The Structure of *NN'*-Ethylenebis(acetylacetoneiminato)phenylaquocobalt(III)

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Summary In *NN'*-ethylenebis(acetylacetoneiminato)-phenylaquocobalt(III), the phenyl group is σ-bonded with a Co–C bond length of 1·93 ± 0·02 Å.

THE cobalt complexes of the quadridentate Schiff bases bis-(salicylaldehyde)ethylenedi-imine (salen H_2) and bis(acetylacetone)ethylenedi-imine (bae H_2) have been extensively studied on account of their ability to stabilise the Co–C bond of the organocobalt derivatives[1] and to enable the cobalt atom to bind molecular oxygen reversibly.[2] The structural features of both these properties are under investigation in our laboratory.[3–6]

We have already determined the crystal structure of the tetra-co-ordinate parent compound Co^{II} bae,[3] and of the hexa-co-ordinate vinylaquo-derivative[4] and the penta-co-ordinate methyl derivative ($MeCo^{III}$ bae).[5] We present here a preliminary account of the crystal structure of the *NN'*-ethylenebis(acetylacetoneiminato)phenylaquocobalt(III).

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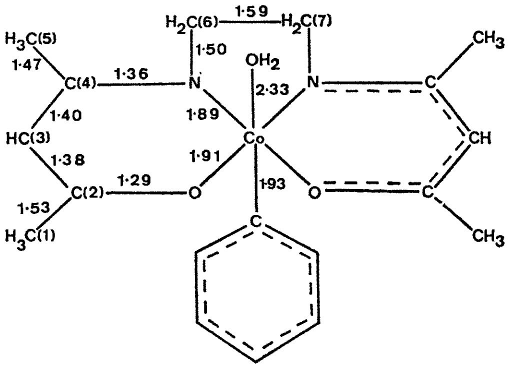
belong to the monoclinic system, space group $C2/c$, with $a = 20{\cdot}04 \pm 0{\cdot}03$, $b = 7{\cdot}22 \pm 0{\cdot}01$, $c = 27{\cdot}87 \pm 0{\cdot}04$ Å, $\beta = 117{\cdot}3 \pm 0{\cdot}3°$, $U = 3583$ Å^3, $Z = 8$, $D_c = 1{\cdot}396$ g. cm^{-3} $D_m = 1{\cdot}390$ g. cm^{-3} (by flotation). The structure analysis was based on 1072 independent reflexions, collected with the equi-inclination Weissenberg method, using Mo-K_α radiation, and estimated visually. The structure was solved by the usual methods and refined by the isotropic block-diagonal least-squares method to the present R-value of 0·11.

The crystal is built up by discrete phenylaquo-Co^{III} bae units, in which the cobalt atom has a distorted octahedral stereochemistry, the bae ligand occupying the four equatorial positions. The axial positions are occupied by the water molecule and by the σ-bonded phenyl group (Figure). The mean values of the bond lengths and angles in the phenyl group are 1·39 Å and 120° respectively.

The two chemically equivalent halves of the bae ligand are bent away from the phenyl group, making a dihedral angle of 8·9°. The phenyl group is nearly parallel to the C–C bond of the ethylene bridge. Such a geometry does not seem ascribable to crystal packing effects because it is in agreement with the model deduced from n.m.r. measurements on some substituted phenyl derivatives of Co bae.[7]

The values of the bond lengths in the ligand are indicative of a delocalisation of the π-electrons in the nearly planar quadridentate ligand as found in similar compounds.[3–5]

The Co–C bond lengths in MeCo^{III} bae,[5] vinylaquo-Co^{III}-bae,[4] and phenylaquo-Co^{III} bae ($1{\cdot}95 \pm 0{\cdot}02$, $1{\cdot}89 \pm 0{\cdot}01$, $1{\cdot}93 \pm 0{\cdot}02$ Å, respectively) show small differences which may lack meaning within the limits of the accuracy of such determinations. However, they suggest that the contribution of π-bonding to the total bond order of the Co–C bond, if any, is rather small. On the other hand, a significant difference is found for the Co–OH_2 distances in the octahedral derivatives ($2{\cdot}221 \pm 0{\cdot}007$ Å in vinylaquo-Co^{III} bae[4] and $2{\cdot}33 \pm 0{\cdot}02$ Å in phenylaquo-Co^{III} bae). Two explanations may be formulated to account for this effect. The first deals with a different *trans*-influence of the vinyl group with respect to that of the phenyl group on the *trans*-water molecule. The alternative explanation rises from the examination of the overall geometry of the bae ligand in the two compounds. Whereas in the phenyl derivative the two chemically equivalent halves of the bae ligand are bent away from the phenyl group, in the vinyl derivative they are slightly bent away from the water molecule, causing less hindrance in the Co–OH_2 bonding.



FIGURE

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