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Bis(dimethylglyoximato-*N*,*N*′)[methyl (*R*)-ethanoato-*C*^{2}][tris(2-cyanoethyl)-phosphine-*P*]cobalt(III)

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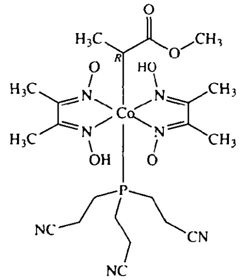
Abstract

The title compound, [Co($C_4H_7N_2O_2$)$_2$($C_4H_7O_2$)($C_9H_{12}N_3P$)], has been analyzed by X-ray diffraction to correlate the structure with the reactivity of the photoracemization on exposure to visible light. Although the crystal decomposed during the racemization, the size of the reaction cavity for the 1-methoxycarbonylethyl group explains the high reactivity.

Comment

It was discovered that the chiral 1-cyanoethyl group bonded to the Co atom in some bis(dimethylglyoximato)cobalt(III) (cobaloxime) complexes is racemized by X-ray or visible-light exposure with retention of the single-crystal form (Ohashi & Sasada, 1977). Such a solid-state process is called a crystalline-state reaction (Ohashi *et al.*, 1981). The relationship between reactivity and crystal structure has been examined for related complex crystals with different axial base ligands. A quantitative relationship between reaction rate and the reaction cavity has been obtained (Ohashi, 1988). When the chiral group was replaced with the (*R*)-1-methoxycarbonylethyl group, two complex crystals with pyridine and 4-chloropyridine as axial base ligands showed crystalline-state racemization only at high temperatures (Kurihara *et al.*, 1984*a*; Kurihara, Ohashi *et al.*, 1983). On the other hand, complex crystals with (*R*)-1-phenylethylamine, (*S*)-1-phenylethylamine and 4-cyanopyridine as axial base ligands showed no reaction (Kurihara *et al.*, 1984, 1984*b*).

In order to analyze the inversion mechanism of the chiral 1-methoxycarbonylethyl group more precisely, 12 1-methoxycarbonylethyl complexes with different axial base ligands were prepared, *i.e.* 3-aminopyridine, 4-methylpyridine, imidazole, tributylphosphine, methylamine, dimethylphenylphosphine, butylamine, propylamine, benzylamine, cyclohexylmethylamine, cyclohexylamine and tris(2-cyanoethyl)phosphine. The powdered samples of the complexes were irradiated with a xenon lamp and the racemization rates observed at constant intervals. The reaction rate at the initial stages was assumed to be first-order kinetics and the rate constants obtained for the 12 complexes varied from 10^{-2} to 10^{-6} s^{-1} (Arai & Ohgo, 1998). The title complex, with tris(2-cyanoethyl)phosphine as the axial base ligand, had the second largest rate constant, 1.52 × 10^{-2} s^{-1}. This brought about an idea that the title crystal would show crystalline-state racemization. However, the crystal decomposed gradually when irradiated with the xenon lamp. This paper reports on the relationship between the reactivity and structure of the title compound, (I).



(I)

The molecular structure of (I) with the atomic numbering is shown in Fig. 1. The Co—C10 bond length, 2.112 (4) Å, is significantly longer than the corresponding bond lengths observed in complexes with the 1-methoxycarbonylethyl group, 2.080 (7)–2.098 (7) Å. The Co—P distance, 2.330 (1) Å, is not significantly

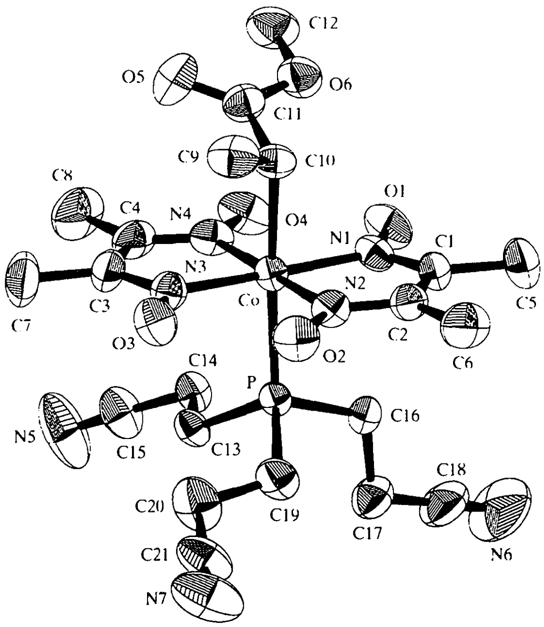


Fig. 1. The molecular structure (*ORTEP*; Johnson, 1965) of the title compound with the atom numbering. Displacement ellipsoids are shown at the 50% probability level.

different from those in cobaloxime complexes with the 1-cyanoethyl group as the alkyl group and phosphine as the axial base ligand: 2.410 (3) and 2.316 (2) Å in the triphenyl- and tributylphosphine complexes, respectively (Kurihara, Uchida *et al.*, 1983), 2.313 (1) and 2.370 (1) Å in the diethylphenyl- and ethyldiphenylphosphine complexes, respectively (Tomotake *et al.*, 1984), and 2.332 (2) Å in the diphenylmethylphosphine complex (Tomotake *et al.*, 1985). The other distances and angles are not significantly different from those in related cobaloxime complexes.

The crystal structure viewed along the *b* axis is shown in Fig. 2. There are no unusually short contacts between molecules. The 1-methoxycarbonylethyl group is surrounded by the axial phosphine ligand and the cobaloxime moieties of neighboring molecules. The cooperative motion of the two reactive groups observed in the pyridine and 4-chloropyridine complexes cannot be expected. This is one reason why the crystal showed no crystalline-state racemization on exposure to visible light. In order to examine the void space around the reactive group, the reaction cavity for the 1-methoxycarbonylethyl group was drawn (Ohashi *et al.*, 1981). The reactive group is packed in the cavity as shown in Fig. 3. The volume of the cavity was calculated to be 26.3 Å^3, which is considerably greater than the volumes observed in the three non-reactive complexes involving (*R*)-1-phenylethylamine, (*S*)-1-phenylethylamine (triclinic and monoclinic forms) and 4-cyanopyridine of 23.8, 24.5 and 21.5, and 18.8 Å^3, respectively. The rate constants of the powdered samples of these crystals were obtained. Since the two forms of the (*S*)-1-phenylethylamine complex were difficult to isolate, a mixed sample of the two forms was used. The rate constants are 2.30×10^{-6}, 9.21×10^{-5} and 1.58×10^{-4} s^{-1} for (*R*)-1-phenylethylamine, (*S*)-1-phenylethylamine and 4-cyanopyridine, respectively. It is clear that the greater rate constant of the title complex is due to the larger reaction cavity for the 1-methoxycarbonylethyl group.

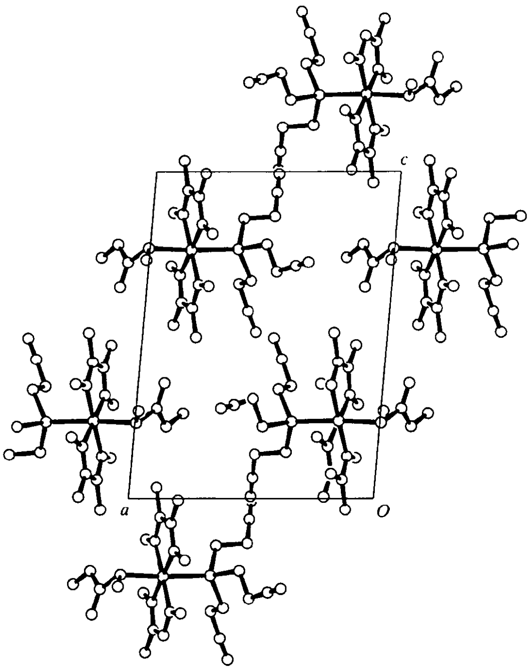


Fig. 2. The crystal structure of the title compound viewed along the *b* axis.

Fig. 3. The reaction cavity for the 1-methoxycarbonylethyl group.

Experimental

Details of the preparation of the title compound will be published elsewhere (Arai & Ohgo, 1998). Crystals were obtained from an aqueous methanol solution.

Crystal data

$[Co(C_4H_7N_2O_2)_2(C_4H_7O_2)$-
$(C_9H_{12}N_3P)]$
$M_r = 569.44$
Monoclinic
$P2_1$
$a = 11.218\ (2)$ Å
$b = 7.991\ (2)$ Å
$c = 15.202\ (2)$ Å
$\beta = 94.95\ (1)°$
$V = 1357.7\ (5)$ Å^3
$Z = 2$
$D_x = 1.393$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.739$ mm^{-1}
$T = 296$ K
Column
0.5 × 0.4 × 0.2 mm
Orange

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scan (North *et al.*, 1968)
$T_{min} = 0.776$, $T_{max} = 0.863$
3350 measured reflections
3350 independent reflections

3237 reflections with $I > 0$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = -19 \rightarrow 19$
3 standard reflections every 100 reflections
intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.095$
$S = 1.05$
3237 reflections
338 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.1868P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (2)

Table 1. *Selected geometric parameters (Å, °)*

Co—N3	1.878 (3)	O5—C11	1.217 (4)
Co—N1	1.884 (3)	O6—C11	1.334 (5)
Co—N4	1.884 (3)	O6—C12	1.441 (6)
Co—N2	1.888 (3)	C9—C10	1.525 (6)
Co—C10	2.112 (4)	C10—C11	1.478 (6)
Co—P	2.330 (1)		
C10—Co—P	176.3 (1)	C9—C10—Co	115.2 (3)
C11—O6—C12	116.1 (3)	O5—C11—O6	121.9 (4)
C11—C10—C9	112.4 (4)	O5—C11—C10	125.6 (5)
C11—C10—Co	108.6 (3)	O6—C11—C10	112.5 (3)

H atoms were refined using a riding model, except for the H atoms of the hydroxy groups, the coordinates and displacement parameters of which were fixed.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SV* (Nemoto & Ohashi, 1993). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1314). Services for accessing these data are described at the back of the journal.

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A Polymorph of Bis(2-pyridylmethyl)amine Iron(III) Chloride

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Abstract

The structure of the orthorhombic modification of an iron(III) chloride complex of bis(2-pyridylmethyl)amine, a potential tridentate N-donor ligand, has been determined, *i.e.* [bis(2-pyridylmethyl)amine-κ^3N]-trichloroiron(III), [$FeCl_3(C_{12}H_{13}N_3)$]. The iron(III) has a rhombically distorted octahedral coordination environment made up of all three N atoms of the capping tridentate ligand and three Cl^- ions.

Comment

Iron(III) complexes incorporating pyridyl and phenolate donors have been synthesized in order to unravel the structure–function relationships of iron(III) tyrosinate proteins (Cox & Que, 1988; Que, 1983). Recently, we reported a series of such iron(III) complexes possessing interesting spectral and structural properties (Viswanathan *et al.*, 1996).

In the crystal of the title compound, (I), there are two crystallographically independent complex molecules in the asymmetric unit, which exhibit the same coordination geometry but slightly different bond lengths and angles.