

Monomeric bis(2,4-pentanedionato)-cobalt(II)

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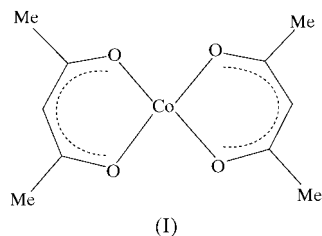
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The title compound, $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2]$, contains isolated molecules. The Co atom is located on a centre of symmetry with the bidentate ligands adopting a square-planar geometry about the Co atom.

Comment

Several 2,4-pentanedionato (acetylacetonate, acacH) complexes of cobalt(II) have been isolated and characterized. Crystal structure determinations have been reported for, *e.g.*, tetranuclear $[\text{Co}_4(\text{acac})_7]$ (Cotton & Elder, 1965), the ${}^n\text{Bu}_4\text{N}^+$ salt of the $[\text{Co}(\text{acac})_3]^-$ anion (Santarsiero *et al.*, 1981), and ternary complexes (adducts) such as $[\text{Co}(\text{acac})_2(\text{py})_2]$ (Elder, 1968) and $[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2]$ (Bullen, 1959), binuclear $[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2]$ (Cotton & Elder, 1966), $[\text{Co}(\text{acac})_2(\text{cyclohexylamine})_2]$ (Bertrand & Kalayanaraman, 1971) and $[\text{Co}_2(\text{acac})_4(\text{Ph}_3\text{AsO})]$ (Binks *et al.*, 1981), and trinuclear $[\text{Co}_3(\text{acac})_6(\text{H}_2\text{O})]$ (Cotton & Eiss, 1968).

We now report the results of an X-ray diffraction determination of the structure of the parent compound, anhydrous mononuclear bis(2,4-pentanedionato)cobalt(II), $[\text{Co}(\text{acac})_2]$,



(I). The structure of (I) consists of monomers stacked in columns parallel to the *y* axis. The Co atom is located on a centre of symmetry and consequently the two chelate rings are coplanar (Fig. 1). The cobalt–oxygen distances, 1.917 (3) and 1.921 (3) Å, may be compared with those of 2.05 (1) and 2.06 (1) Å in $[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2]$, of 2.034 (3) Å in $[\text{Co}(\text{acac})_2(\text{py})_2]$ and 2.06 (1) Å in the $[\text{Co}(\text{acac})_3]^-$ anion (Santarsiero *et al.*, 1981), and with the ranges of 1.93 (3)–2.14 (3) Å (mean 2.06 Å) and 1.89 (3)–2.14 (3) Å (mean

2.02 Å) observed in $[\text{Co}_4(\text{acac})_7]$ and $[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2]$, respectively.

There are, surprisingly, no significant intermolecular interactions. The shortest non-bonded contact distance between pairs of molecules is 2.93 Å, between Co and the H5A atom of an adjacent molecule (the sum of the van der Waals radii of cobalt and hydrogen is 3.17 Å). There is no indication of any interaction at the fifth and sixth coordination positions of the cobalt – the shortest intermolecular Co···O contact is at 4.08 Å (the sum of the van der Waals radii of cobalt and oxygen is 3.57 Å) – with Co···O making an angle of 60.5° with the plane of the molecule. The coordination geometry about the Co atom is thus square-planar rather than the expected pseudo-octahedral, tetragonal or tetrahedral (Wells, 1984).

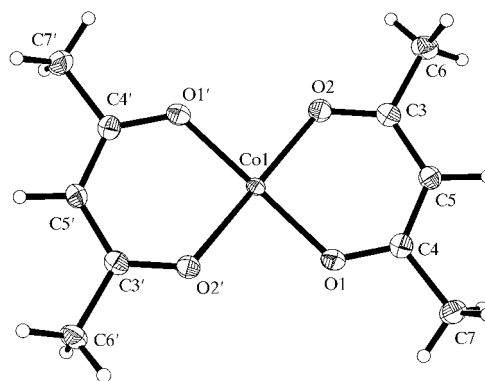


Figure 1

The molecular structure of (I) showing the atom-numbering scheme and 30% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

The few other square-planar cobalt(II) complexes are those of ligands such as maleonitriledithiolate, which impose square-planar geometry at many metal centres, and the tetradentate ligand salicylaldehylenediimine, where steric factors control the coordination geometry (Martell & Calvin, 1952; Wells, 1984).

The lack of Co–O–Co bridging in anhydrous $[\text{Co}(\text{acac})_2]$ may be contrasted with the presence of such bridges in the binuclear complexes $[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2]$, $[\text{Co}(\text{acac})_2(\text{cyclohexylamine})_2]$ and $[\text{Co}_2(\text{acac})_4(\text{Ph}_3\text{AsO})]$. In all three cases there are two Co–O–Co bridges linking the pairs of cobalt atoms through coordinating oxygen; the triphenylarsine adduct has an additional Co–O–Co bridge through the Ph_3AsO oxygen.

Experimental

The crystal used in this structure determination was obtained adventitiously from an attempted preparation of a cobalt(II)–Schiff base complex in which cobalt(II) acetate (1.0 g), aniline (2.5 g) and 2,4-pentanedione (2.5 g) were refluxed in ethanol for 1 h. The reaction mixture was left to cool and then to stand for 2 d. One of the small number of green plate-like crystals formed was used for the crystal structure determination.

Crystal data

[Co(C₅H₇O₂)₂]
M_r = 257.14
 Monoclinic, *P*2₁/*n*
a = 10.276 (2) Å
b = 4.677 (1) Å
c = 11.296 (2) Å
 β = 92.22 (2)°
V = 542.49 (18) Å³
Z = 2

D_x = 1.574 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 36 reflections
 θ = 5.71–12.35°
 μ = 1.572 mm⁻¹
T = 190 (2) K
 Plate, green
 0.52 × 0.26 × 0.08 mm

Data collection

Bruker *P4* diffractometer
 ω scans
 Absorption correction: 548 ψ -scan data (*XEMP* in *SHELXL97*; Sheldrick, 1997), merging *R* = 0.123 before correction and 0.044 after correction
*T*_{min} = 0.55, *T*_{max} = 0.91
 1410 measured reflections
 956 independent reflections

787 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.027
 θ _{max} = 25°
h = -1 → 12
k = -1 → 5
l = -13 → 13
 3 standard reflections every 100 reflections
 intensity decay: <1%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.052
wR(*F*²) = 0.140
S = 1.104
 956 reflections
 72 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0983P)^2 + 0.1697P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.005$
 $\Delta\rho_{\max} = 0.98 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.11 \text{ e \AA}^{-3}$

H atoms were treated as riding with a C—H distance of 0.96 Å.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1084). Services for accessing these data are described at the back of the journal.

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