# Preparation, *X*-Ray Crystal Structure, and Magnetic Properties of a Trinuclear Cobalt(II) Carboxylate

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*Summary* The trinuclear complex $[Co_3(quin)_2(PhCO_2)_6]$ is produced by the slow reaction of quinoline with ethanolic cobalt(II) benzoate; its molecular structure, determined by *X*-ray methods, consists of a linear array of cobalt atoms bridged by benzoate groups, but the compound is only very weakly antiferromagnetic.

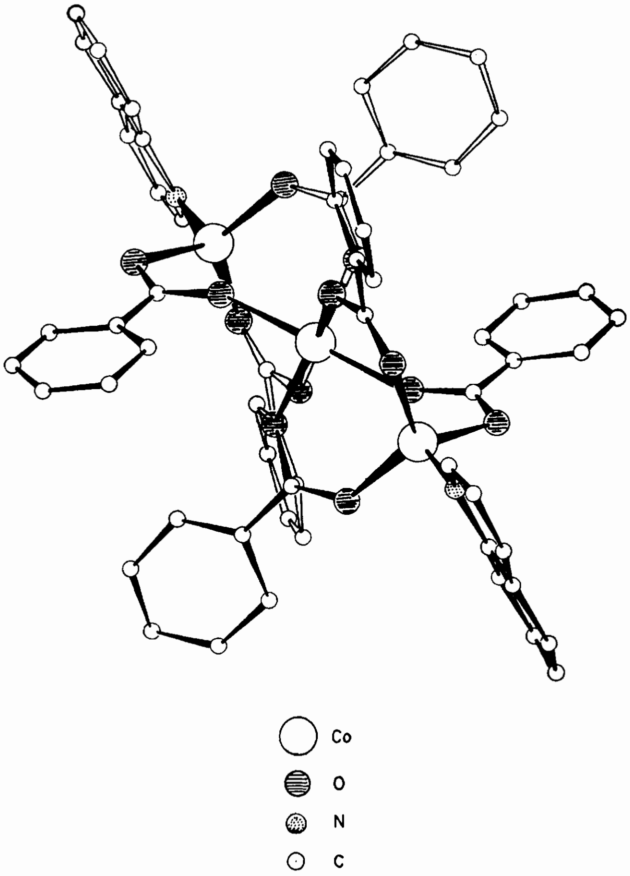
During our study[1] of cobalt(II) carboxylates we found that $[Co_2(quin)_2(PhCO_2)_4]$ was formed by refluxing quinoline with ethanolic cobalt(II) benzoate. If this green complex is then crystallised from ethanol or if the preparation is carried out at room temperature violet crystals of $[Co_3(quin)_2(PhCO_2)_6]$ are formed. Satisfactory C, Co, H, and N analyses have been obtained. We have determined its structure by single crystal *X*-ray analysis.

*Crystal data:* $C_{60}H_{44}Co_3O_{12}N_2$, $M = 1133{\cdot}81$, triclinic, $a = 10{\cdot}782$, $b = 10{\cdot}977$, $c = 10{\cdot}916$ Å, $\alpha = 83{\cdot}53$, $\beta = 98{\cdot}10$, $\gamma = 94{\cdot}85°$, $D_m = ca.\ 1{\cdot}50$, $Z = 1$, $D_c = 1{\cdot}48$, $\mu(Cu\text{-}K_\alpha) = 79{\cdot}89\ cm^{-1}$, space group $P\bar{1}$. Intensity data were recorded on a General Electric XRD6 manual diffractometer using the stationary-crystal-stationary-counter technique and Cu-$K_\alpha$ radiation. From a total of 1587 reflections measured out to a $2\theta$ limit of 80°, 1139 had significant ($>3\sigma$) intensities. The structure was solved by Patterson and Fourier methods and refined by least squares to a present $R$ of 0·10.

The molecular structure (Figure) consists of a centrosymmetric, and thus linear, array of three cobalt atoms with three bridging benzoate groups between adjacent pairs. The outer cobalt atoms [Co(2)] are each co-ordinated to a quinoline molecule to give four-co-ordination, but the angles are significantly different from those of a regular tetrahedron, with $\angle$O–Co–O 111—121° and $\angle$N–Co–O 92—104°. The central cobalt atom Co(1) has almost regular octahedral co-ordination of oxygen atoms, and is 3·56 Å distant from the other cobalt atoms. This is a much greater distance than that of 2·83 Å found in $\mathrm{Co_2(quin)_2(PhCO_2)_4}$, and is also longer than the 3·3 Å found for the metal–metal separations in the triangular clusters $[\mathrm{M^{III}_3O(MeCO_2)_6L_3}]^+$, (M = Cr[2], Mn[3], Fe[4]). This is the first example of a linear structure for a trinuclear carboxylate cluster, the first carboxylate cluster containing metal atoms in different co-ordination numbers, and the first system in which a ligand forms different clusters in different compounds with the same metal carboxylate.

The 'tetrahedral' Co–O distances (1·96—1·99, average 1·975 Å) are, as expected, significantly different from those for the octahedral Co atom (2·08—2·15, average 2·110 Å).

The trinuclear complex is only slightly antiferromagnetic down to 98 K, the magnetic moment being 4·87 B.M. per cobalt at 298 K and 4·58 B.M. at 98 K, and the Weiss constant has the small value of 19°. These results show that any magnetic exchange is smaller even than the weak antiferromagnetism found in the dimeric cobalt(II) carboxylate[1] or in the triangular clusters of trivalent chromium and iron.[5]



FIGURE

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