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Tetra-μ-benzoato-bis(4-methylquinoline)dicobalt(II)

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Abstract. $C_{48}H_{38}Co_2N_2O_8$, triclinic, $P\bar{1}$; $a = 10{\cdot}098$ (10), $b = 10{\cdot}869$ (11), $c = 11{\cdot}981$ (12) Å, $\alpha = 106{\cdot}65$ (7), $\beta = 122{\cdot}86$ (8), $\gamma = 92{\cdot}84$ (7)°, $U = 1023{\cdot}4$ Å^3, $Z = 1$, $D_x = 1{\cdot}442$ g cm^{-3}. The structure was determined by direct methods and refined to an R of 0·050 for 2625 unique diffractometer data. The structure is analogous to that of Co_2(benzoate)$_4$(quinoline)$_2$, with Co $\cdots$ Co 2·861 (5) Å.

Introduction. The structure of the green Co^{II} dimer Co_2(benzoate)$_4$(quinoline)$_2$ was reported by Drew, Hursthouse, Thornton & Welch (1973), who prepared it by adding quinoline to an ethanolic solution of Co^{II} benzoate. Attempts to study the nature of the magnetic exchange in this compound (Boyd, Davies & Gerloch, 1977) have been frustrated by the difficulty of obtaining suitable crystals (1–5 mg) and pure powder samples; invariably, the product is contaminated with the purple trimer Co_3(benzoate)$_6$(quinoline)$_2$ (Catterick, Hursthouse, New & Thornton, 1974). The analogous reaction of 4-methylquinoline yields the dimer exclusively, and crystals of mass exceeding 2 mg can be obtained by slow addition of 4-methylquinoline to an ethanolic solution of Co^{II} benzoate at room temperature. In view of this, we have determined the crystal structure of Co_2(benzoate)$_4$(4-methylquinoline)$_2$ as a preliminary to magnetic anisotropy measurements.

Intensities were determined with a Syntex $P2_1$ four-circle diffractometer, Mo $K\alpha$ radiation, a graphite monochromator and a crystal 0·3 × 0·3 × 0·25 mm. 3855 reflexions were measured; averaging equivalent reflexions gave 2625 unique data with $F > 4\sigma(F)$ based on counting statistics. No corrections were made for absorption ($\mu = 8{\cdot}11$ cm^{-1}). The structure was

Table 1. *Atom coordinates* ($\times 10^4$)

	x	y	z
Co	283 (1)	225 (1)	4018 (1)
O(11)	−709 (4)	1739 (3)	4463 (3)
O(12)	−1114 (3)	1421 (3)	6018 (3)
O(21)	−2447 (3)	−1339 (3)	4131 (3)
O(22)	−2046 (3)	−972 (3)	2593 (3)
C(10)	−1146 (4)	2059 (4)	5287 (4)
C(11)	−1731 (4)	3308 (4)	5409 (4)
C(12)	−1669 (5)	4095 (4)	4711 (4)
C(13)	−2216 (6)	5241 (4)	4805 (5)
C(14)	−2833 (6)	5585 (4)	5597 (5)
C(15)	−2893 (6)	4813 (5)	6292 (5)
C(16)	−2350 (5)	3659 (4)	6202 (4)
C(20)	−2860 (5)	−1535 (4)	2888 (4)
C(21)	−4421 (5)	−2555 (4)	1675 (4)
C(22)	−4921 (6)	−2858 (5)	286 (5)
C(23)	−6332 (7)	−3868 (6)	−836 (5)
C(24)	−7210 (7)	−4536 (5)	−544 (6)
C(25)	−6723 (7)	−4214 (5)	836 (6)
C(26)	−5334 (5)	−3231 (4)	1934 (5)
N	355 (4)	811 (3)	2540 (3)
C(31)	−928 (5)	1197 (4)	1686 (4)
C(32)	−1034 (5)	1734 (4)	724 (4)
C(33)	231 (6)	1918 (4)	623 (4)
C(34)	1636 (5)	1508 (4)	1511 (4)
C(35)	3019 (6)	1632 (5)	1499 (5)
C(36)	4308 (7)	1204 (6)	2323 (6)
C(37)	4310 (5)	614 (5)	3232 (5)
C(38)	2999 (5)	493 (4)	3297 (4)
C(39)	1640 (5)	944 (4)	2440 (4)
C(40)	127 (7)	2530 (5)	−386 (5)

Table 2. *Anisotropic temperature factors* (Å^2 × 10^3)

The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \cdots\cdots + 2U_{12}hka^*b^*)$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	53 (1)	45 (1)	46 (1)	25 (1)	37 (1)	20 (1)
O(11)	92 (2)	58 (2)	77 (2)	36 (2)	68 (2)	43 (2)
O(12)	73 (2)	50 (2)	63 (2)	35 (1)	47 (2)	29 (1)
O(21)	57 (2)	67 (2)	51 (2)	13 (1)	32 (2)	7 (2)
O(22)	51 (2)	70 (2)	77 (2)	36 (2)	41 (2)	12 (2)
C(10)	41 (2)	41 (2)	44 (2)	17 (2)	24 (2)	13 (2)
C(11)	43 (2)	41 (2)	41 (2)	17 (2)	25 (2)	14 (2)
C(12)	71 (3)	52 (3)	67 (3)	31 (2)	47 (3)	27 (2)
C(13)	88 (3)	50 (3)	75 (3)	34 (2)	49 (3)	30 (3)
C(14)	81 (3)	48 (3)	60 (3)	15 (2)	32 (3)	31 (2)
C(15)	92 (4)	70 (3)	66 (3)	24 (3)	53 (3)	42 (3)
C(16)	65 (3)	58 (3)	51 (2)	22 (2)	38 (2)	26 (2)
C(20)	45 (2)	48 (2)	56 (2)	23 (2)	34 (2)	21 (2)
C(21)	42 (2)	47 (2)	47 (2)	17 (2)	28 (2)	16 (2)
C(22)	62 (3)	99 (4)	59 (3)	26 (3)	40 (3)	24 (3)
C(23)	82 (4)	111 (5)	48 (3)	8 (3)	31 (3)	38 (4)
C(24)	73 (4)	66 (4)	94 (4)	4 (3)	36 (3)	9 (3)
C(25)	83 (4)	68 (3)	88 (4)	25 (3)	41 (3)	0 (3)
C(26)	59 (3)	52 (3)	63 (3)	20 (2)	32 (2)	1 (2)
N	52 (2)	45 (2)	45 (2)	22 (2)	35 (2)	17 (2)
C(31)	57 (3)	54 (3)	54 (2)	28 (2)	37 (2)	22 (2)
C(32)	73 (3)	53 (3)	49 (2)	25 (2)	37 (2)	24 (2)
C(33)	86 (3)	37 (2)	46 (2)	12 (2)	41 (2)	5 (2)
C(34)	61 (3)	41 (2)	39 (2)	6 (2)	35 (2)	−3 (2)
C(35)	73 (3)	86 (4)	62 (3)	21 (3)	47 (3)	−3 (3)
C(36)	57 (3)	130 (5)	74 (3)	26 (3)	47 (3)	2 (3)
C(37)	49 (3)	107 (4)	65 (3)	27 (3)	35 (3)	15 (3)
C(38)	48 (3)	68 (3)	49 (2)	22 (2)	30 (2)	14 (2)
C(39)	48 (2)	41 (2)	40 (2)	9 (2)	29 (2)	2 (2)
C(40)	120 (4)	70 (3)	62 (3)	32 (3)	57 (3)	8 (3)

solved by multisolution Σ_2 sign expansion; all but four non-hydrogen atoms were found in the best E map. The structure was refined by blocked cascade least squares, with isotropic temperature factors for the H atoms and the remaining atoms anisotropic. H atoms were inserted in geometrically calculated positions and refined subject to the constraint that the C—H vectors remained constant (with C—H 1·08 Å). Complex neutral-atom scattering factors were employed; the weighting scheme was $w = 1/[\sigma^2(F) + 0{\cdot}0003F^2]$. The refinement converged to $R' = \Sigma\, w^{1/2} \Delta / \Sigma\, w^{1/2} |F_o| = 0{\cdot}045$ and $R = 0{\cdot}050$. Positional and thermal parameters are given in Tables 1–3, and the resulting bond lengths and angles in Tables 4 and 5.*

Table 3. *Hydrogen atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2 $\times$ 10^3)

	x	*y*	*z*	*U*
H(12)	−1187	3820	4086	66 (10)
H(13)	−2160	5856	4258	100 (12)
H(14)	−3271	6471	5669	80 (10)
H(15)	−3367	5098	6921	117 (12)
H(16)	−2414	3046	6748	87 (11)
H(22)	−4230	−2317	58	84 (11)
H(23)	−6721	−4119	−1927	137 (13)
H(24)	−8293	−5321	−1403	125 (13)
H(25)	−7433	−4732	1063	130 (13)
H(26)	−4959	−2988	3020	95 (11)
H(31)	−1960	1084	1738	91 (11)
H(32)	−2131	2008	53	97 (11)
H(35)	3049	2076	811	125 (13)
H(36)	5245	1323	2261	79 (10)
H(37)	5343	260	3874	94 (11)
H(38)	3002	54	4001	64 (9)
H(401)	1243	2593	−315	195 (15)
H(402)	−48	3514	−102	191 (15)
H(403)	−888	1925	−1468	234 (15)

Table 4. *Bond lengths* (Å)

Co—O(11)	2·058 (6)	Co—O(12*)	2·013 (5)
Co—O(21*)	2·024 (4)	Co—O(22)	2·051 (5)
Co—N	2·081 (6)	O(11)—C(10)	1·257 (8)
O(12)—C(10)	1·252 (7)	O(21)—C(20)	1·254 (7)
O(22)—C(20)	1·250 (8)	C(10)—C(11)	1·508 (8)
C(11)—C(12)	1·378 (9)	C(12)—C(13)	1·387 (8)
C(13)—C(14)	1·374 (11)	C(14)—C(15)	1·361 (10)
C(15)—C(16)	1·394 (8)	C(16)—C(11)	1·378 (9)
C(20)—C(21)	1·497 (5)	C(21)—C(22)	1·375 (9)
C(22)—C(23)	1·401 (7)	C(23)—C(24)	1·361 (13)
C(24)—C(25)	1·366 (11)	C(25)—C(26)	1·372 (6)
C(26)—C(21)	1·364 (10)	N—C(31)	1·328 (6)
N—C(39)	1·371 (8)	C(31)—C(32)	1·392 (9)
C(32)—C(33)	1·358 (10)	C(33)—C(34)	1·428 (7)
C(34)—C(35)	1·405 (10)	C(34)—C(39)	1·415 (8)
C(35)—C(36)	1·347 (9)	C(36)—C(37)	1·413 (12)
C(37)—C(38)	1·369 (10)	C(38)—C(39)	1·415 (7)
C(33)—C(40)	1·498 (10)	Co—Co*	2·861 (5)

Discussion. The molecule (Fig. 1) possesses a crystallographic centre of symmetry, and an overall geometry similar to that reported by Drew *et al.* for the analogous quinoline derivative. The Co···Co distances [4-methylquinoline derivative 2·861 (5); quinoline derivative 2·832 (2) Å] are longer than most metal–metal distances in carboxylate-bridged dimers, but shorter than the Co(O)Co distances in di-μ-acetato-tetrakis[μ_3-methoxo-2,4-pentanedionato-cobalt(II,III)] (mean Co···Co 3·075; Bertrand & Hightower, 1973) and in dimeric bis(2,4-pentanedionato)cyclohexylaminecobalt(II) [Co···Co 3·332 (2) Å; Bertrand & Kalyanaraman, 1971]. Further in-

Table 5. *Bond angles* (°)

O(11)—Co—O(22)	87·4 (2)	O(11)—Co—O(21*)	87·1 (2)
O(11)—Co—O(12*)	162·0 (2)	O(22)—Co—O(12*)	88·6 (2)
O(12*)—Co—O(21*)	91·3 (2)	O(22)—Co—O(21*)	161·9 (2)
O(11)—Co—N	92·5 (3)	N—Co—O(12*)	105·4 (3)
N—Co—O(21*)	101·6 (2)	O(22)—Co—N	95·9 (2)
Co—O(22)—C(20)	126·4 (4)	C(20)—O(21)—Co*	126·3 (4)
Co—O(11)—C(10)	132·2 (3)	C(10)—O(12)—Co*	121·1 (4)
Co—N—C(31)	116·2 (5)	Co—N—C(39)	126·7 (4)
C(21)—C(20)—O(22)	124·9 (4)	O(22)—C(20)—C(21)	118·0 (5)
O(21)—C(20)—C(21)	117·0 (6)	C(20)—C(21)—C(22)	120·3 (6)
C(20)—C(21)—C(26)	120·6 (5)	C(22)—C(21)—C(26)	119·0 (5)
C(21)—C(22)—C(23)	119·9 (7)	C(22)—C(23)—C(24)	119·7 (7)
C(23)—C(24)—C(25)	120·1 (5)	C(24)—C(25)—C(26)	120·1 (8)
O(11)—C(10)—C(11)	117·3 (5)	O(12)—C(10)—C(11)	118·1 (6)
C(10)—C(11)—C(12)	120·1 (6)	C(10)—C(11)—C(16)	120·3 (5)
O(11)—C(10)—O(12)	124·7 (5)	C(21)—C(26)—C(25)	121·1 (7)
C(12)—C(11)—C(16)	119·7 (5)	C(11)—C(12)—C(13)	120·6 (7)
C(12)—C(13)—C(14)	119·5 (7)	C(13)—C(14)—C(15)	120·2 (6)
C(14)—C(15)—C(16)	120·8 (7)	C(11)—C(16)—C(15)	119·3 (6)
C(31)—N—C(39)	116·9 (5)	N—C(31)—C(32)	124·3 (6)
C(31)—C(32)—C(33)	120·6 (5)	C(32)—C(33)—C(34)	117·2 (6)
C(33)—C(34)—C(39)	118·9 (6)	N—C(39)—C(34)	122·0 (5)
C(33)—C(34)—C(35)	122·9 (6)	C(35)—C(34)—C(39)	118·2 (5)
C(34)—C(35)—C(36)	121·4 (8)	C(35)—C(36)—C(37)	120·8 (8)
C(36)—C(37)—C(38)	119·8 (6)	C(37)—C(38)—C(39)	119·9 (6)
C(34)—C(39)—C(38)	119·9 (6)	N—C(39)—C(38)	118·2 (6)
C(32)—C(33)—C(40)	120·3 (5)	C(34)—C(33)—C(40)	122·4 (7)

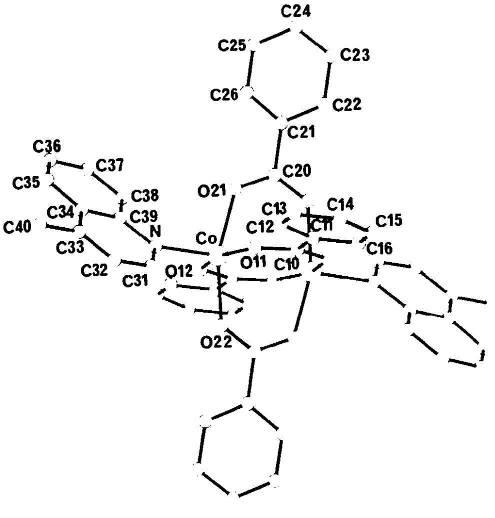

Fig. 1. The molecule of tetra-μ-benzoato-bis(4-methylquinoline)-dicobalt(II).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31993 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

sight into these distances must await the magnetic anisotropy studies (Boyd, Davies & Gerloch, 1977).

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Crystallographic Studies on Metal–Nucleotide Base Complexes. VIII. Tetraaquabis(9-methylhypoxanthine)copper(II) Sulphate

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Abstract. $[(C_6H_6N_4O)_2Cu(H_2O)_4]SO_4$, monoclinic, space group $P2_1/c$, $a = 8{\cdot}709$ (3), $b = 13{\cdot}348$ (3), $c = 16{\cdot}778$ (1) Å, $\beta = 105{\cdot}44$ (2)°, $Z = 4$, $D_m = 1{\cdot}879$ (7), $D_x = 1{\cdot}85$ (3) g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å. The structure was refined by full-matrix least squares to an R of 0·040. The complex unit has both a pseudo two-fold axis and a pseudo mirror plane. The Cu ion is octahedrally surrounded, the guanine bases binding equatorially through N(7) with four water molecules completing the coordination sphere.

Introduction. The compound was synthesized according to a procedure described by Weiss & Venner (1965). Single crystals suitable for X-ray work appeared overnight. The experimental procedure for data collection and processing is described elsewhere (Sletten, 1974). Within the sphere of reflexion limited at $\sin\theta/\lambda = 0{\cdot}56$, 4144 unique reflexions were recorded. Of these, 1107 were less than the threshold value. The least-squares refinement converged slowly owing to pseudosymmetry, to an R of 0·040. Atomic parameters are listed in Table 1.*

Discussion. The molecular dimensions of the complex and the sulphate ion are shown in Fig. 1. The hypoxanthine ligands are coordinated equatorially and arranged in an *anti* configuration while in the analogous guanine complex the purine ligands are *syn* (Sletten & Fløgstad, 1976). Apart from the metal–nucleic acid interaction it is also of interest to elucidate the role of anions in these systems. In the present compound the sulphate serves as a hydrogen-bond bridge between crystallographically independent hypoxanthine ligands (Fig. 2). Guanine is the only purine able to establish a true di-hydrogen bond to oxyanions; however, the connexion between sulphate and hypoxanthine ligand A is similar in nature, regarding C(2)–H···O(5) as a hydrogen bond. The interaction between sulphate and ring B is through a bifurcated hydrogen bond involving N(1)–H

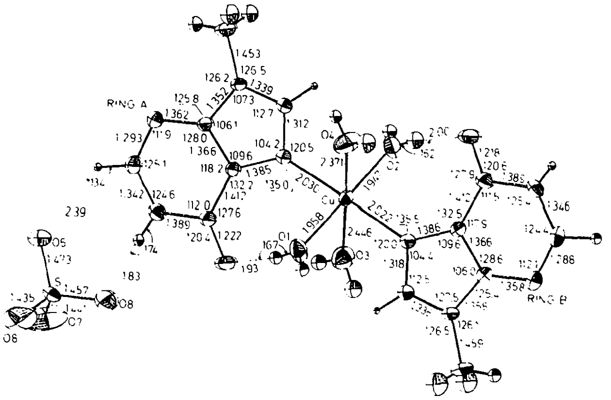

Fig. 1. Interatomic distances and angles in the complex unit. The σ's in bond lengths are: Cu–O(N) 0·002 Å, C–C(N)(O) 0·003–0·004 Å. The σ's for angles involving non-hydrogen atoms are in the range 0·04–0·4°. The thermal spheres of the H atoms correspond to ¼ of the U values.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31994 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.