Preparation, Crystal Structure, and Magnetic Properties of a Binuclear Cobalt(II) Carboxylate

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Summary The reaction of quinoline with ethanolic cobalt(II) benzoate produces the dimeric complex $Co_2(quin)_2(C_6H_5CO_2)_4$, whose molecular structure, determined by *X*-ray methods, shows a long cobalt–cobalt distance of 2·83 Å, consistent with the compound's weak antiferromagnetism.

The recent discussion[1,2] of the origin of the antiferromagnetism of dimeric carboxylates has been confined to copper(II) species, as similar complexes of other metals have proved diamagnetic, and it has not hitherto been possible to use this structure to test more advanced theories of magnetic exchange involving spins greater than $\frac{1}{2}$[3] or extensive orbital contributions.[4] High spin Co^{2+} is a suitable ion for studying these developments, and we have found that addition of quinoline to the filtrate from the reaction of cobalt(II) carbonate with benzoic acid in ethanol gives the dimeric complex $Co_2(quin)_2(C_6H_5CO_2)_4$, for which satisfactory C, Co, H, and N analyses have been obtained.

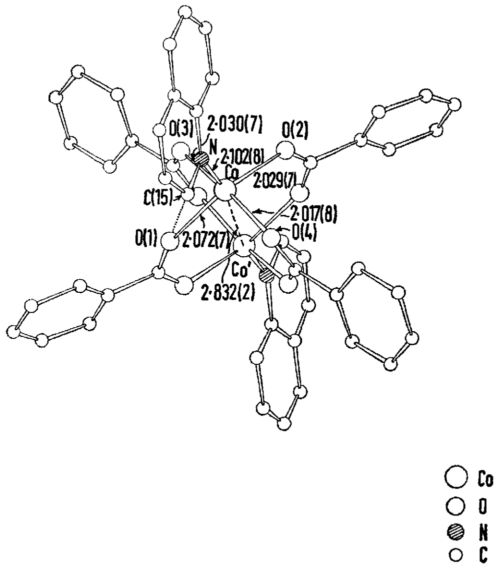

FIGURE. *View of the dimer, as seen in* c *axis projection. Bond lengths are in* Å. *The* N–Co–O(*n*) *angles are* 92·52(30), O(1); 104·19(30), O(2); 99·30(30), O(3); 96·88(29), O(4). *The* Co–Co–N *angle is* 168·31(30).

The complex exhibits the expected antiferromagnetism, with the moment falling from 4·11 B.M. at 293 K to 1·71 B.M. at 98 K, the susceptibility showing a maximum at 268 K. However, the data show the interaction to be comparatively weak (J *ca.* $-19\ cm^{-1}$). The detailed interpretation of the magnetism will be reported elsewhere, but it is clear that the reduction in magnetic moment at room temperature from the value of 5·05 B.M.[5] in the magnetically dilute $[Co(2\text{-picoline})(C_6H_5CO_2)_2]$ or of 5·07 B.M.[6] in the square-pyramidal $[Co(Ph_2MeAsO)_4(NO_3)]^+$ represents a fall of about one-third in the room-temperature susceptibility. This is less than the 50% fall in susceptibility found in copper(II) carboxylates (J *ca.* $-150\ cm^{-1}$), and indicates a far weaker interaction than the complete pairing of spins which occurs in carboxylates of bivalent chromium, molybdenum, and rhodium.[7]

Crystal data: $C_{46}H_{34}O_8N_2Co$, $M = 860{\cdot}64$, orthorhombic, $a = 17{\cdot}150(10)$, $b = 19{\cdot}703(11)$, $c = 11{\cdot}655(7)$, $D_m = 1{\cdot}49$, $Z = 4$, $D_c = 1{\cdot}50$, $\mu(\text{Cu-}K_\alpha) = 71{\cdot}7\ \text{cm}^{-1}$, space group *Pcab*. Intensity data were recorded on a G.E. XRD6 manual diffractometer using the stationary-crystal–stationary-counter technique and Cu-K_α radiation. From a total of 1750 reflections investigated, 1221 had intensities significantly ($> 3\sigma$) above background. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to a present R of 0·079. The structure found is shown in the Figure, which includes some of the more relevant bond lengths and angles.

The most striking dimension in the dimeric molecule is the cobalt–cobalt distance of 2·83 Å, which is the longest metal–metal distance yet found in this type of structure, being significantly longer than the strong multiple bond of length 2·36 Å found[8] in $Cr_2(H_2O)_2(CH_3CO_2)_4$, and also longer than the copper–copper distance of 2·6—2·7 Å in copper(II) carboxylates.

Also of interest is the inequality of the Co–O distances. The variations appear to be caused, at least in part, by the contact distances of the oxygens with carbon atoms of the quinoline molecules. Thus O(1), the oxygen furthest from Co, is the one closest to quinoline, being 3·03 Å distant from C(15), but the other O–C (quinoline) contacts are all longer than 3·2 Å.

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