σ-Bonded Dioxygen. *X*-Ray Crystal Structure of $[NEt_4]_3[Co(CN)_5(O_2)],5H_2O$

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Summary The crystal and molecular structure of a dioxygen adduct of $[Co(CN)_5]^{3-}$ has been determined, the complex is best formulated as a nearly linear superoxide complex of Co^{III} with a Co–O–O angle of 175°.

BECAUSE of the role played in biological oxygen transport, the mode of bonding of dioxygen in transition-metal complexes has been studied for many years. The resolution of the *X*-ray diffraction analyses of the oxygen-transport

proteins oxymyoglobin and oxyhaemoglobin is not sufficient to determine the mode of bonding of dioxygen to the iron atom.[1] The suggested mode of bonding has ranged from the linear σ Fe–O–O structure (I) first proposed by Pauling[2] to the π Fe $\leftarrow$ $\begin{matrix} \\ | \\ \mathrm{O} \end{matrix}$ structure (II) proposed by Griffith[3] or the superoxide structure proposed by Weiss.[4] Pauling[5] subsequently proposed a bent σ structure (III) with an Fe–O–O bond angle of 120°. Only recently dioxygen complexes of iron in model compounds have been prepared,[6] although there are many examples of stable O_2 adducts of low-spin Co^{II} complexes, and the structures of two such adducts have been reported recently.[7] In both cases the Co–O–O angle is *ca.* 126°, structure (III). This also appears to be the geometry of the model iron complexes.[8] The properties of oxycobaltmyoglobin and oxycobalthaemoglobin indicate that dioxygen binds to cobalt in the same way that it binds to iron in the native proteins.[9] We report here a preliminary account of the structure of a simple yet unusual cobalt complex of dioxygen, the $[Co(CN)_5(O_2)]^{3-}$ anion.

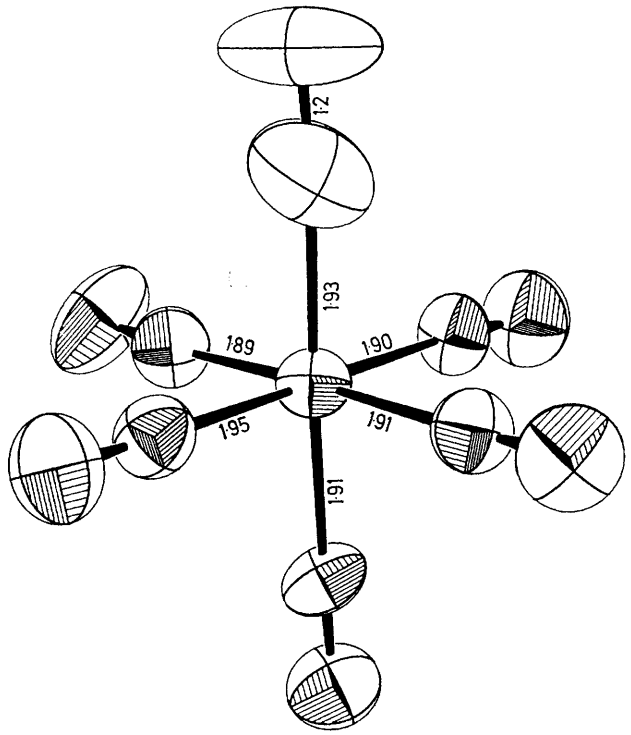

FIGURE. Structure of the anion in $[NEt_4]_3[Co(CN)_5(O_2)]$, $5H_2O$.

Exposure to air of an anhydrous solution of $[NEt_4]_3[Co(CN)_5]$ in dimethylformamide gave a red-brown solution of the $[Co(CN)_5(O_2)]^{3-}$ salt.[10] After this was left in ambient atmosphere of moderate humidity red-brown crystals of $[NEt_4)_3[Co(CN)_5(O_2)],5H_2O$ deposited. *Crystal data:* space group $P2_1$, $a = 10{\cdot}444(4)$, $b = 14{\cdot}105(8)$, $c = 14{\cdot}392(6)$ Å, $\beta = 108{\cdot}63(2)°$, D_m (flotation) = 1·15 g cm^{-3}, D_c = 1·16 g cm^{-3} for $Z = 2$. Intensity data were collected by automated diffractometer methods. Full-matrix least-squares refinement for the 2315 reflections with $F^2 > 3\sigma(F^2)$ gave $R = 6{\cdot}90\%$ and $R_w = 7{\cdot}33\%$. Several types of trial models in the refinement have shown conclusively that the structure is ordered.

The Figure shows the molecular geometry of the $[Co(CN)_5(O_2)]^{3-}$ ion. The mode of bonding of the O_2 group is essentially linear, with a Co–O–O bond angle of 175(2)°. This bond angle and the O–O distance of 1·13(2) Å are to some extent affected by the high thermal motion of the O_2 group. The best estimate of the O–O distance, when corrected for thermal motion,[11] is 1·2—1·3 Å. The complex may be formulated as a low-spin octahedral Co^{III} complex of the superoxide anion, O_2^-. This is also consistent with the solution e.s.r. spectrum.[10,12] The Co–O distance is 1·93(2) Å. The five Co–C bond lengths average 1·92(1) Å, with average C–N bond lengths of 1·10(2) Å.

A recent report on the e.s.r. spectra of oxycobaltmyoglobin and oxycobalthaemoglobin proposed the π structure (II).[13] The similarity of oxycobaltmyoglobin and $[Co(CN)_5(O_2)]^{3-}$, the structure reported here, and the preliminary information for the crystalline iron model compound[8] instead suggest that dioxygen binds to all such Fe^{II} and Co^{II} complexes through only one oxygen atom.

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