

distance is shorter than the corresponding one [3.03 (1) Å] found for the As₂S analogue, probably owing to the smaller overall size of the P₂S group. Actually, the latter group is more strained than the As₂S one after bond cleavage, as revealed by the value of the angle lying opposite the elongated bond in each unit [P₂S, 81.7 (3); As₂S, 80.4 (1)°]. The dihedral angle between the plane of the triatomic unit and the least-squares plane through the four atoms surrounding Pt, of 131.4 (3)°, does not differ considerably from that of 127.6 (3)° detected for the As₂S isomorph. We expect to obtain more information from additional compounds of this series.

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Structure and Chirality of (–)₅₄₆-Bis(2,4-pentanedionato)(3-formyl-2,4-pentanedionato)cobalt(III)

BY MARIO BONAMICO, VINCENZO FARES AND PATRIZIA IMPERATORI

Istituto di Teoria, Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del CNR, Area della Ricerca di Roma, CP n. 10, 00016 Monterotondo Stazione, Roma, Italy

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Abstract. [Co(C₅H₇O₂)₂(C₆H₇O₃)], *M_r* = 384.27, trigonal, *P*3₁21, *a* = 12.094 (3), *c* = 11.144 (3) Å, *V* = 1411.6 (7) Å³, *Z* = 3, *D_m* = 1.35, *D_x* = 1.357 g cm^{−3}, λ(Mo *K*α) = 0.7107 Å, μ = 9.8 cm^{−1}, *F*(000) = 600, *T* ≈ 300 K, final *R* = 0.034 for 1677 unique reflections. The (–) isomer has the *A* chirality and the Co atom is chelated in a distorted octahedron by the three ligands. Molecular symmetry contains a twofold axis parallel to the *x* axis: the formyl group is outside the plane of the formylate ligand (with twofold disorder) and is responsible for a perturbation in the chelate ring.

Introduction. The title compound was synthesized in an optically pure form by La Torre and is of interest as chiral chromatographic support (La Torre, Prosperi, Bonamico & Fares, 1985). The formyl group should affect the size of the 'twist angle' which is important in defining CD signal energies (Peacock, 1983); single-crystal CD spectra studies are in progress by Prosperi.

Here we report the determination by X-ray analysis of the structural chirality and the molecular structure of the (–) isomer of the formyl derivate of tris(2,4-pentanedionato)cobalt(III), Co(pd)₃.

Experimental. The crystals are black prisms, *D_m* by flotation. A specimen with dimensions ca 0.3 × 0.3 × 0.3 mm was selected for the intensity measurements

and mounted on a Nicolet *P3m* computer-controlled four-circle diffractometer with graphite-monochromated Mo *K*α radiation. Cell parameters were determined by least squares from the measured *θ* values of 15 selected reflections, *θ* range 11–17°. Intensities were measured in the *θ*–2*θ* scan mode. Two standard reflections (006 and 130) were re-measured after every 30 reflections: no significant loss in intensity throughout data collection. 6575 reflections were measured, 2*θ*_{max} = 55°, 4590 with *I* > 3σ(*I*) observed, index range *h* = 0 to 15, *k* = −7 to 7, *l* = −14 to 14. Intensities were corrected for Lorentz–polarization factors; semiempirical absorption correction, based on a 360° scan around the scattering vector of a pair of selected reflections, was applied: ratio between max. and min. values was 1.15; no other absorption correction was applied. 1677 independent reflections were obtained by averaging and merging equivalent reflections (*R*_{int} = 0.040).

Structure was solved by Patterson and Fourier methods. Origin at 3₂21. Subsequent difference Fourier maps revealed a twofold positional disorder for the formyl group (see later). The methyl H atoms were found to be disordered over two alternate staggered and eclipsed positions.

Positional and anisotropic thermal parameters for non-H atoms were refined by full-matrix least squares, minimizing Σ*w*(|*F_o*| – *k*|*F_c*|)², *w* = 1/σ(*F_o*)².

H-atom positional parameters were introduced in fixed calculated positions (C—H = 1.0 Å) in the final cycles, with occupancy 0.5 for the disordered ones and fixed isotropic B equal to the B_{eq} of C atoms to which they are linked. Refinement converged in the space group $P3_121$ to $R = 0.0343$, $wR = 0.0261$ and $S = 1.60$; the number of observations per refined parameters was 1677/119 = 14.1 and $(\Delta/\sigma)_{max} < 0.01$. The peaks in the final $\Delta\rho$ map were between 0.3 and $-0.2 \text{ e } \text{\AA}^{-3}$ except in the region around the Co atom, where peaks of $+1.2$ and $-0.4 \text{ e } \text{\AA}^{-3}$ were observed [$\sigma(\rho) = 0.06 \text{ e } \text{\AA}^{-3}$]; this could be due to the lack of absorption correction. Atomic scattering factors for Co, C and O and the anomalous-dispersion corrections added to the scattering factors of Co from *International Tables for X-ray Crystallography* (1974); for H from Hanson, Herman, Lea & Skillman (1964). At the final stage a new refinement was carried out in $P3_121$: the R and wR values were 0.0456 and 0.0411 respectively, indicating $P3_121$ to be the true space group of the crystal. Application of the R -factor-ratio test showed that the space group $P3_121$ can be rejected at the 0.005 level (Hamilton, 1965).

Table 1. Observed (Cu $K\alpha$ radiation) and calculated structure-factor relations between some Bijvoet pairs

h	k	l	$F_o(hkl)$	$F_o(\bar{h}\bar{k}\bar{l})$	$F_c(hkl)$	$F_c(\bar{h}\bar{k}\bar{l})$
2	1	3	32.7	18.9	30.2	21.8
4	1	1	18.9	34.4	24.4	33.7
4	1	4	25.7	34.7	28.6	34.4
5	2	4	15.6	20.8	15.2	23.4
6	3	2	25.4	16.3	25.7	18.1
6	3	3	29.7	38.8	30.1	36.3
6	2	3	28.6	17.9	27.2	18.1
6	2	5	28.7	34.9	27.9	31.7
8	4	0	28.2	22.4	30.9	24.5

Table 2. Final fractional coordinates ($\times 10^5$) with e.s.d.'s in parentheses and equivalent isotropic temperature factors, $B_{eq} (\text{\AA}^2)$, for non-H atoms

	x	y	z	B_{eq}
Co†	36459 (3)	0*	66667*	3.8
O(1)	34167 (10)	-3375 (11)	83266 (9)	4.6
O(2)	41605 (13)	-11869 (14)	63061 (10)	4.3
O(3)	32122 (15)	12784 (14)	69035 (12)	5.3
O(4)†	-11775 (44)	-6518 (63)	61182 (55)	13.1
C(1)	38277 (19)	-9872 (20)	88604 (16)	4.6
C(2)	43677 (22)	-16355 (22)	83240 (17)	5.5
C(3)	44950 (21)	-17146 (21)	70967 (18)	4.7
C(4)	21228 (30)	11554 (28)	68555 (21)	6.2
C(5)†	9870 (29)	0*	66667*	7.9
C(6)†	-1093 (83)	1931 (149)	63186 (84)	9.4
C(11)	36882 (24)	-10360 (25)	102078 (18)	6.8
C(31)	50537 (33)	-24970 (30)	66264 (19)	7.6
C(41)	21608 (31)	24159 (30)	70164 (28)	10.1

* These coordinates were held fixed during the refinement.

† Atoms with occupancy factor = 0.5.

The structural chirality A was also clearly confirmed by a comparison of some observed and calculated hkl and $\bar{h}\bar{k}\bar{l}$ reflections, taken with Cu $K\alpha$ radiation ($f' = -2.464$, $f'' = 3.608$) (see Table 1).

The atomic parameters are listed in Table 2.*

Computations were performed on a Data General computer with a set of programs *CAOS* written by Cerrini & Spagna (1977).

* Lists of structure factors, anisotropic temperature factors, least-squares planes and deviations, calculated H-atom coordinates and normal intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43768 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

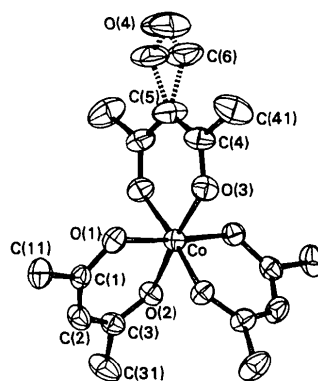


Fig. 1. A perspective drawing of the molecule with thermal ellipsoids (30% probability level) and the numbering scheme (H atoms not shown). The formyl-group bonding is shown with dashed lines and placed in the two disordered positions.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Co—O(1)	1.885 (1)	C(1)—C(2)	1.382 (3)
Co—O(2)	1.872 (1)	C(2)—C(3)	1.385 (3)
Co—O(3)	1.883 (1)	C(4)—C(5)	1.402 (6)
O(1)—C(1)	1.268 (2)	C(1)—C(11)	1.509 (3)
O(2)—C(3)	1.267 (2)	C(3)—C(31)	1.505 (4)
O(3)—C(4)	1.251 (4)	C(4)—C(41)	1.513 (5)
O(4)—C(6)	1.201 (20)	C(5)—C(6)	1.508 (10)
O(1)—Co—O(2)	96.54 (5)	O(1)—C(1)—C(2)	126.2 (2)
O(3)—Co—O(3')	92.89 (9)	O(2)—C(3)—C(2)	125.3 (2)
O(1)—Co—O(3)	88.23 (6)	O(3)—C(4)—C(5)	125.0 (3)
O(1)—Co—O(1')	175.55 (6)	C(1)—C(2)—C(3)	124.5 (2)
O(1)—Co—O(2')	86.66 (6)	C(4)—C(5)—C(4')	122.4 (3)
O(1)—Co—O(3')	88.71 (7)	C(4)—C(5)—C(6)	112.6 (8)
O(2)—Co—O(3)	174.72 (8)	C(4')—C(5)—C(6)	122.6 (8)
O(2)—Co—O(2')	88.54 (8)	C(5)—C(6)—O(4)	124.8 (15)
O(2)—Co—O(3')	89.48 (8)	O(1)—C(1)—C(11)	114.8 (2)
Co—O(1)—C(1)	122.3 (1)	C(2)—C(1)—C(11)	118.9 (2)
Co—O(2)—C(3)	123.3 (1)	O(2)—C(3)—C(31)	115.6 (2)
Co—O(3)—C(4)	127.3 (3)	C(2)—C(3)—C(31)	119.2 (2)
		O(3)—C(4)—C(41)	112.1 (4)
		C(5)—C(4)—C(41)	122.9 (3)

Atoms numbered as (N') are related to atoms (N) by a twofold axis (symmetry code: $x-y, -y, \frac{1}{2}-z$) in the table and throughout the text.

Discussion. Fig. 1 shows a perspective view of the molecule along the pseudo-threefold axis. Bond lengths and angles are listed in Table 3.

The Co atom is surrounded octahedrally by six O atoms with an average Co—O distance of 1.880 (6) Å.* The interchelate O...O distances, particularly in the non-formylated rings, are significantly longer than the others, leading to a distortion around the Co atom (see Table 4) as seen in *rac*-Co(pd)₃ by Hon & Pfluger (1973) and Kruger & Reynhardt (1974).

Each pentanedionato—Co ring is almost planar: however, planarity is not equivalent for all the rings; in the two non-formylated rings the Co atom does not lie in the ligand least-squares plane, the chelate ring being bent by 11.9 (1)° along a line through the two chelate O atoms. A similar situation is present in Co(pd)₃ and has been noted in studies of several pentanedionate complexes [see Ito & Toriumi (1980) for Ge(pd)₃ and references therein].

The two methyl groups C(11) and C(31) are both a little out of the plane of the pentanedionato—Co ring on the opposite side to the Co atom, while in the formylated ring, which lies across the crystallographic twofold rotation axis, the methyl groups are displaced above and below the plane.

As noted before, the formyl group occupies two equivalent positions at 50% occupation but this disorder does not affect the atomic positions of the rest of the molecule. Only the B_{eq} values for the atoms belonging to the ligand containing the formyl group are considerably higher than those of the corresponding atoms in the other ligands.

The introduction as a substituent of a formyl group in a position 'ortho' to the two methyl groups leads, however, to a peculiar situation in the present structure.

As already known, formyl and carboxyl groups as substituents interact with the π system to which they are linked and the twist angle τ provides a measure of the extent of this interaction (Domenicano & Vaciago, 1979), in the sense that the smaller the angle the larger the interaction. In the absence of other substituents at 'ortho' positions, these groups are almost coplanar, as found in *p*-hydroxybenzaldehyde by Iwasaki (1977) with $\tau = 1.3^\circ$, and in 3,5-dimethylbenzoic acid by Colapietro, Domenicano, Marciante & Portalone (1984) with $\tau = 0.4^\circ$.

In the presence of two methyl groups in the 'ortho' positions, τ for the carboxyl group increases to 53.5° as found in 2,6-dimethylbenzoic acid by Anca, Martinez-Carrera & Garcia-Blanco (1967).

A different situation occurs when the methyl groups are in asymmetric positions with respect to the carboxyl group. In 2,3-dimethylbenzoic acid, Smith, Florencio & Garcia-Blanco (1971) found that the position of the

Table 4. Oxygen—oxygen distances (Å).

Bite separations			
O(1)...O(2)	2.803 (2)		
O(3)...O(3')	2.729 (3)		
Other separations			
O(1)...O(2')	2.578 (3)	O(2)...O(3')	2.643 (2)
O(1)...O(3)	2.623 (2)	O(3)...O(1')	2.634 (2)
O(1)...O(3')	2.634 (2)	O(3)...O(2')	2.643 (2)
O(2)...O(1')	2.577 (2)	O(1')...O(3')	2.623 (3)
O(2)...O(2')	2.613 (3)		

carboxyl group is distorted, having a deformation of the external angle and the τ value is 10.1°; however, the C atom of —COOH is still coplanar with the benzene ring.

In the present structure, the presence of the asymmetric formyl group might be expected to give rise to an angular distortion and a twist angle comparable with those observed in the 2,6-dimethylbenzoic acid mentioned above. On the contrary, not only is there a deformation of the external angles, but also a lack of coplanarity: in fact the C(5)—C(6) bond forms an angle of *ca* 16° with respect to the least-squares plane of the ring, while the twist angle τ is nearly 0°. Even allowing for the disorder of the formyl group, the C(5)—C(6) bond length of 1.51 (1) Å still appears to be greater than the corresponding values of 1.464 and 1.463 Å reported for *p*-hydroxybenzaldehyde by Iwasaki (1977) and for 3-hydroxy-4-methoxybenzaldehyde by Iwasaki (1973) respectively. An analogous increase is noticed when the carboxyl group is in an 'ortho' position to the methyl groups, as in 2,3-dimethylbenzoic acid cited above. The interference between the —CHO and the —CH₃ groups is also shown by the opening of the bond angle C(6)—C(5)—C(4') which has a value of 123 (1)°.

Bond distances and angles in the non-formylated rings are in reasonable agreement with those determined for *rac*-Co(pd)₃ (see references above).

The most significant differences in the formylated ligand are: (1) the coplanarity of the Co atom with the chelate ring; (2) the variation in the O(3)—Co—O(3') bond angle, which is 3.7° smaller than the O(1)—Co—O(2) angle; (3) the enlargement by more than 4° of the Co—O—C angles; and (4) the shortening of —C=O bond distances by about 0.02 Å. These effects are probably derived from an electronic perturbation in the π system caused by the non-planarity of the formyl group.

As far as we are aware there are no similar examples of chelate rings in coordination compounds nor in the simpler π systems of polysubstituted benzene derivatives.

The packing consists of infinite spirals of molecules along the symmetry axis $A3_2$ which is parallel to the crystallographic *c* axis and almost parallel to the octahedral axis O(1)—Co—O(1'), while the formylated

* The e.s.d.'s of the average values have been calculated by $[\sum_i (x_i - \bar{x})^2 / n - 1]^{1/2}$.

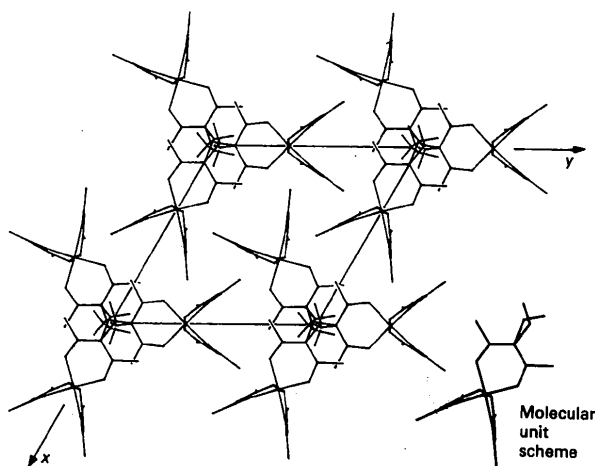


Fig. 2. A view of the crystal structure along the *c* axis.

ring is almost coplanar with (001). In Fig. 2 is shown the superposition of the formyl groups. The shortest intermolecular contacts were observed between methyl C and formyl O atoms: C(41)···O(4)* = 3.25 (1) Å. Other intermolecular contacts, involving C(6) with C(4), C(5), C(6) and O(4); or O(4) with C(4) and C(5); or methyl groups with other methyl groups or with O(1), are not remarkable, being in the range 3.44–3.79 Å.

* In the equivalent position $y - x, -x, \frac{1}{2} + z$.

All the molecules overlapping in the same spiral must have the formyl group disordered in the same position to avoid steric hindrance.

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Structure of (Cycloocta-1,5-diene)(tolan)nickel*

BY RICHARD GODDARD, BRIGITTE APOTECHE AND HEINZ HOBERG

Max-Planck-Institut für Kohlenforschung, Lembkestraße 5, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

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Abstract. [Ni(C₁₄H₁₀)(C₈H₁₂)], *M_r* = 345.13, monoclinic, *P*2₁/*c*, *a* = 11.429 (2), *b* = 8.648 (1), *c* = 17.724 (3) Å, β = 89.26 (1)°, *V* = 1751.6 Å³, *Z* = 4, *D_x* = 1.31 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 11.08 cm⁻¹, *F*(000) = 728, *T* = 291 K. Final *R* = 0.044 (*wR* = 0.051) for 2490 unique observed reflections. The Ni atom has an approximately trigonal planar coordination geometry, with the C=C bonds of the coordinated cycloocta-1,5-diene and the C≡C triple

bond of the tolan ligand occupying the three coordination sites. The central C—C bond of the coordinated tolan molecule lies approximately parallel to the coordination plane of the metal.

Introduction. In tris(ligand) complexes of the *d*¹⁰ transition metals, single-faced π-acceptor ligands adopt a conformation in which the π-acceptor orbital of the ligand aligns itself parallel to the coordination plane of the metal (Hartley, 1972). Tris(ethylene)platinum (Howard, Mason & Spencer, 1983) and tris(ethylene)-

* Tolan is diphenylethyne.