Crystal and Molecular Structure of Tetra-μ-benzoato-bisquinolinedicobalt(II), a Binuclear Cobalt(II) Carboxylate

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The structure of the title compound has been determined by three-dimensional *X*-ray crystal structure analysis. The crystals are orthorhombic with unit cell dimensions a = 17.150(10), b = 19.703(11), c = 11.655(7) Å, Z = 4, space group *Pcab*. Full-matrix least-squares refinement using 1 221 reflections reached R = 0.061. The centrosymmetric molecule comprises two cobalt ions bridged by four benzoate anions with the two oxygen atoms of each benzoate group bonded to different cobalt ions. Square-pyramidal five-co-ordination of cobalt is completed by a quinoline molecule, but steric effects cause significant deviations from regularity with N–Co–O angles from 92 to 104°, Co–O distances from 2.017 to 2.072 Å, Co–O–C angles from 119.1 to 130.3°, and an included Co–Co–N angle of 168.3°. The Co–Co separation is 2.832 Å.

SINCE the original report [1] of the two-dimensional *X*-ray determination of the molecular structure of copper(II) acetate monohydrate confirmed the prediction [2] from e.s.r. data that the compound adopted a binuclear con-

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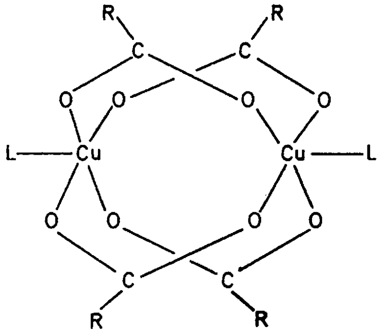
figuration, there have been many[3] studies of the magnetic and spectral properties of compounds having the general formula $[Cu_2L_2(RCO_2)_4]$. The first structure has been redetermined both by *X*-ray[4] and neutron diffraction[5] methods and complete structure determinations have been made[6-20] on many other dimeric copper(II) carboxylates.

In all these molecules the general structure is as shown in (1), the four carboxylate groups acting as bridging ligands and the terminal ligand L rendering the copper atoms five co-ordinate with the copper–copper separation ranging from 2.58 Å (L = ½ dioxan, R = H, ref. 8) to 2.747 Å (L = 2-picoline, R = CH_2Cl, ref. 13). The compounds all have magnetic moments at room temperature which are significantly below the spin-only value for one unpaired electron, and this value falls with decreasing temperature. The structure is also associated with a characteristic e.s.r. spectrum and its peculiar temperature dependence.



(1)

The many theoretical discussions[3] of the nature of the interaction between the copper ions which gives rise to these characteristic properties makes it desirable that more paramagnetic compounds having the same basic structure should be prepared and identified. Unfortunately most binuclear carboxylates other than those of copper are diamagnetic. However two vanadium(III) carboxylates, $[V_2(\eta\text{-}C_5H_5)_2(RCO_2)_4]$, where R = CF_3 or furan-2-yl, have been shown[21,22] to adopt the binuclear configuration and to have appropriate magnetic properties. As part of our study[20,23-26] of carboxylate complexes of the transition elements just preceding copper in the periodic table we now report the details of the *X*-ray study of the crystal and molecular structure of $[Co_2(quin)_2(C_6H_5CO_2)_4]$ (quin = quinoline), of which a preliminary account has already appeared.[27]

EXPERIMENTAL

Tetra-μ-benzoato-bisquinolinedicobalt(II) was precipitated in a suitably crystalline form from the reaction of quinoline with ethanolic cobalt(II) benzoate as dark green truncated octahedra.[26,27]

Crystal Data.—$C_{46}H_{34}Co_2N_2O_8$, $M = 860.6$, Orthorhombic, $a = 17.150(10)$, $b = 19.703(11)$, $c = 11.655(7)$ Å, $U = 3\,949$ Å, D_m (by flotation) = 1.49 g cm^{-3}, $Z = 4$, $D_c = 1.500$ g cm^{-3}, $F(000) = 1\,768$. The space group was shown to be *Pcab* from the systematic absences: $0kl$ for $l = 2n + 1$, $h0l$ for $h = 2n + 1$, and $hk0$ for $k = 2n + 1$. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 71.7 cm^{-1}.

Intensity data were recorded for a crystal of approximate size 0.25 × 0.3 × 0.3 mm mounted along the *a* axis using a General Electric XRD6 diffractometer equipped with manual goniometer, pulse-height analyser, and scintillation counter. The stationary-crystal–stationary-counter technique was used with a counting time of 10 s. A total of 1 750 reflections were recorded for $2\theta \leqslant 120°$, of which 1 221 had $I_{net} > 3\sigma$. Background readings were taken for all reflections and were subtracted from the observed reflections to give I_{net}.

Structure Analysis.—The position of the independent cobalt atom was determined from a Patterson synthesis and those of the lighter atoms from three successive difference syntheses. Least-squares refinement, with isotropic temperature factors for all atoms, reduced *R* to 0.092. Correction of the data absorption, followed by further isotropic refinement gave $R = 0.090$. Refinement with anisotropic temperature factors for all atoms (except hydrogen, for which no allowance was made) and use of the weighting scheme $\omega^{\frac{1}{2}} = 1$ for $F_o < F^*$ and $\omega^{\frac{1}{2}} = F_o/F^*$ for $F_o > F^*$, with $F^* = 65.0$ on an absolute scale, gave a final *R* value of 0.061. At this point all shifts were $<0.2\sigma$ and a difference map showed no area of significant electron density. The final fractional co-ordinates and their standard deviations are listed in Table 1, and Table 2 gives the

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U_{ij} coefficients in the expression for the anisotropic temperature factor $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Observed and calculated structure factors are deposited as Supplementary Publication No. SUP 21893 (4 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates *

	X	Y	Z
Co	−0.011 1(1)	0.040 6(1)	0.098 9(1)
N	−0.043 1(4)	0.085 1(4)	0.255 9(6)
O(1)	0.106 1(4)	0.024 4(3)	−0.100 9(6)
O(2)	0.090 8(4)	0.086 8(4)	0.057 3(6)
O(3)	−0.074 9(4)	0.099 3(4)	−0.009 2(6)
O(4)	−0.054 9(4)	0.034 6(4)	−0.165 2(6)
C(1)	0.088 7(5)	−0.081 4(6)	0.110 2(10)
C(2)	0.149 9(5)	−0.122 6(6)	0.172 6(8)
C(3)	0.167 8(6)	−0.188 6(6)	0.139 7(10)
C(4)	0.190 2(6)	−0.089 2(6)	0.261 9(9)
C(5)	0.251 3(7)	−0.126 9(7)	0.320 9(9)
C(6)	0.266 7(6)	−0.194 8(7)	0.289 7(12)
C(7)	0.226 1(7)	−0.226 6(6)	0.200 4(14)
C(8)	0.129 3(5)	0.065 1(5)	−0.027 6(10)
C(9)	0.212 2(6)	0.091 2(5)	−0.035 7(9)
C(10)	0.246 6(6)	0.125 4(6)	0.057 1(9)
C(11)	0.325 5(7)	0.143 7(6)	0.052 1(11)
C(12)	0.369 9(6)	0.128 7(7)	−0.046 1(12)
C(13)	0.336 5(6)	0.094 7(6)	−0.139 6(11)
C(14)	0.256 7(7)	0.074 8(5)	−0.134 3(10)
C(15)	−0.071 3(6)	0.039 0(7)	0.331 1(9)
C(16)	−0.103 3(7)	0.063 0(8)	0.439 8(11)
C(17)	−0.105 9(7)	0.130 6(9)	0.463 6(11)
C(18)	−0.076 2(6)	0.176 7(6)	0.381 5(10)
C(19)	−0.077 9(6)	0.248 4(8)	0.402 1(11)
C(20)	−0.047 0(7)	0.295 6(7)	0.321 3(13)
C(21)	−0.015 6(6)	0.268 1(6)	0.215 8(12)
C(22)	−0.013 3(6)	0.198 2(6)	0.193 3(10)
C(23)	−0.043 7(5)	0.153 2(5)	0.276 7(9)

* Estimated standard deviations are given in parentheses throughout this paper.

TABLE 2

Anisotropic thermal parameters (× 10^3)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	37(1)	35(1)	34(1)	1(1)	2(1)	−5(1)
N	43(4)	29(5)	35(5)	5(4)	5(4)	−6(4)
O(1)	52(4)	46(4)	50(5)	−13(4)	−1(4)	−12(4)
O(2)	35(4)	58(6)	49(5)	−6(4)	8(3)	−8(4)
O(3)	45(4)	58(5)	43(5)	9(4)	−9(4)	−2(4)
O(4)	59(5)	47(4)	47(4)	15(4)	3(4)	−2(4)
C(1)	27(6)	39(9)	40(8)	−9(5)	3(6)	10(7)
C(2)	32(6)	35(8)	34(6)	3(6)	6(5)	10(6)
C(3)	52(8)	37(9)	78(9)	4(6)	16(7)	−7(7)
C(4)	42(6)	62(9)	42(7)	6(6)	1(6)	8(7)
C(5)	47(7)	81(10)	46(7)	−6(8)	3(6)	23(7)
C(6)	33(7)	71(12)	92(11)	6(7)	3(6)	17(9)
C(7)	41(8)	55(11)	121(13)	14(7)	−4(8)	20(9)
C(8)	33(6)	22(8)	46(7)	6(5)	0(6)	7(6)
C(9)	38(6)	25(7)	48(7)	1(6)	0(6)	7(6)
C(10)	39(7)	65(7)	47(9)	−12(7)	−9(6)	−9(6)
C(11)	68(9)	52(10)	68(9)	−11(7)	−6(8)	−2(7)
C(12)	41(7)	64(10)	73(10)	−8(7)	4(7)	−7(8)
C(13)	44(8)	60(10)	73(9)	−4(7)	4(7)	12(8)
C(14)	43(7)	40(7)	56(8)	7(6)	7(6)	1(6)
C(15)	52(7)	91(11)	31(6)	−6(7)	0(6)	1(7)
C(16)	70(9)	78(13)	55(9)	−3(8)	13(7)	13(8)
C(17)	62(9)	87(13)	50(8)	−7(9)	10(7)	3(9)
C(18)	44(7)	24(8)	54(8)	5(6)	−18(6)	−19(7)
C(19)	42(6)	71(11)	55(8)	5(7)	−10(7)	−22(9)
C(20)	52(8)	68(12)	74(10)	18(8)	−26(8)	−36(9)
C(21)	48(7)	40(11)	89(10)	−8(7)	−11(7)	−23(7)
C(22)	52(7)	23(9)	54(7)	−14(7)	−11(6)	7(6)
C(23)	29(5)	20(8)	46(7)	12(5)	−8(5)	−20(6)

All calculations were performed on the University of London CDC 6600 computer using the 'X-Ray '67' system,[28] except the absorption corrections, which were computed using the programme 'ICABS', a local version prepared by Dr. P. G. H. Troughton of Imperial College of the original programme of Coppens *et al.*[29] Scattering factors for neutral atoms were taken from ref. 30.

DISCUSSION

This analysis shows the molecule to be a centrosymmetric dimer with four bidentate benzoate groups acting as bridging ligands between the two cobalt atoms, to each of which a quinoline molecule is also co-ordinated. The structure thus resembles those of the dimeric copper(II) carboxylates and this is the first compound of cobalt(II) found to have this structure. Figure 1 shows the structure of one molecule of $[Co_2(quin)_2(C_6H_5CO_2)_4]$ viewed along the *c* axis and includes the atomic numbering scheme. Figure 2 is a view of the unit-cell contents in projection down the *c* axis. A list of the bond lengths and bond angles, together with standard deviations, is given in Table 3.

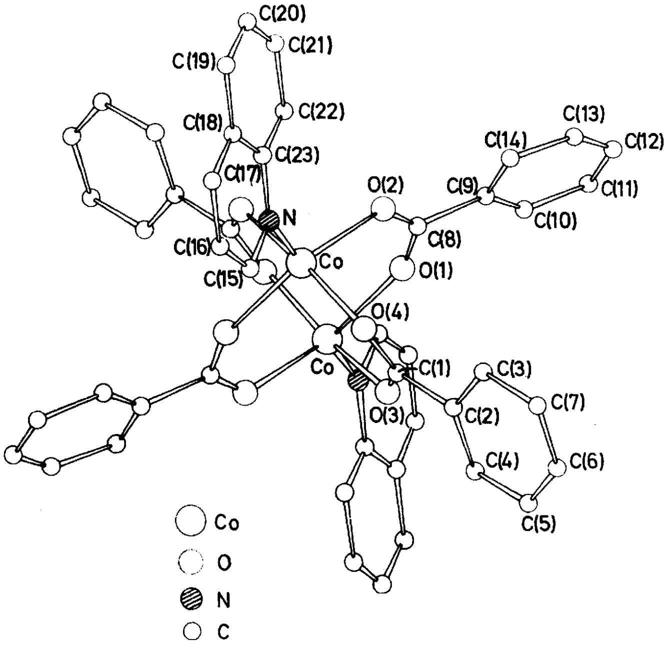

FIGURE 1 Molecular structure of $[Co_2(quin)_2(C_6H_5CO_2)_4]$ projected along the *c* axis

The co-ordination about each cobalt atom is square pyramidal, with four oxygen atoms from four different benzoate groups forming the basal plane and the nitrogen atom from a quinoline molecule occupying the axial position. The cobalt atom is located out of the O_4 plane and toward the nitrogen, as shown by the obtuse N–Co–O angles (mean value, 98.2°). The wide range of values for this angle also indicates significant distortions

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

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from idealised C_{4v} symmetry round the cobalt atom, which are mainly due to steric hindrance between the quinoline ligand and one of the benzoate groups. Thus the Co–O distances range from 2.017 to 2.072 Å (mean 2.037 Å) with the longest of these to O(1), the oxygen atom closest to the quinoline group [O(1)—C(15) 3.03 Å]. Another manifestation of the steric effect of the quinoline group is the difference in the Co–O–C angles, that at O(1) being 130.3°, 3.5° larger than any of the others.

The Co′–Co–N grouping is non-linear with an included angle of 168.3°. This is significantly smaller than any value recorded for this angle in $[M_2L_2(RCO_2)_4]$ compounds, and also reflects the difficulty of accommodating the bulky and rigid quinoline ligand.

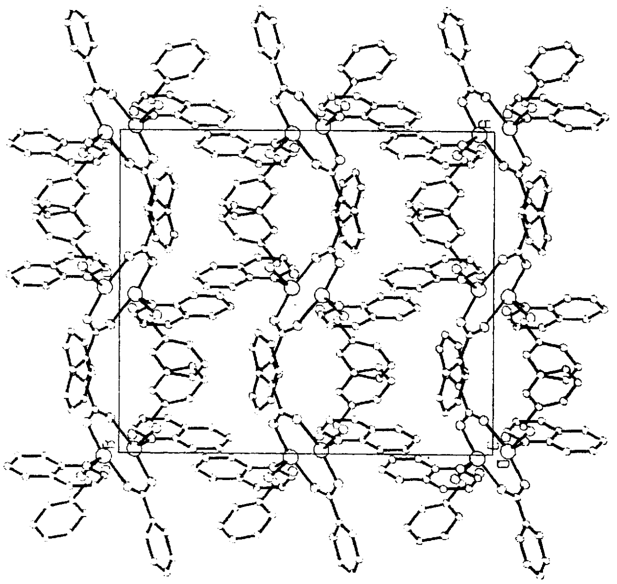

FIGURE 2 A view of the unit-cell contents, in projection down the *c* axis

The only other first-row transition-metal dimer involving an arylcarboxylate for which full structure data are available is $[Cu_2(OH_2)_2(2\text{-}BrC_6H_4CO_2)_4]$.[16] The mean bond distances and angles found for the carboxylate ligand there and in our compound show no significant differences. Also the geometry of the quinoline group is similar to that found in other quinoline containing complexes.[31,32]

As we are interested in comparing the physical properties of $[Co_2(quin)_2(C_6H_5CO_2)_4]$ with those of molecules containing single cobalt atoms, it is interesting to note that the cobalt–cobalt separation is 2.832 Å. This is much longer than the 2.36 Å found[33] for the multiple Cr–Cr bond in $[Cr_2(OH_2)_2(CH_3CO_2)_4]$. It is also longer than the copper–copper separation in dimeric copper(II) carboxylates (2.58—2.747 Å) but much shorter than the very long V–V distances of 3.704 and 3.625 Å found for cyclopentadienylvanadium(III) trifluoroacetate[21] and 2-carboxyfuran[22] respectively. However, the mean Co–O–C–O–Co 'super-exchange pathway', 6.584 Å, is of the same order as the average value for the corresponding distance in dimeric carboxylates of copper(II) (6.45 Å) and vanadium(III) (6.58 Å). In keeping with these results the cobalt complex is antiferromagnetic[27] and not diamagnetic.

TABLE 3

Bond lengths and angles in the complex

(*a*) Bond lengths (Å)			
Co(1)–C(1′)	2.832(2)	Co(1)–O(2)	2.029(7)
Co(1)–N(1)	2.102(8)	Co(1)–O(3)	2.030(7)
Co(1)–O(1)	2.072(7)	Co(1)–O(4)	2.017(8)
Quinoline group			
N(1)–C(15)	1.355(14)	C(19)–C(20)	1.425(20)
C(15)–C(16)	1.459(17)	C(20)–C(21)	1.446(20)
C(16)–C(17)	1.363(25)	C(21)–C(22)	1.404(17)
C(17)–C(18)	1.413(19)	C(22)–C(23)	1.414(15)
C(18)–C(19)	1.436(20)	C(23)–N(1)	1.362(13)
Benzoate group (1)			
O(1)–C(8)	1.237(13)	C(11)–C(12)	1.404(18)
O(2)–C(8)	1.265(13)	C(12)–C(13)	1.402(18)
C(8)–C(9)	1.515(14)	C(13)–C(14)	1.426(16)
C(9)–C(10)	1.405(15)	C(14)–C(9)	1.415(16)
C(10)–C(11)	1.402(17)		
Benzoate group (2)			
O(3)–C(1)	1.252(14)	C(4)–C(5)	1.457(16)
O(4)–C(1)	1.264(13)	C(5)–C(6)	1.413(21)
C(1)–C(2)	1.514(15)	C(6)–C(7)	1.400(20)
C(2)–C(3)	1.390(17)	C(7)–C(3)	1.437(18)
C(2)–C(4)	1.412(18)		
(*b*) Bond angles (°)			
N(1)–Co(1)–O(2)	104.2(3)	O(1)–Co(1)–O(3)	86.3(3)
N(1)–Co(1)–O(3)	99.3(3)	O(1)–Co(1)–O(4)	89.1(3)
N(1)–Co(1)–O(1)	92.5(3)	O(2)–Co(1)–O(3)	93.4(3)
N(1)–Co(1)–O(4)	96.9(3)	O(2)–Co(1)–O(4)	86.3(3)
Quinoline group			
C(15)–N(1)–C(23)	122.9(9)	C(18)–C(19)–C(20)	121.5(11)
C(16)–C(15)–N(1)	118.7(12)	C(19)–C(20)–C(21)	117.2(12)
C(15)–C(16)–C(17)	120.4(13)	C(20)–C(21)–C(22)	122.5(11)
C(16)–C(17)–C(18)	118.5(12)	C(21)–C(22)–C(23)	118.3(10)
C(17)–C(18)–C(19)	120.6(12)	C(22)–C(23)–N(1)	119.4(9)
Benzoate group (1)			
Co(1)–O(1)–C(8)	130.3(7)	C(9)–C(10)–C(11)	119.6(10)
Co(1)–O(2)–C(8)	119.1(7)	C(10)–C(11)–C(12)	120.4(11)
O(1)–C(8)–O(2)	126.2(9)	C(11)–C(12)–C(13)	120.7(11)
O(1)–C(8)–C(9)	118.7(9)	C(12)–C(13)–C(14)	119.4(11)
O(2)–C(8)–C(9)	115.1(9)	C(13)–C(14)–C(9)	119.2(10)
C(10)–C(9)–C(14)	120.7(9)		
Benzoate group (2)			
Co(1)–O(3)–C(1)	121.7(7)	C(2)–C(4)–C(5)	117.4(10)
Co(1)–O(4)–C(1)	126.8(7)	C(4)–C(5)–C(6)	119.8(11)
O(3)–C(1)–O(4)	126.5(10)	C(5)–C(6)–C(7)	121.5(12)
O(3)–C(1)–C(2)	115.6(9)	C(3)–C(7)–C(6)	118.6(12)
O(4)–C(4)–C(2)	117.8(10)	C(2)–C(3)–C(7)	120.4(11)
C(3)–C(2)–C(4)	122.2(10)		

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