Crystal and Molecular Structure of a Tetranuclear Cobalt(II)–Tropolonate Complex: $[Co_4(C_7H_5O_2)_8(H_2O)_2]$

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Crystals of the title compound are monoclinic, a = 13.341(5), b = 18.634(9), c = 11.603(5) Å, β = 171.43(3)°, Z = 2, space group $P2_1/c$. The structure was determined from X-ray diffractometer data by Patterson and Fourier syntheses, and refined by full-matrix least-squares calculations to R 0.067 for 2 070 observed reflections. There are two distinct cobalt atoms in the structure, both achieving a co-ordination number of six but with considerably distorted octahedral geometry. Of the four independent tropolone ligands in the asymmetric unit, three chelate and have one bridging oxygen atom while the other ligand chelates and does not bridge. A water molecule completes the co-ordination polyhedra. The Co–O distances vary from 2.051(6) to 2.149(9) Å, with mean distances corresponding to whether the ligand chelates (2.060 Å), chelates and bridges (2.084 Å), or forms a bridging bond (2.137 Å). The molecules are hydrogen-bonded *via* the water molecules and tropolone oxygen atoms. The stability of the structure is due to efficient lattice packing and hydrogen bonding, both facilitated by the compact planar structure of the ligand.

TROPOLONE has been shown,[1,2] in $[\{NiT_2(H_2O)\}_2]$ (T = tropolonate anion), to form an oxygen-bridged structure in the solid state, and molecular association has been reported[3] for other substituted tropolone chelates in solution. The number of complexes formed by tropolone[3-5] approaches that known for acetylacetone and it is reasonable to suspect that other bridged structures exist. Although tropolone behaves similarly to the smaller β-diketones[2,6] in many ways, the bridged structures of the former appear to exhibit greater stability, and the present compound has been studied to further investigate the characteristics of tropolone as a bridging ligand.

EXPERIMENTAL

The title compound was prepared by the addition of an aqueous solution of cobalt(II) nitrate to an excess of tropolone in aqueous ethanol. Sodium acetate solution was then added dropwise until the reaction mixture darkened. On heating, a dark red precipitate formed which was washed and dried (silica gel). From aqueous methanol, red transparent crystals were obtained which were elongated along b (Found: C, 54.10; H, 3.60. Calc. for $C_{56}H_{44}Co_4O_{18}$: C, 54.20; H, 3.58%). The space group and preliminary cell dimensions were determined from precession and Weissenberg photographs.

Crystal Data.—$C_{56}H_{44}Co_4O_{18}$, M = 1240.72, Monoclinic, a = 13.341(5), b = 18.634(9), c = 11.603(5) Å, β = 117.43(3)°, U = 2 560.1 Å^3, D_c = 1.57, Z = 2, D_m = 1.58(1) (by flotation in aqueous $ZnCl_2$), $F(000)$ = 1264. Mo-K_α radiation, λ = 0.71069 Å; μ(Mo-K_α) = 13.7 cm^{-1}. Space group $P2_1/c$ from systematic absences: $0k0$ when k is odd, $h0l$ when l is odd.

A crystal with dimensions *ca.* 0.2 × 0.4 × 0.1 mm was mounted with the b axis nearly coincident with the instrument ϕ-axis of a Stoe computer-controlled four-circle diffractomer. Accurate cell parameters and the crystal orientation matrix were then obtained by a least-squares treatment of 12 general hkl reflections of moderate intensity, by use of Mo-K_α radiation from a graphite monochromator. Intensity data were collected for all reflections having $2\theta(\text{Mo-}K_\alpha) \leqslant 45°$, employing the θ—2θ scanning technique with a scan width of 1.6°. The detector was of the scintillation type and pulse-height discrimination was applied to all measurements. A check reflection was monitored every 30 reflections for scaling purposes. Of the reflections measured, 2 070 were considered observed, while those which had intensities with $I < 3\sigma(I)$ [$\sigma(I)$ is defined by $\sigma^2(I)$ =

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[1] R. J. Irving, M. L. Post, and D. C. Povey, *J.C.S. Dalton*, 1973, 697.

[2] M. L. Post, Ph.D. Thesis, University of Surrey, 1971.

[3] E. L. Muetterties, H. Roesky, and C. M. Wright, *J. Amer. Chem. Soc.*, 1966, **88**, 4856.

[4] B. E. Bryant, W. C. Fernelius, and B. E. Douglas, *J. Amer. Chem. Soc.*, 1953, **75**, 3784.

[5] B. E. Bryant, J.-C. Pariaud, and W. C. Fernelius, *J. Org. Chem.*, 1954, **19**, 1889.

[6] D. W. Thompson, *Structure and Bonding*, 1971, **9**, 27.

$S + B$ where S = scan count and B = background] were considered unobserved and were excluded from subsequent calculations. Lorentz and polarisation corrections were applied and relative structure factors derived. No absorption or extinction corrections were made.

Structure Determination and Refinement.—The positions of the two independent cobalt atoms were determined from a Patterson synthesis and from a subsequent Fourier synthesis all remaining oxygen and carbon atoms were located. Following two cycles of full-matrix least-squares refinement, employing isotropic temperature factors, R was 0.091. A further four cycles of full-matrix refinement, using anisotropic thermal parameters, reduced R to 0.067; in the last cycle no parameter shift was $>0.5\sigma$. Scattering factors were taken from ref. 7. Unit weights were used throughout, a plot of ΔF *vs.* F_o showing that this was satisfactory. A final difference-Fourier synthesis indicated no electron density >0.9 eÅ^{-3} other than in the region of the cobalt atoms. Final positional and thermal parameters are shown in Tables 1 and 2, while measured and calculated structure factors are listed in Supplementary Publication No. SUP 21358 (20 pp., 1 microfiche).*

TABLE 1

Final positional parameters ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
Co(1)	1 723(1)	4 243(1)	5 022(2)
Co(2)	3 679(1)	5 115(1)	4 681(2)
O(a1)	5 258(5)	5 593(4)	5 717(7)
O(a2)	3 380(6)	5 975(4)	5 663(9)
C(a1)	5 314(8)	6 165(6)	6 362(10)
C(a2)	4 224(10)	6 390(6)	3 306(12)
C(a3)	4 036(11)	7 019(7)	6 868(14)
C(a4)	4 779(11)	7 516(7)	7 666(13)
C(a5)	5 959(11)	7 552(7)	8 206(14)
C(a6)	6 621(11)	7 111(7)	7 864(15)
C(a7)	6 346(10)	6 514(7)	7 052(13)
O(b1)	3 465(6)	4 409(4)	5 991(7)
O(b2)	2 163(6)	3 883(5)	6 876(7)
C(b1)	3 916(10)	4 308(6)	7 206(11)
C(b2)	3 167(10)	4 010(6)	7 722(12)
C(b3)	3 462(11)	3 867(7)	9 021(13)
C(b4)	4 503(13)	3 914(8)	10 128(13)
C(b5)	5 577(12)	4 135(9)	10 280(15)
C(b6)	5 802(11)	4 358(8)	9 280(14)
C(b7)	5 090(10)	4 454(7)	7 974(14)
O(c1)	2 002(5)	4 799(5)	3 572(7)
O(c2)	3 119(6)	5 739(6)	3 023(9)
C(c1)	1 400(10)	5 224(6)	2 619(12)
C(c2)	2 065(10)	5 729(7)	2 278(11)
C(c3)	1 627(12)	6 210(8)	1 198(14)
C(c4)	520(14)	6 334(8)	299(15)
C(c5)	−515(14)	6 021(9)	153(16)
C(c6)	−597(12)	5 510(8)	964(16)
C(c7)	209(10)	5 141(7)	2 027(14)
O(d1)	48(5)	3 966(4)	4 082(8)
O(d2)	1 764(6)	3 268(4)	4 193(9)
C(d1)	−178(10)	3 411(6)	3 336(12)
C(d2)	816(10)	3 024(6)	3 426(12)
C(d3)	768(12)	2 389(7)	2 695(13)
C(d4)	−135(13)	1 996(7)	1 797(14)
C(d5)	−1 305(12)	2 119(8)	1 298(14)
C(d6)	−1 803(12)	2 676(8)	1 634(15)
C(d7)	−1 321(11)	3 248(7)	2 523(13)
O(w)	1 468(7)	5 297(4)	5 562(12)

TABLE 2

Final anisotropic thermal parameters ($\beta_{ij} \times 10^4$), with estimated standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	16(1)	12(1)	61(2)	−3(1)	21(1)	−6(1)
Co(2)	10(1)	12(1)	43(2)	2(1)	13(1)	2(1)
O(a1)	16(5)	18(3)	70(9)	−3(3)	19(6)	−12(4)
O(a2)	22(5)	17(3)	92(12)	−3(3)	25(6)	−15(5)
C(a1)	25(8)	13(4)	55(12)	0(4)	19(4)	−1(6)
C(a2)	27(9)	12(4)	86(15)	0(5)	27(10)	3(6)
C(a3)	45(11)	18(5)	95(17)	0(6)	38(12)	0(7)
C(a4)	43(11)	19(5)	70(16)	−6(6)	19(11)	−1(7)
C(a5)	53(12)	13(4)	82(16)	−5(6)	21(12)	1(7)
C(a6)	48(11)	10(4)	127(19)	−8(6)	34(12)	1(7)
C(a7)	33(10)	16(4)	88(16)	−5(5)	22(11)	−8(8)
O(b1)	20(5)	13(3)	52(9)	−6(3)	12(6)	−2(4)
O(b2)	41(6)	35(4)	51(9)	−19(4)	31(6)	0(5)
C(b1)	42(10)	15(4)	38(12)	4(5)	26(10)	−5(6)
C(b2)	38(9)	14(4)	51(13)	−15(5)	24(9)	−9(6)
C(b3)	62(12)	22(5)	64(15)	−15(6)	34(11)	−7(7)
C(b4)	91(16)	25(5)	69(17)	1(7)	34(14)	2(8)
C(b5)	63(13)	41(7)	75(17)	−3(8)	21(12)	−5(9)
C(b6)	42(11)	28(6)	76(17)	6(6)	12(11)	−4(7)
C(b7)	35(10)	20(5)	76(16)	−3(6)	24(11)	−8(7)
O(c1)	19(5)	21(3)	57(8)	0(3)	10(5)	5(4)
O(c2)	28(5)	35(4)	76(11)	10(4)	25(6)	19(6)
C(c1)	54(11)	11(4)	67(15)	11(5)	34(11)	2(6)
C(c2)	50(10)	15(4)	54(14)	4(5)	25(10)	1(6)
C(c3)	68(13)	27(5)	70(16)	14(7)	19(12)	10(8)
C(c4)	91(15)	27(6)	78(18)	16(8)	24(14)	9(8)
C(c5)	83(16)	27(6)	106(21)	26(7)	14(15)	−1(9)
C(c6)	47(12)	26(6)	124(20)	12(7)	7(13)	13(9)
C(c7)	29(10)	17(4)	102(17)	9(6)	−4(10)	−1(7)
O(d1)	20(5)	16(3)	97(11)	−8(3)	31(6)	−21(4)
O(d2)	21(5)	14(3)	92(12)	1(3)	10(6)	−16(5)
C(d1)	29(9)	15(4)	74(15)	1(5)	23(10)	−4(6)
C(d2)	45(10)	11(4)	55(14)	5(5)	27(10)	9(6)
C(d3)	68(12)	19(5)	64(15)	−5(6)	29(12)	−7(7)
C(d4)	76(14)	17(5)	77(17)	5(6)	22(13)	9(7)
C(d5)	73(13)	21(5)	81(17)	−19(7)	38(13)	−11(7)
C(d6)	54(12)	28(6)	103(18)	−17(7)	27(13)	−6(8)
C(d7)	46(11)	20(5)	76(16)	−8(6)	21(11)	−6(7)
O(w)	57(7)	17(3)	223(21)	−8(4)	100(11)	−28(6)

Thermal parameters are in the form: $\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

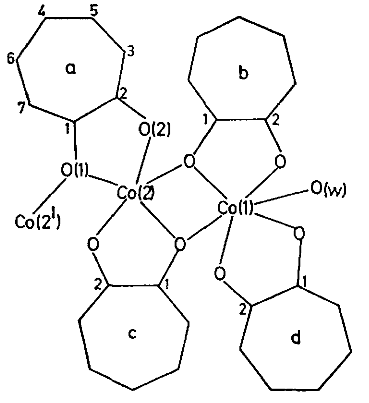

FIGURE 2 The atom numbering scheme for the complex. Each tropolone ring has a literal subscript, the atoms then being numbered as shown in a

DISCUSSION

The details of the structure are shown in Figure 1, and the atom numbering scheme for the molecule in Figure 2. Tables 3 and 4 list bond lengths and angles, while Table 5 gives some mean planes.

The molecule itself is centrosymmetric with the centre of symmetry lying between atoms Co(2) and Co(2$^{\text{I}}$).

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[7] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

Each of the cobalt atoms achieves a co-ordination number of six, Co(1) through five tropolonate oxygen atoms and one water molecule at O(w), while Co(2) is co-ordinated by tropolonate oxygen atoms alone. In both cases, however, the co-ordination geometry is considerably distorted octahedral, a result of the rigid ligand and its chelation angle, mean 76.7°. The distances Co(1)$\cdots$Co(2) [3.249(3) Å] and Co(2)$\cdots$Co(2^I) [3.277(3) Å] indicate that no metal–metal interaction is occurring, and can be contrasted with that [2.524 Å] in dicobalt octacarbonyl,[8] in which the Co–Co interaction is of structural importance. The four cobalt atoms in the present structure are not linearly arranged, the angle Co(1)–Co(2)–Co(2^I) being 138.4(2)°.

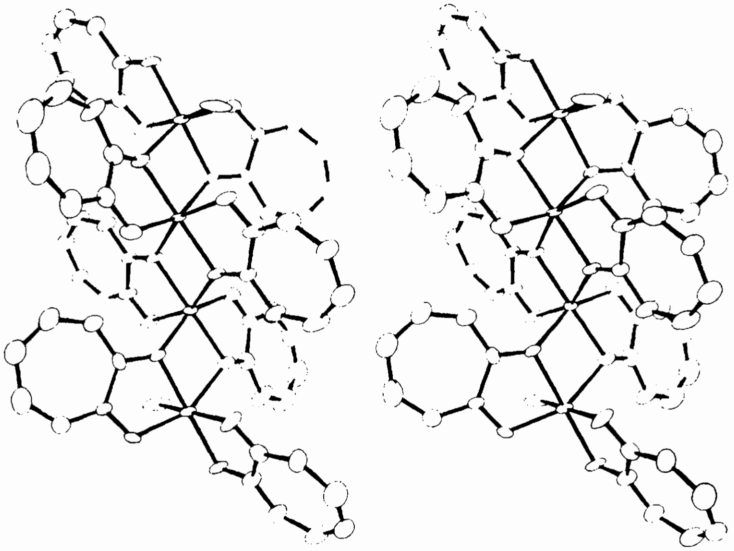

FIGURE 1 Stereoscopic view of the complex. All atoms are represented by 50% probability thermal ellipsoids

TABLE 3

Bond distances (Å), with estimated standard deviations * in parentheses

Co(1)–O(b1)	2.086(7)	C(b2)–C(b3)	1.397(20)
Co(1)–O(b2)	2.064(8)	C(b3)–C(b4)	1.394(16)
Co(1)–O(c1)	2.149(9)	C(b4)–C(b5)	1.422(25)
Co(1)–O(d1)	2.051(6)	C(b5)–C(b6)	1.389(27)
Co(1)–O(d2)	2.068(9)	C(b6)–C(b7)	1.380(18)
Co(1)–O(w)	2.136(9)	C(b7)–C(b1)	1.428(16)
Co(2)–O(a1)	2.084(6)	O(c1)–C(c1)	1.295(13)
Co(2)–O(a2)	2.109(9)	O(c2)–C(c2)	1.266(13)
Co(2)–O(b1)	2.127(9)	C(c1)–C(c2)	1.467(20)
Co(2)–O(c1)	2.088(6)	C(c2)–C(c3)	1.429(19)
Co(2)–O(c2)	2.070(10)	C(c3)–C(c4)	1.380(19)
Co(2^I)–O(a1)	2.136(8)	C(c4)–C(c5)	1.435(27)
O(a1)–C(a1)	1.284(14)	C(c5)–C(c6)	1.378(26)
O(a2)–C(a2)	1.284(13)	C(c6)–C(c7)	1.388(18)
C(a1)–C(a2)	1.486(19)	C(c7)–C(c1)	1.419(17)
C(a2)–C(a3)	1.419(20)	C(d1)–C(d1)	1.292(14)
C(a3)–C(a4)	1.361(17)	O(d2)–C(d2)	1.249(13)
C(a4)–C(a5)	1.402(19)	C(d1)–C(d2)	1.471(19)
C(a5)–C(a6)	1.391(23)	C(d2)–C(d3)	1.440(19)
C(a6)–C(a7)	1.395(20)	C(d3)–C(d4)	1.385(18)
C(a7)–C(a1)	1.395(19)	C(d4)–C(d5)	1.411(22)
O(b1)–C(b1)	1.266(14)	C(d5)–C(d6)	1.381(24)
O(b2)–C(b2)	1.266(12)	C(d6)–C(d7)	1.415(19)
C(b1)–C(b2)	1.488(22)	C(d7)–C(d1)	1.407(16)

* Estimated standard deviation calculated from full covariance matrix. Superscript I denotes atom at $1 - x$, $1 - y$, $1 - z$.

It is apparent from Figures 1 and 2 that, with respect to co-ordination characteristics, there are two types of tropolone ligand in the molecule. One type (a—c)

TABLE 4

Co-ordination and bond angles, with estimated standard deviations in parentheses

O(b1)–Co(1)–O(b2)	77.0(3)	C(a3)–C(a4)–C(a5)	130.8(15)
O(b1)–Co(1)–O(c1)	78.4(3)	C(a4)–C(a5)–C(a6)	125.0(12)
O(b1)–Co(1)–O(d1)	174.0(3)	C(a5)–C(a6)–C(a7)	131.3(12)
O(b1)–Co(1)–O(d2)	96.9(3)	C(a6)–C(a7)–C(a1)	130.0(14)
O(b1)–Co(1)–O(w)	89.6(3)	C(a7)–C(a1)–C(a2)	125.5(11)
O(b2)–Co(1)–O(c1)	154.7(3)	Co(1)–O(b1)–C(b1)	114.7(9)
O(b2)–Co(1)–O(d1)	100.9(4)	Co(1)–O(b2)–C(b2)	116.0(9)
O(b2)–Co(1)–O(d2)	98.3(4)	O(b1)–C(b1)–C(b2)	116.1(9)
O(b2)–Co(1)–O(w)	90.0(5)	O(b2)–C(b2)–C(b1)	115.1(11)
O(c1)–Co(1)–O(d1)	104.1(3)	C(b1)–C(b2)–C(b3)	126.7(10)
O(c1)–Co(1)–O(d2)	90.4(4)	C(b2)–C(b3)–C(b4)	130.4(16)
O(c1)–Co(1)–O(w)	84.0(5)	C(b3)–C(b4)–C(b5)	130.7(16)
O(d1)–Co(1)–O(d2)	77.7(3)	C(b4)–C(b5)–C(b6)	125.2(12)
O(d1)–Co(1)–O(w)	96.1(3)	C(b5)–C(b6)–C(b7)	130.7(14)
O(d2)–Co(1)–O(w)	170.4(4)	C(b6)–C(b7)–C(b1)	131.5(15)
O(a1)–Co(2)–O(a2)	75.9(3)	C(b7)–C(b1)–C(b2)	124.6(11)
O(a1)–Co(2)–O(b1)	106.6(3)	Co(2)–O(c1)–C(c1)	114.9(8)
O(a1)–Co(2)–O(c1)	171.1(3)	Co(2)–O(c2)–C(c2)	116.0(9)
O(a1)–Co(2)–O(c2)	97.6(3)	O(c1)–C(c1)–C(c2)	114.1(9)
O(a1)–Co(2)–O($a1^I$)	78.1(3)	O(c2)–C(c2)–C(c1)	116.4(10)
O(a2)–Co(2)–O(b1)	87.8(4)	C(c1)–C(c2)–C(c3)	125.8(11)
O(a2)–Co(2)–O(c1)	97.5(3)	C(c2)–C(c3)–C(c4)	129.1(16)
O(a2)–Co(2)–O(c2)	89.9(4)	C(c3)–C(c4)–C(c5)	131.2(16)
O(a2)–Co(2)–O($a1^I$)	153.6(3)	C(c4)–C(c5)–C(c6)	125.0(13)
O(b1)–Co(2)–O(c1)	78.9(3)	C(c5)–C(c6)–C(c7)	132.6(15)
O(b1)–Co(2)–O(c2)	154.3(3)	C(c6)–C(c7)–C(c1)	127.8(15)
O(b1)–Co(2)–O($a1^I$)	95.4(3)	C(c7)–C(c1)–C(c2)	128.3(11)
O(c1)–Co(2)–O(c2)	76.1(3)	Co(1)–O(d1)–C(d1)	114.8(8)
O(c1)–Co(2)–O($a1^I$)	108.8(3)	Co(1)–O(d2)–C(d2)	114.6(8)
O(c2)–Co(2)–O($a1^I$)	97.9(4)	O(d1)–C(d1)–C(d2)	114.8(9)
Co(1)–O(b1)–Co(2)	100.9(3)	O(d2)–C(d2)–C(d1)	117.2(10)
Co(1)–O(c1)–Co(2)	100.1(3)	C(d1)–C(d2)–C(d3)	124.5(10)
Co(2)–O(a1)–Co(2^I)	101.9(3)	C(d2)–C(d3)–C(d4)	131.7(15)
Co(2)–O(a1)–C(a1)	117.6(7)	C(d3)–C(d4)–C(d5)	129.6(15)
Co(2)–O(a2)–C(a2)	116.0(9)	C(d4)–C(d5)–C(d6)	126.2(13)
O(a1)–C(a1)–C(a2)	114.6(8)	C(d5)–C(d6)–C(d7)	131.0(13)
O(a2)–C(a2)–C(a1)	115.7(11)	C(d6)–C(d7)–C(d1)	129.7(14)
C(a1)–C(a2)–C(a3)	126.2(12)	C(d7)–C(d1)–C(d2)	127.2(11)
C(a2)–C(a3)–C(a4)	130.3(14)		

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[8] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732.

chelates a cobalt atom and has one trigonal bridging oxygen atom, while the other (d) does not take part in bridging and chelates Co(1) alone. There does appear to be some correlation between the co-ordination role of the oxygen atoms, and Co–O distances. Thus the shorter distances occur for ligand d (2.051 and 2.068 Å), and the longest distances correspond to bridging interactions (2.136, 2.127, and 2.149 Å), while those for the chelation bonds of the bridging ligands a—c are intermediate (2.064—2.109 Å). Mean distances for these three bond types are 2.060, 2.137, and 2.084 Å, the differences probably being of significance to the manner in which tropolone behaves as a ligand. The longer bridging bonds suggest a slightly weaker interaction than is found with ligand d, for instance, and lengthening of the chelate bonds in the bridging ligands may well be due to an electron delocalisation mechanism, facilitating formation of the bridge. Such a delocalised system is thought to exist over the ligand,[9,10] but excluding the C(1)–C(2) bonds, and its extension into the chelate ring [11] has supporting evidence. In the present complex, this delocalisation would also include the bridging bonds. In this context the π-system of the carbon ring could be considered as a reservoir of electron density, enhancing the co-ordination ability of the oxygen atoms, and effectively allowing bridging oxygen atoms to become bidentate. The ligand bites in the complex are 2.578(12), 2.584(13), 2.563(14), and 2.585(12) Å (for ligands a—d), which, together with the O(1)–C(1)–C(2) and O(2)–C(2)–C(1) angles, indicate that the co-ordination system in the ligand is rigid even when it bridges. Similar values have been reported [10,12] for other tropolonate structures. Of the other oxygen–oxygen distances in the co-ordination polyhedra, O(al)···O(al^{I}) and O(b1)···O(c1) [2.659(15) and 2.678(9) Å] are less than would be expected for van der Waals interaction alone. This effect has been noted previously,[1] and is probably a consequence of the bridging character of the atoms.

TABLE 5

Equations of some weighted least-squares mean planes, (X, Y, Z, in Å based on an orthogonal co-ordinate system a, b, c^*), together with atom displacements (Å) from the planes

Plane (1): (Ligand a)

$$0.2027X + 0.5592Y - 0.8039Z - 1.8855 = 0$$

Plane (2): (Ligand b)

$$0.3364X - 0.9312Y - 0.1403Z + 8.0287 = 0$$

Plane (3): (Ligand c)

$$0.4123X - 0.6771Y - 0.6095Z + 8.0274 = 0$$

Plane (4): (Ligand d)

$$0.3781X + 0.5712Y - 0.7286Z - 0.3663 = 0$$

Atom displacements (Å) from respective planes:

Atom	Ligand a	Ligand b	Ligand c	Ligand d
O(1)	0.012	−0.001	0.044	−0.009
O(2)	−0.047	0.032	−0.061	0.009
C(1)	0.019	−0.026	−0.015	−0.004
C(2)	0.011	−0.012	0.003	0.001
C(3)	0.090	−0.054	0.071	−0.002
C(4)	0.061	−0.027	0.068	−0.021
C(5)	−0.086	0.023	0.018	−0.006
C(6)	−0.048	0.060	−0.071	0.016
C(7)	0.016	−0.002	−0.063	0.021
Co(1) *		−0.189	−0.637	0.235
Co(2) *	0.057	−0.713	0.371	
Co(2^{I}) *	−0.066			

* Not included in mean plane calculations.

The tropolone ligands, with the exception of d, show some significant deviations from planarity (Table 5). The mode of distortion cannot be analysed as a ligand twist or fold, as has been possible in some other tropolonate structures,[12-14] and in this case appears to be more random. The normals to the planes defined by each carbon ring and the corresponding moieties O(1), C(1), C(2), O(2) of rings a—c are at angles of 3.8, 3.0, and 4.3°, respectively, while angles between normals to the ligand planes and Co, O(1), O(2) planes are 2.9, 7.1, 13.0, and 8.4° (a—d). Similar values have been reported for other tropolonate structures in which the ligands have been bridging [1,2] and non-bridging,[12-14] and in the present structure, as has been concluded with the majority of the others, it is more likely that the ligand distortions are due to the constraints of lattice packing than to inherent chemical behaviour. There is no definite evidence for bond-length alternation around the periphery of the carbon rings, and the inequality in what would be equivalent bonds should electron delocalisation be occurring is taken up by the standard deviations. Excluding the longer bonds C(1)–C(2) which are not involved in electron delocalisation and have values close to those expected for an sp^2–sp^2 single bond, the mean C–C lengths for the rings are 1.394, 1.402, 1.405, and 1.407 Å (a—d), quite close to the expected aromatic value.[15]

Figures 3 and 4 show the lattice packing of the molecules. The manner in which the tropolone rings of different molecules lie between one another is clearly visible (Figure 3). The minima of non-bonded intermolecular contacts for all ring carbon atoms are <3.97 Å, these distances being <3.7 Å if atoms of the type C(1) and C(2) are excluded. Figure 4 shows the positions of the hydrogen-bonds which link each molecule into chains lying approximately perpendicular to bc. The hydrogen-bonds are between the water molecules and atoms of the type O(d1) on adjacent complex molecules, the distance O(w)···O(d1) [2.631(14) Å] indicating a relatively strong interaction.

In common with the dimeric structure found [1,2] for $[\{NiT_2(H_2O)\}_2]$, the present structure has no β-diketone analogue. The tetrameric cobalt(II) acetylacetonate [16] is anhydrous and, in air, reverts to a hydrate, which is

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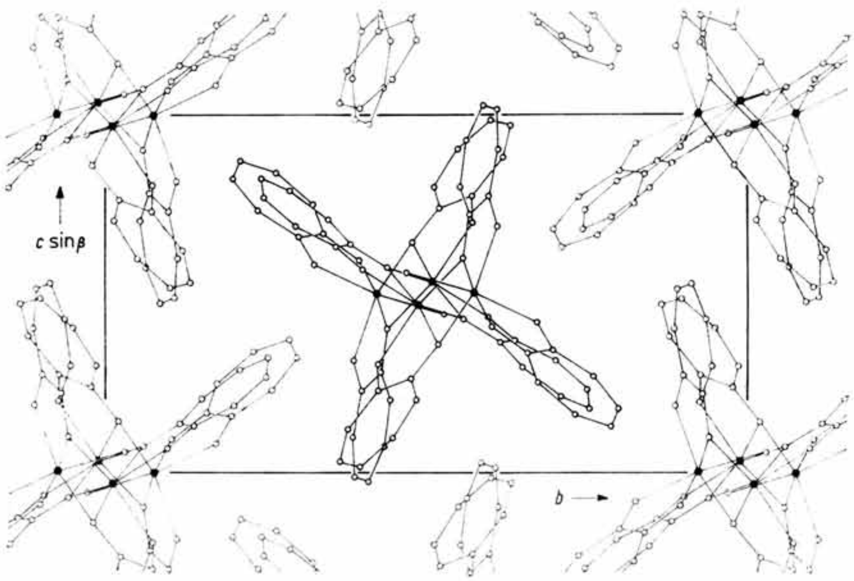

FIGURE 3 A projection of the lattice, viewed down the *a* axis

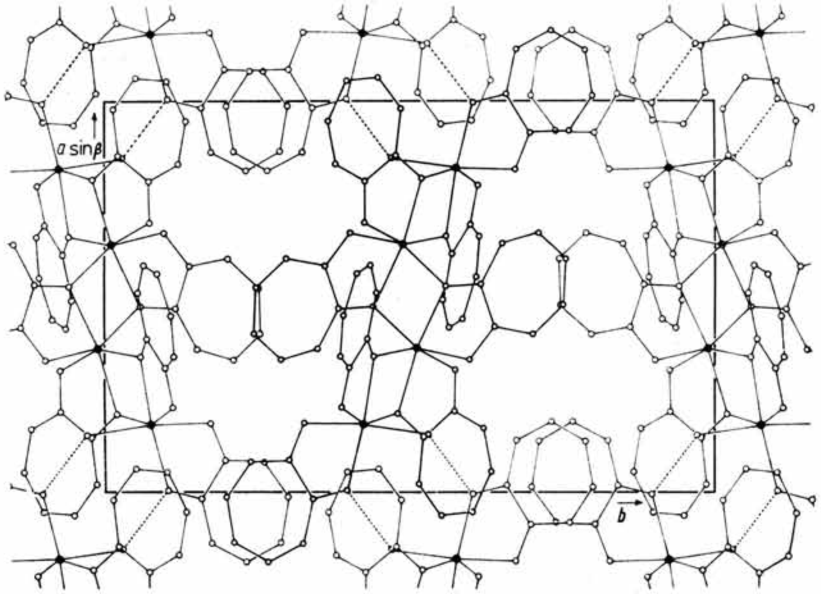

FIGURE 4 A projection of the lattice, viewed along the *c* axis from O to +*c*. Broken lines denote hydrogen bonds

probably [Co(acac)$_2$(H$_2$O)$_2$]. Other hydrated forms of [Co(acac)$_2$] do exist but these have been shown[17] to be di- and tri-meric. The structural stability of the bridged tropolonate hydrates is almost certainly governed by the compact nature of the ligand facilitating efficient lattice packing and hydrogen-bonded interaction, with a possible further chemical contribution by extension of electron delocalisation, from the carbon rings, over the metal–tropolone bonds.

We thank the S.R.C. for a maintenance grant (to M. L. P)., Dr. Peter Pauling for making the *X*-ray equipment available, and Professor J. Trotter for some computing time. The programs used are given in ref. 1.

[4/2317 *Received*, 17*th November*, 1974]

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