Instrumental Achievements

Crystal Structure of (Aqua)bis(dimethylglyoximate)((*Z*)-2-phenylethen-1-yl)cobalt(III)hydrate

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Many photoreactions of cobaloxime complexes in the solid or crystalline state have been found: *e.g.* photo-racemization¹ and photoisomerization.² Since it is expected that the cobaloxime complex having an alkyl group with C–C double bonds will show photoreactivity in the solid state, the alkenyl cobaloxime, ((*Z*)-2-phenylethen-1-yl)cobaloxime complex³, attracted our attention.

The title compound was prepared in a similar way to that reported previously. Single crystals suitable for X-ray work were obtained from an aqueous methanol solution. The crystal is photostable to the irradiation of a Xe-lamp. The crystal data and the experimental details are listed in Table 1. The molecular and crystal structures are shown in Figs. 1 and 2, respectively. The atomic coordinates are listed in Table 2. The configuration of the alkenyl moiety is *Z*, which is consistent with the result from the ¹H NMR measurement.⁴ The molecule has an expanded alkenyl moiety; the bond angle Co1–C9=C10, C9=C10–C11 and O5–Co1–C9 are

135.6(2)°, 133.1(3)° and 176.2(1)°, respectively. The cobaloxime plane is distorted like a propeller because of the close contact with the alkenyl group; the torsion angles between two dimethylglyoxime moieties O1–N1...N4–O4 and O2–N2...N3–O3 are 5.4(2)° and

Fig. 1 ORTEP⁸ drawing with the numbering of the atoms. Thermal ellipsoids scaled to enclose 50% probability.

Table 1 Crystal and experimental data

Formula	C ₁₆ H ₂₅ O ₆ N ₄ Co·H ₂ O
<i>M_r</i> =428.33	
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> =10.405(5) Å	α =94.95(4)°
<i>b</i> =13.032(5) Å	β =102.08(4)°
<i>c</i> =7.507(4) Å	γ =104.07(3)°
<i>V</i> =955.3(7) Å ³	<i>Z</i> =2
<i>D_x</i> =1.489 Mg m ⁻³	
λ =0.71073 Å (Mo K α)	
<i>T</i> =296 K	
Diffractometer	Rigaku AFC-5
Crystal size	0.62×0.30×0.12 mm
Crystal color	red
Crystal description	plate
$\omega/2\theta$ scans	
$\theta_{\max}$ =27.52°	4390 independent reflections
250 parameters	3295 observed reflections [$>2\sigma(I)$]
$R(F>4\sigma(F))$ =0.048	
$wR(F^2)$ =0.119	
Structure determination	SHELXS-86 ⁶
Refinement	SHELXL-93 ⁷

Fig. 2 Crystal structure viewed along the *c* axis. Inter-molecular hydrogen bonds are indicated by dotted lines.

Table 2 Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for non-hydrogen atoms

Atom	x	y	z	U_{eq}
Co(1)	0.4230(1)	0.2036(1)	0.1563(1)	0.027
O(1)	0.6286(3)	0.3910(2)	0.3513(4)	0.056
O(2)	0.4176(2)	-0.0157(2)	0.1742(3)	0.037
O(3)	0.2070(2)	0.0175(2)	-0.0175(3)	0.043
O(4)	0.4337(2)	0.4209(2)	0.1279(3)	0.046
O(5)	0.5120(3)	0.1959(2)	-0.0633(3)	0.048
O(6)	0.4090(4)	0.6266(2)	0.2242(4)	0.078
N(1)	0.5916(2)	0.2825(2)	0.3123(4)	0.037
N(2)	0.4894(2)	0.0866(2)	0.2329(3)	0.031
N(3)	0.2542(2)	0.1259(2)	0.0022(3)	0.031
N(4)	0.3612(2)	0.3191(2)	0.0707(3)	0.032
C(1)	0.6689(3)	0.2287(3)	0.3933(4)	0.038
C(2)	0.6108(3)	0.1119(2)	0.3429(4)	0.034
C(6)	0.6845(4)	0.0328(3)	0.4132(5)	0.048
C(5)	0.8015(4)	0.2777(3)	0.5308(6)	0.058
C(7)	0.0544(3)	0.1275(3)	-0.2353(5)	0.051
C(3)	0.1844(3)	0.1788(2)	-0.0975(4)	0.034
C(4)	0.2487(3)	0.2950(2)	-0.0566(4)	0.034
C(8)	0.1900(4)	0.3767(3)	-0.1474(5)	0.052
C(9)	0.3511(3)	0.2115(2)	0.3732(4)	0.034
C(10)	0.2489(3)	0.2445(3)	0.4176(4)	0.042
C(11)	0.1361(3)	0.2819(3)	0.3101(4)	0.036
C(12)	0.0186(3)	0.2092(3)	0.2019(5)	0.046
C(13)	-0.0895(4)	0.2436(3)	0.1109(6)	0.054
C(14)	-0.0840(4)	0.3508(3)	0.1273(6)	0.058
C(15)	0.0307(4)	0.4238(3)	0.2361(6)	0.059
C(16)	0.1398(4)	0.3895(3)	0.3270(5)	0.046

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j).$$

4.2(2)°, respectively. The phenyl group is almost parallel to the cobaloxime plane and nearly perpendicular to the alkenyl plane; the torsion angle C9=C10-C11-C12 is 80.9(5)°, showing that the conjugation is

interrupted between the phenyl and the vinyl group. The geometry of the alkenyl group is almost the same as that of [1-chloro-2,2-bis(*p*-chlorophenyl)vinyl]bis(dimethylglyoximate)pyridine cobalt(III) reported previously⁵, in which one of the *p*-chlorophenyl groups was imposed to be *cis* to the cobaloxime plane.

Figure 2 shows the crystal structure. The phenyl group is parallel to the cobaloxime plane of the adjacent molecules. The solvent water molecule O6 is hydrogen-bonded to the cobaloxime plane O4 and the axial water ligand O5; O6...O4, and O6[1-x, 1-y, -z]...O5 are 2.80, and 2.73 Å respectively. These hydrogen bonds make a dimer around the inversion center (0.5, 0.5, 0).

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