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New Investigation of the Structure of Trisacetylacetonatocobalt(III)

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Abstract. $Co(C_5O_2H_7)_3$, monoclinic, $P2_1/c$, $a=13{\cdot}90$ (7), $b=7{\cdot}47$ (4), $c=16{\cdot}21$ (7) Å, $\beta=98{\cdot}4$ (1)°, $Z=4$, $D_c=1{\cdot}40$ g cm^{-3}, $D_m=1{\cdot}41$ g cm^{-3}, final $R=0{\cdot}038$. All hydrogen atoms were located and their positions refined. The compound is isomorphous with the manganese(III) and chromium(III) complexes. The distortion of the octahedral configuration of oxygen ligands is similar to that found in the manganese(III) complex.

Experimental. Dark green crystals were grown from acetone. Intensities and cell dimensions were measured on a Philips PW 1100 single-crystal diffractometer with a crystal of dimensions 0·3 × 0·2 × 0·2 mm. Systematic absences $h0l$, $l\neq 2n$ and $0k0$, $k\neq 2n$ confirm space group $P2_1/c$. Data were collected to a maximum 2θ value of 40° with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å, ω–2θ scan, scan-width = 1·2°, scan speed = 0·04° s^{-1}). The background was counted for half the total scanning time on each side of the reflexion. 1550 unique reflexions were measured of which 1424 were considered to be observed with $I/\sigma(I)>1{\cdot}65$ where $\sigma(I)=[(0{\cdot}02S)^2+S+B]^{1/2}$, S = scan count and B = total background count. Corrections for Lorentz and polarization effects were applied, but no absorption correction was made.

A Patterson synthesis confirmed that the cobalt atom is in the same position as that found for chromium in trisacetylacetonatochromium(III) (Morosin, 1965). Full-matrix least-squares refinement of all the atomic positions from that structure led to smooth convergence and an R of 0·050 with anisotropic thermal parameters. The positions of all the hydrogen atoms were located from a difference synthesis. They were included during further refinement in which their positional parameters were allowed to vary but their isotropic thermal parameters kept constant at $U=0{\cdot}034$ Å^2, the value of the overall temperature factor estimated from a Wilson plot.

The weighting scheme was $w=(\sin\theta/0{\cdot}2)\times(80{\cdot}0/F_o)$ for reflections with $\sin\theta<0{\cdot}2$ and/or $F_o>80{\cdot}0$.

The final discrepancy indices are $R=0{\cdot}038$ and $R_w=0{\cdot}040$ where

$$R=\sum(|F_o|-|F_c|)/\sum F_o$$

and

$$R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}\,.$$

The 'goodness of fit' defined as $[\sum w(|F_o|-|F_c|)^2/(n_{\rm ref}-n_{\rm var})]^{1/2}$ is 1·45. Atomic coordinates and temperature factors are listed in Tables 1 and 2, and bond lengths and angles in Tables 3 and 4.* The numbering of the

Table 1. *Fractional coordinates with e.s.d'.s*

	x/a	y/b	z/c
Co	0·2420 (1)	0·2691 (1)	0·4687 (1)
O(1)	0·1225 (3)	0·3406 (5)	0·4075 (2)
O(2)	0·1916 (3)	0·1918 (5)	0·5645 (2)
O(3)	0·3645 (3)	0·1880 (5)	0·5191 (2)
O(4)	0·3017 (3)	0·3563 (5)	0·3791 (2)
O(5)	0·2179 (3)	0·0353 (5)	0·4268 (2)
O(6)	0·2528 (3)	0·5016 (5)	0·5150 (2)
C(1)	0·3082 (4)	0·2648 (8)	0·3140 (3)
C(2)	0·2357 (4)	−0·0156 (7)	0·3557 (4)
C(3)	0·2768 (4)	0·0897 (9)	0·3004 (3)
C(4)	0·3564 (5)	0·3568 (9)	0·2507 (4)
C(5)	0·2085 (4)	−0·2068 (8)	0·3357 (4)
C(6)	0·3294 (5)	0·5613 (7)	0·5584 (3)
C(7)	0·4289 (4)	0·2897 (9)	0·5590 (3)
C(8)	0·4150 (4)	0·4678 (9)	0·5781 (4)
C(9)	0·5250 (4)	0·2016 (9)	0·5880 (4)
C(10)	0·3211 (5)	0·7481 (8)	0·5891 (4)
C(11)	0·0413 (5)	0·3161 (9)	0·4319 (4)
C(12)	0·1018 (5)	0·1863 (8)	0·5688 (4)
C(13)	0·0280 (4)	0·2420 (11)	0·5072 (4)
C(14)	−0·0441 (5)	0·3725 (12)	0·3703 (4)
C(15)	0·0778 (6)	0·1160 (14)	0·6495 (5)
H(3)	0·285 (3)	0·044 (6)	0·249 (3)
H(41)	0·337 (3)	0·329 (6)	0·200 (3)
H(42)	0·335 (3)	0·466 (6)	0·243 (3)
H(43)	0·409 (3)	0·404 (6)	0·262 (3)
H(51)	0·225 (3)	−0·234 (6)	0·288 (3)
H(52)	0·142 (3)	−0·220 (6)	0·326 (3)
H(53)	0·242 (3)	−0·278 (6)	0·374 (3)
H(8)	0·462 (3)	0·524 (6)	0·608 (3)
H(91)	0·570 (3)	0·267 (6)	0·607 (3)
H(92)	0·547 (3)	0·133 (6)	0·546 (3)
H(93)	0·513 (3)	0·093 (6)	0·625 (3)
H(101)	0·373 (3)	0·791 (6)	0·613 (3)
H(102)	0·298 (3)	0·817 (6)	0·548 (3)
H(103)	0·281 (3)	0·761 (6)	0·627 (3)
H(13)	−0·034 (3)	0·223 (6)	0·516 (3)
H(141)	−0·099 (3)	0·368 (6)	0·394 (3)
H(142)	−0·040 (3)	0·309 (6)	0·316 (3)
H(143)	−0·037 (3)	0·471 (7)	0·346 (3)
H(151)	0·017 (4)	0·086 (7)	0·646 (3)
H(152)	0·128 (4)	0·022 (7)	0·675 (3)
H(153)	0·100 (4)	0·178 (7)	0·692 (3)

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30300 (11 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

atoms and the thermal motion in the molecule are illustrated in Fig. 1, drawn with the plot program *ORTEP* (Johnson, 1965). All other computations were done with the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The atomic scattering factors used were those of Cromer & Mann (1968) except for hydrogen where those of Stewart, Davidson & Simpson (1965) were used. The components of the anomalous dispersion correction used for the cobalt atom are those listed in *International Tables for X-ray Crystallography* (1962).

Discussion. Although the crystal and molecular structures of the trivalent metal acetylacetonates have been investigated by several workers (Morosin & Brathovde, 1964; Morosin, 1965; Roof, 1956), the available information on the structure of the cobalt complex (Padmanabhan, 1958; Shkolnikova & Shugam, 1961) is inadequate to interpret n.m.r. results obtained by Reynhardt (1973). For example, electric field gradient calculations and the interpretation of the anisotropic chemical shift at the ^{59}Co nuclei require accurate information on the distortion of the octahedral configuration of oxygen ligands surrounding the cobalt nuclei.

The distortion around the cobalt atom is evident from the bond lengths and angles listed in Tables 3 and 4, and from the distances between the oxygen atoms forming the edges of the octahedron listed in Table 5. The intrachelate oxygen–oxygen distances are significantly longer than the others, resulting in point group symmetry $C3$ for the octahedron. This distortion is similar to that of the manganese(III) complex (Morosin & Brathovde, 1964). The cobalt complex is diamagnetic and not susceptible to a Jahn–Teller distortion. The distortion in the manganese complex is therefore not the result of a Jahn–Teller mechanism as predicted by Dunitz & Orgel (1957). Bond lengths and angles for some metal acetylacetonates are compared in Table 6. While the intrachelate oxygen–oxygen distances are the same within the estimated standard deviations, there is a relatively wide spread in the oxygen–metal–oxygen bond angles, illustrating that the wider 'bite' of the bidentate ring is retained in preference to the preservation of cubic symmetry.

The large anisotropic motion of carbon atoms C(13), C(14) and C(15) was also found in the chromium(III)

Table 3. *Intramolecular distances* (Å)

Co—O(1)	1·883 (4)	C(3)—H(3)	0·92 (4)
Co—O(2)	1·885 (4)	C(8)—H(8)	0·86 (4)
Co—O(3)	1·889 (4)	C(13)–H(13)	0·90 (4)
Co—O(4)	1·892 (4)	C(4)—H(41)	0·86 (4)
Co—O(5)	1·887 (4)	C(4)—H(42)	0·87 (5)
Co—O(6)	1·890 (4)	C(4)—H(43)	0·81 (5)
Average	1·888	C(5)—H(51)	0·86 (5)
		C(5)—H(52)	0·93 (4)
O(1)—C(11)	1·262 (8)	C(5)—H(53)	0·90 (4)
O(2)—C(12)	1·262 (8)	C(14)–H(141)	0·91 (5)
O(3)—C(7)	1·267 (8)	C(14)–H(142)	1·00 (5)
O(4)—C(1)	1·272 (7)	C(14)–H(143)	0·85 (5)
O(5)—C(2)	1·272 (7)	C(15)–H(151)	0·87 (6)
O(6)—C(6)	1·268 (7)	C(15)–H(152)	1·03 (5)
Average	1·267	C(15)–H(153)	0·84 (5)
		C(10)–H(101)	0·84 (4)
C(11)–C(13)	1·377 (10)	C(10)–H(102)	0·87 (4)
C(12)–C(13)	1·387 (9)	C(10)–H(103)	0·89 (4)
C(7)—C(8)	1·387 (9)	C(9)—H(91)	0·82 (4)
C(6)—C(8)	1·378 (9)	C(9)—H(92)	0·94 (5)
C(1)—C(3)	1·386 (9)	C(9)—H(93)	1·03 (5)
C(2)—C(3)	1·378 (9)	Average	0·90
Average	1·382		
C(11)–C(14)	1·497 (9)		
C(12)–C(15)	1·492 (11)		
C(7)—C(9)	1·502 (8)		
C(1)—C(4)	1·476 (9)		
C(2)—C(5)	1·502 (8)		
C(6)—C(10)	1·492 (8)		
Average	1·494		

Table 2. *Mean square atomic vibrations in* Å^2 ($\times 10^4$) *with e.s.d'.s*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	352 (5)	321 (5)	230 (5)	42 (4)	39 (3)	−15 (3)
O(1)	446 (26)	448 (25)	348 (22)	102 (21)	−51 (20)	−19 (19)
O(2)	408 (26)	484 (25)	300 (22)	11 (20)	77 (17)	15 (18)
O(3)	341 (22)	399 (23)	367 (23)	95 (20)	7 (18)	−21 (19)
O(4)	500 (24)	391 (23)	286 (23)	−11 (19)	90 (18)	−3 (20)
O(5)	529 (25)	381 (23)	329 (24)	−14 (19)	57 (19)	−46 (19)
O(6)	447 (25)	363 (23)	317 (21)	100 (20)	29 (20)	−44 (18)
C(1)	349 (33)	482 (42)	242 (33)	81 (30)	9 (26)	26 (33)
C(2)	335 (32)	351 (37)	340 (37)	128 (28)	−126 (28)	−80 (32)
C(3)	581 (39)	483 (43)	236 (32)	38 (34)	69 (29)	−93 (31)
C(4)	723 (43)	683 (45)	385 (36)	−168 (37)	137 (32)	−33 (34)
C(5)	445 (36)	532 (43)	477 (37)	83 (31)	−158 (28)	−84 (32)
C(6)	540 (43)	297 (35)	232 (31)	−51 (34)	106 (31)	24 (27)
C(7)	297 (35)	523 (45)	264 (31)	52 (34)	99 (27)	82 (31)
C(8)	386 (39)	468 (45)	469 (37)	−54 (33)	23 (29)	−72 (32)
C(9)	374 (36)	734 (49)	673 (43)	52 (35)	74 (31)	−3 (38)
C(10)	790 (45)	463 (42)	453 (36)	−49 (36)	90 (33)	−82 (33)
C(11)	389 (42)	666 (46)	462 (43)	129 (34)	−35 (34)	−185 (35)
C(12)	539 (45)	532 (42)	364 (37)	−77 (34)	127 (34)	−67 (31)
C(13)	324 (39)	1187 (63)	511 (44)	−101 (40)	128 (36)	−100 (46)
C(14)	524 (42)	1152 (63)	617 (45)	185 (43)	−107 (36)	−91 (45)
C(15)	569 (49)	1180 (75)	568 (49)	−190 (51)	136 (42)	25 (47)

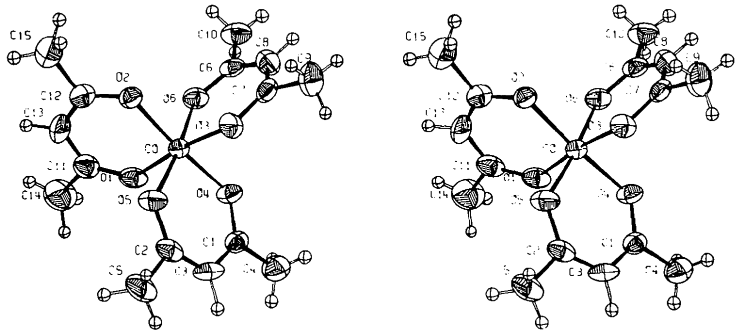

Fig. 1. Molecular structure and atomic nomenclature. Thermal ellipsoids for the non-hydrogen atoms are drawn at 50% probability.

Table 4. *Intramolecular bond angles* (°)

O(1)-Co—O(2)	96·7 (2)	O(1)—C(11)-C(14)	114·1 (6)
O(3)-Co—O(6)	96·2 (2)	O(2)—C(12)-C(15)	114·2 (5)
O(4)-Co—O(5)	96·7 (2)	O(3)—C(7)—C(9)	114·7 (5)
Average	96·5	O(4)—C(1)—C(4)	114·9 (5)
		O(5)—C(2)—C(5)	113·9 (5)
Co—O(1)-C(11)	123·6 (4)	O(6)—C(6)—C(10)	114·6 (5)
Co—O(2)-C(12)	123·0 (3)	Average	114·4
Co—O(3)-C(7)	123·2 (4)		
Co—O(4)-C(1)	123·0 (4)	C(1)—C(3)—C(2)	125·9 (5)
Co—O(5)-C(2)	123·8 (4)	C(6)—C(8)—C(7)	125·3 (5)
Co—O(6)-C(6)	123·8 (4)	C(11)-C(13)-C(12)	125·3 (6)
Average	123·4	Average	125·5
O(1)-C(11)-C(13)	125·4 (5)	C(3)—C(2)—C(5)	121·1 (5)
O(2)-C(12)-C(13)	125·7 (6)	C(3)—C(1)—C(4)	119·6 (5)
O(3)-C(7)—C(8)	125·5 (5)	C(8)—C(6)—C(10)	120·2 (5)
O(4)-C(1)—C(3)	125·5 (5)	C(8)—C(7)—C(9)	119·8 (5)
O(5)-C(2)—C(3)	124·9 (5)	C(13)-C(12)-C(15)	120·1 (7)
O(6)-C(6)—C(8)	125·2 (5)	C(13)-C(11)-C(14)	120·6 (6)
Average	125·4	Average	120·2

and manganese(III) complexes and was considered by Morosin (1965) to be the result of the particular stacking of the molecules in the crystal.

Table 5. *Oxygen–oxygen distances* (Å)

O(1)-O(2)	2·815 (5)
O(3)-O(6)	2·813 (6)
O(4)-O(5)	2·823 (6)
Average	2·817
O(1)-O(4)	2·601 (6)
O(4)-O(6)	2·633 (6)
O(6)-O(1)	2·615 (6)
O(1)-O(5)	2·634 (6)
O(3)-O(4)	2·632 (6)
O(2)-O(6)	2·631 (6)
O(2)-O(3)	2·626 (6)
O(3)-O(5)	2·617 (7)
O(5)-O(2)	2·593 (6)
Average	2·620

Table 6. *Selected bond distances and angles for some metal acetylacetonates*

	Metal–oxygen distance (Å)	Intrachelate oxygen–oxygen distance (Å)	Oxygen–metal–oxygen bond angle (°)
Cr	1·951 (7)	2·786 (13)	91·2
Fe	1·95 (1)	2·80 (1)	90·0
Co	1·888 (4)	2·817 (6)	96·5
Mn	1·872 (8)	2·805 (10)	97·0

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