and the delocalized orbitals of the octenyl, C_8H_{12} being in the boat form and C_8H_{13} the tub form.

π-CYCLO-OCTENYL-π-CYCLO-OCTA-1,5-DIENECOBALT has been obtained by direct interaction of cyclo-octa-1,5-diene with $CoCl_2$ in the presence of metallic sodium. This compound readily loses hydrogen atoms, and Otsuka and Rossi suggested two possible molecular structures in which two hydrogen atoms are located at exceptionally short distances from the cobalt atom.[1] We have undertaken a three-dimensional *X*-ray crystal analysis of $Co(C_8H_{13})(C_8H_{12})$.

The crystals are brilliant black plates. As they are moderately sensitive to air, specimens were sealed in glass capillaries for use. Crystal data: monoclinic, space group $P2_1/c$; $a = 10{\cdot}78 \pm 0{\cdot}03$, $b = 7{\cdot}30 \pm 0{\cdot}02$, $c = 17{\cdot}81 \pm 0{\cdot}03$ Å, $\beta = 104{\cdot}2 \pm 0{\cdot}1°$; $Z = 4$, $D_c = 1{\cdot}31$ g.cm.$^{-3}$, $\mu = 29{\cdot}6$ cm.$^{-1}$ (for Fe-K_α). Multiple-film equi-inclination Weissenberg photographs were taken using Mn-filtered Fe-K_α radiation about the *a*- and *b*-axes, and intensities of 1043 independent reflections were obtained by visual estimation.

Approximate co-ordinates of the cobalt atom were obtained by a three-dimensional sharpened Patterson function. All of the sixteen carbon atoms were located by successive Fourier analyses. The positional and anisotropic thermal parameters were refined by least-squares methods. The convergence was slow and the *R* factor ceased to decrease at around 0·141, presumably because of imperfections in the crystal structure. The standard deviations in the positional parameters are about 0·003 Å for the cobalt atom and 0·03 Å for the carbon atoms.

The molecular structure is shown in the Figure. The cobalt atom lies between the C_8H_{13} and the C_8H_{12}. The C_8H_{13} ligand is in the tub form and the C_8H_{12} ligand in the boat form. Atoms Co, C(1), C(3), and the respective centres of the two double bonds, C(9)–C(16) and C(12)–C(13), in the C_8H_{12} ring are coplanar to within 0·08 Å. Thus, the cobalt atom can be said to form a planar configuration if we take the two π-bonds extending from the diene together with the delocalized orbitals arising from the octenyl. The average value of the seven nearest Co–C distances is 2·06 Å. The bond lengths in the two ligands are normal. Few of the bond angles are definitely larger either than 109·5° for sp^3 or than 120° for sp^2. Large bond-angles similar to those found in this investigation have already been reported for $Ni(C_8H_{12})_2$[2] and $[RhCl(C_8H_{12})]_2$.[3]

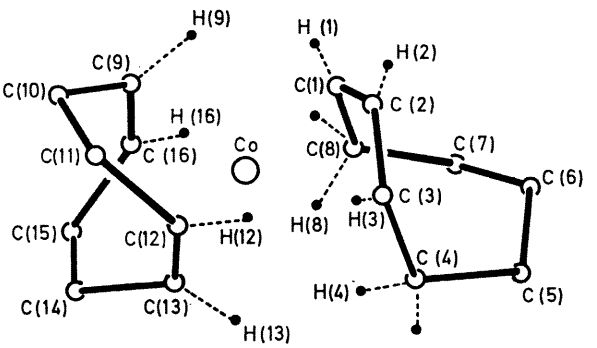

FIGURE. *The molecular structure viewed along the* b *axis. Hydrogen atom positions are postulated.*

Atoms C(9), C(12), C(13), and C(16) deviate by only 0·02 Å from a least-squares plane, and atoms C(1), C(3), C(4), and C(8) are also approaching planarity. These two planes are nearly perpendicular to the plane containing Co, C(1), C(3), and the two double-bond centres. Two parts of the ligand, C(8)–C(1)–C(2)–C(3) and C(1)–C(2)–C(3)–C(4), deviate from the planar *cis*-conformation. The C(1)–C(2) and C(2)–C(3) bond lengths are 1·46 and 1·38 Å,

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and the angles of twist around these two bonds are 40° and 33°, respectively.

The conformation of C(9)–C(10)–C(11)–C(12) is incompletely eclipsed, the angle of twist around the C(10)–C(11) bond being 22°. This twisting probably arises from the repulsion between hydrogen atoms attached to the carbon atoms concerned. The conformation of C(13)–C(14)–C(15)–C(16) is similar to that of C(9)–C(10)–C(11)–C(12).

Positions of the hydrogen atoms attached to all the sixteen carbon atoms were calculated using conventional bond distances and bond angles. No abnormally short interatomic distances between Co and H have been found. However, there are two short interatomic distances between hydrogen atoms: H(3) · · · H(12) and H(4) · · · H(8) are 1·72 and 1·85 Å, respectively, which are comparable to those found in $Ni(C_8H_{12})_2$.[2]

The four cobalt atoms lie on the general positions with *x ca.* 1/4, *y ca.* 0, *z ca.* 1/4, and form almost a face-centred lattice. The molecules are packed together mainly by the van der Waals forces and there are no abnormal short interatomic distances between them.

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