Cobaloxime and DDT. *X*-Ray Crystal Structure of an Unexpected Vinyl-Cobalt(III) Complex

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Summary The crystal structure of the product of the reaction between bis(dimethylglyoximato)pyridinecobalt-(I) and the insecticide 1,1-bis-(*p*-chlorophenyl)-2,2,2-trichloroethane (*p,p'*-DDT) shows the presence of a chlorovinyl group σ-bonded to cobalt.

WE have been studying the possible involvement of alkyl–cobalt species in the biological reactions of DDT.[1] Because of analogies between the chemistry of cobaloximes and cobalamins,[2] the reaction of the former with DDT, and the structure of the product, were of interest. Pyridinatocobaloxime(I) was prepared in methanol by the published method,[3] and treated *in situ* with 1 equiv. of *p,p'*-DDT. After warming to 40° for 3 h, a 55% yield of a yellow-orange solid had precipitated. Crystals of this compound were grown from methanol.‡

Crystal data: $C_{27}H_{27}N_5Cl_3O_4Co$ is orthorhombic, space group $Pn2_1a$; $a = 25{\cdot}50(2)$, $b = 23{\cdot}13(2)$, $c = 9{\cdot}728(7)$ Å; D_m (flotation) $= 1{\cdot}48$; $D_c = 1{\cdot}507$ g cm^{-3} for $Z = 8$. Intensity data were collected using an automated two-circle diffractometer (Mo-K_α radiation) and corrected for absorption. Data collected about two axes were merged to give 3545 unique observed reflexions. The structure was solved by interpretation of a multiple superposition Patterson minimum function and successive electron density syntheses. Anisotropic temperature factors were employed for cobalt and chlorine atoms only. All four crystallographically independent hydrogen-bonded hydrogen atoms were found in symmetrical O···H···O locations in a difference electron density map [mean O···O 2·50(1) Å]. At the present stage of refinement the conventional R factor is 0·049.

The asymmetric unit contains two molecules, each with octahedral co-ordination of cobalt, which differ significantly only in the relative orientations of the aromatic rings and the effect this has on the equatorial plane. This probably

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‡ Satisfactory analyses were obtained for this compound.

assists the crystal packing of this bulky complex. Although several σ-bonded vinyl–Co^{III} complexes have been prepared by reactions of Co^{I} species with vinyl halides or acetylenes,[4] no such compound has previously been produced from a fully saturated organic molecule. The C=C distance of 1·37(2) Å compares with the distances of 1·333(15) and 1·31(3) Å found in σ-vinyl complexes of Co^{III}bae[5] and Co^{III}salen[6] [bis(acetylacetone)- and bis(salicylaldehyde)-ethylenedi-iminato dianions].

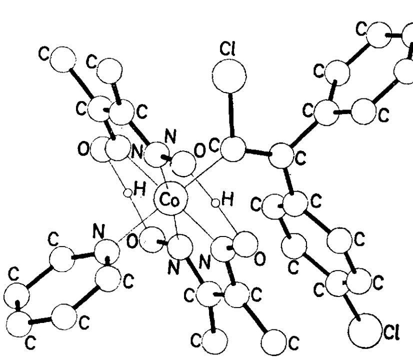

FIGURE. One molecule of the complex. Some average bond lengths and angles for the two crystallographically different molecules are: C=C 1·37(2), C–Cl(vinyl) 1·80(1), C–Cl(aromatic) 1·76(2), C–C(vinyl) 1·50(4), C–C(oxime) 1·43(2), C=N(oxime) 1·30(2), N–O 1·35(2), O · · · O 2·50(1), Co–N(oxime) 1·88(1), Co–N(py) 2·04(1), Co–C 1·97(1) Å; Co–C=C 133·8(12), Cl–C–Co 115·0(5), Cl–C=C 110·6(8)°.

Since DDT itself is stable to base-induced elimination of HCl under the reaction conditions employed,[7] this complex must have been produced by elimination of HCl from the first-formed product of S_N2 attack by Co^{I} on C(2) of DDT. This elimination is driven by the conjugation in the product between the vinylic double bond and the benzene rings, and the Co–C bond is stabilised by the presence of the vinylic chlorine.[8] In the light of this result, the mechanism suggested[1] for the formation of a previously reported cobalt–DDT product must be considered incorrect; however, an important new pathway for the chemical degradation of DDT has been established.

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