

Dichloro[(1*E*,1'*E*)-1,1'-(pyridine-2,6-diyl)diethanone bis(*O*-methyloxime)- κ^3N^1,N^2,N^6]cobalt(II)

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Received 3 July 2006

Accepted 11 July 2006

Online 11 August 2006

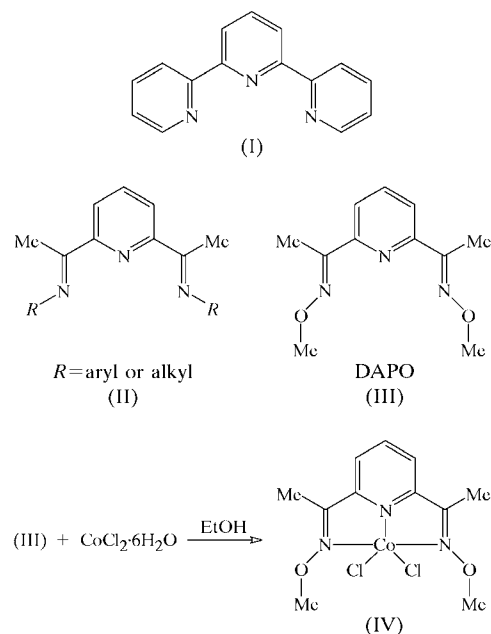
In the title compound, [CoCl₂(C₁₁H₁₅N₃O₂)], the Co^{II} ion is five-coordinated in a strongly distorted square-pyramidal arrangement, with one of the two Cl atoms located in the apical position, and the other Cl atom and the three N-donor atoms of the tridentate methyloxime ligand located in the basal plane. The non-H atoms, except for the Cl atoms, lie on a mirror plane. The two equatorial Co—N_{oxime} distances are almost equal (mean 2.253 Å) and are substantially longer than the equatorial Co—N_{pyridine} bond [2.0390 (19) Å]. The structure is stabilized by intra- and intermolecular C—H⋯Cl contacts, which involve one of the methyl C atoms belonging to the methyloxime groups.

Comment

Complexes of transition metals with tridentate Schiff bases are of considerable interest due to their structural and material properties and their potential as catalysts for a variety of organic reactions (Small & Brookhart, 1998; Britovsek *et al.*, 1999). For instance, the terpyridine molecule, (I), has been the subject of numerous studies concerning analytical applications (Togni & Venanzi, 1994). Various 2,6-diacetylpyridine diimines, (II), have also been studied as catalysts for the polymerization and epoxidation of alkenes (Tellmann *et al.*, 2005, and references therein; Small & Brookhart, 1999; Griffiths *et al.*, 1999; Harman *et al.*, 1997; Small *et al.*, 1998; Dias *et al.*, 2001; Çetinkaya *et al.*, 1999; Bianchini & Lee, 2000). We report here the synthesis and characterization of a cobalt(II) complex derived from the related tridentate ligand 1,1'-(pyridine-2,6-diyl)diethanone bis(*O*-methyloxime) (DAPO), (III).

The tridentate Schiff base (III), derived from the condensation of 2,6-diacetylpyridine with *O*-methylhydroxylamine, reacted with cobalt(II) chloride hydrate to give a mononuclear complex of formula [CoCl₂(DAPO)], (IV).

The molecular structure of complex (IV), together with the atom-labelling scheme and the intramolecular hydrogen bonding, are shown in Fig. 1. Selected geometric parameters are listed in Table 1. The structure is composed of a DAPO



ligand with a Co^{II} metal centre and two Cl ligands. As expected, complex (IV) does not crystallize with solvent molecules, and the DAPO ligand, with its two imine groups in *ortho* positions with respect to the pyridine N atom, behaves as a symmetrical *N,N',N'*-tridentate chelate. The Co^{II} ion is five-coordinated by two methyloxime N atoms, one pyridine N atom and two Cl atoms (Fig. 1). The molecule lies with all non-H atoms, except atom Cl1, on a crystallographic mirror plane so that the complex is strictly planar.

Recently, we have reported a complex of (III) with copper(II), [CuCl₂(DAPO)] (Özdemir *et al.*, 2006). On the basis of the estimated 'effective' ionic radii for Cu²⁺ (0.65 Å) and Co²⁺ (0.67 Å) in a five-coordinate environment (Shannon, 1976), the corresponding *M*—N and *M*—Cl bond distances in [CuCl₂(DAPO)] and [CoCl₂(DAPO)], would be expected to be fairly similar in magnitude. This premise is clearly not supported by a comparison of the *M*—N and *M*—Cl bond distances in both complexes. The Cu—Cl distances in [CuCl₂(DAPO)] are *ca* 0.04 and 0.07 Å longer than their respective Co—Cl bond distances in [CoCl₂(DAPO)]. Conversely, the Co—N_{pyridine} and Co—N_{oxime} bond distances in [CoCl₂(DAPO)] are *ca* 0.06 and 0.16 Å longer than their respective Cu—N bond distances in [CuCl₂(DAPO)]. These unusually long Co—N bond distances strongly suggest that the angular overlap between the available metal orbitals and the N-donor orbitals of the oxime ligand is relatively poor in this five-coordinate Co complex.

The coordination polyhedron about the Co atom is concluded to be a highly distorted square pyramid on the basis of the τ parameter of 0.46 calculated for this complex [for a square pyramid $\tau = 0$ and for a trigonal-bipyramid $\tau = 1$; $\tau = (\beta - \alpha)/60^\circ$, α and β being the two largest angles around the

central atom (Addison *et al.*, 1984)]. In contrast, the τ value for the Cu analogue was 0.53, indicating a geometry slightly more towards the trigonal-bipyramidal ideal. The apex of the square pyramid in (IV) is occupied by a chloride ligand, and the four basal positions consist of the other chloride ligand and the three N-donor atoms of the tridentate methyloxime ligand [Clⁱ; symmetry code: (i) $x, \frac{1}{2} - y, z$]. The maximum deviation from the ideal value of 90° of the valency angles involving the transition metal atom is 16.18 (8)° for N1—Co1—N3. A comparison of the appropriate bond distances and angles in [CoCl₂(DAPO)] indicates that the molecule possesses *C_s* symmetry with a non-crystallographic mirror plane passing through atoms Co, Cl1, Cl2 and N1. The axial-equatorial (ax-eq) angles fall into two groups, with Cl_{ax}—Co—N_{eq} angles in the range 97.92 (3)–121.129 (15)° and a Cl_{ax}—Co—Cl_{eq} angle of 117.74 (3)°.

The most predominant feature of this five-coordinate cobalt complex is the significantly different Co—N distances in the basal plane. The Co1—N2 and Co1—N3 bond distances are longer than the Co1—N1 bond (Table 1). Since the electronic ground state in this Co^{II} complex is not likely to be degenerate, the observed variations in these bond distances are probably due to a second-order Jahn–Teller effect of the *d*⁷ metal atom (Pearson, 1969). The displacement parameters for atoms N2 and N3 suggest a slight dynamic component to the Jahn–Teller effect, as the values of $\Delta(\text{MSDA})$ (MSDA is mean-square displacement amplitude; Hirshfeld, 1976) for the Co1—N2 and Co1—N3 bonds are 0.0050 (12) and 0.0071 (14) Å², respectively, which are significantly larger than those for all of the other bonds in the structure. In the electronic spectrum, a weak band at 630 nm corresponds to a *d*–*d* transition (dichloromethane solution). A less intense band at 361 nm is due to the Jahn–Teller effect in the complex. The absorption band below 345 nm results from the overlap of a low-energy π – π^* transition mainly localized within the imine chromophore and the ligand-to-metal charge transfer bands (LMCT). The magnetic moment of 4.9 BM observed for the

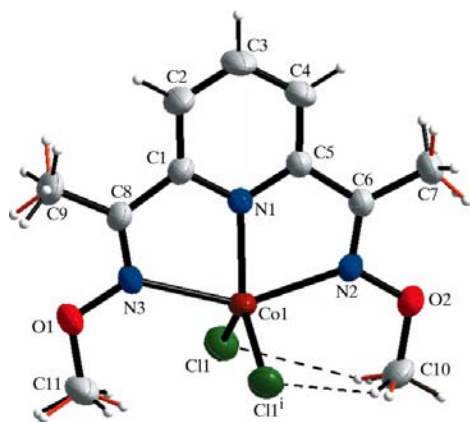


Figure 1
A view of the molecule of (IV), showing 40% probability displacement ellipsoids and the atom-numbering scheme. Intramolecular C—H...Cl contacts are represented by dashed lines. [Symmetry code: (i) $x, -y + \frac{1}{2}, z$]. Both orientations of the disordered methyl H atoms are shown.

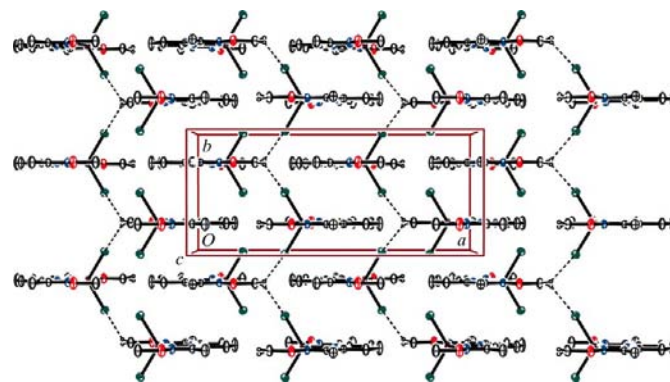


Figure 2
A projection of (IV), viewed along the *c* axis. Dashed lines show the C—H...Cl interactions. For clarity, only H atoms involved in hydrogen bonding have been included.

complex indicates the high spin state. The electrochemical parameters of the complex were measured in dichloromethane *versus* tetrabutylammonium hexafluorophosphate using a gold electrode and ferrocene as the internal standard. The couples at +0.91 V and –0.21 V are attributed to Co^{III/II} and Co^{II/I}, respectively.

Similar to the Cu^{II} complex, two intramolecular interactions are observed between the methyl H and the Cl atoms in the molecular structure of (IV), forming six-membered rings. Despite the similar chemical compositions of the Cu^{II} and Co^{II} complexes, the packing patterns of the molecules in the crystal structures are quite different. In contrast to the columnar packed structure observed in [CuCl₂(DAPO)], the molecules of (IV) pack in layers parallel to the *ac* plane. The Cu^{II} complexes are connected to one another by the molecules packed in 2₁ screw symmetry-related columns, forming pairs of C—H...Cl contacts between two neighbouring molecules. However, in (IV), there are no intermolecular interactions between the Co^{II} complex molecules in each layer nor in the *c* direction. The intermolecular contacts between the layers are formed by the methyl C atoms belonging to one of the methyloxime groups and by the Cl atoms, forming a two-dimensional network (Fig. 2 and Table 2).

Experimental

CoCl₂·6H₂O (Panreac), diacetylpyridine (Fluka) and methoxylamine hydrochloride (Acros) were used as received. Compound (III) was prepared by a modification of literature methods (Çetinkaya *et al.*, 1999; Bianchini & Lee, 2000). Solvents were of analytical grade and distilled after drying. A solution of CoCl₂·6H₂O (238 mg, 1 mmol) in EtOH (10 ml) was added dropwise to a solution of DAPO (221 mg, 1 mmol) in ethanol (10 ml). The resulting green solution was refluxed for 4 h and then concentrated (5 ml). Et₂O was added, with stirring, to a final volume of 20 ml, causing a green powder to precipitate. The precipitate was filtered off, washed with Et₂O and dried. X-ray quality crystals were grown from CH₂Cl₂–Et₂O (15 ml, 1:2 *v/v*) (yield 240 mg, 68%; m.p. 515–517 K). Analysis calculated for C₁₁H₁₅Cl₂·CoN₃O₂: C 37.63, H 4.31, N 11.97%; found: C 37.23, H 4.49, N 12.32%. IR (KBr): 1637 ($\nu_{\text{C=N}}$) cm^{–1}.

Crystal data

[CoCl ₂ (C ₁₁ H ₁₅ N ₃ O ₂)]	Z = 4
<i>M_r</i> = 351.09	<i>D_x</i> = 1.577 Mg m ⁻³
Orthorhombic, <i>Pnma</i>	Mo <i>Kα</i> radiation
<i>a</i> = 18.0255 (11) Å	μ = 1.52 mm ⁻¹
<i>b</i> = 7.6426 (5) Å	<i>T</i> = 296 K
<i>c</i> = 10.7325 (8) Å	Plate, green
<i>V</i> = 1478.53 (17) Å ³	0.41 × 0.28 × 0.05 mm

Data collection

Stoe IPDS-II diffractometer	9341 measured reflections
ω scans	1406 independent reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	1161 reflections with <i>I</i> > 2 σ (<i>I</i>)
<i>T_{min}</i> = 0.564, <i>T_{max}</i> = 0.926	<i>R_{int}</i> = 0.050
	θ_{max} = 25.0°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{\text{max}} = 0.001$
<i>S</i> = 1.00	$\Delta\rho_{\text{max}} = 0.20 \text{ e } \text{Å}^{-3}$
1406 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{Å}^{-3}$
117 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0037 (7)

Table 1

Selected geometric parameters (Å, °).

Co1—N1	2.0390 (19)	O1—N3	1.391 (3)
Co1—N2	2.220 (2)	O2—N2	1.388 (3)
Co1—Cl1	2.2366 (5)	N2—C6	1.286 (3)
Co1—N3	2.286 (2)	N3—C8	1.281 (3)
N1—Co1—N2	74.64 (7)	N2—Co1—N3	148.46 (7)
N1—Co1—Cl1	121.129 (15)	Cl1—Co1—N3	98.23 (3)
N2—Co1—Cl1	97.92 (3)	N2—C6—C5	114.3 (2)
Cl1—Co1—Cl1 ⁱ	117.74 (3)	N3—C8—C1	114.8 (2)
N1—Co1—N3	73.82 (8)		

Symmetry code: (i) *x*, $-y + \frac{1}{2}$, *z*.

Table 2

Short-contact geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C10—H10C...Cl1 ⁱ	0.96	2.77	3.611 (3)	147
C10—H10A...Cl1 ⁱⁱ	0.96	2.79	3.650 (3)	149

Symmetry codes: (i) *x*, $-y + \frac{1}{2}$, *z*; (ii) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $z + \frac{1}{2}$.

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96 and 0.93 Å for methyl and aromatic H atoms, respectively. The *U*_{iso}(H) values were set at 1.2 (aromatic) or 1.5 (methyl) times *U*_{eq}(C). Riding methyl H atoms were allowed to rotate freely during refinement using the AFIX 137

command of *SHELXL97* (Sheldrick, 1997). The H atoms of the four methyl groups were disordered over two symmetry-related positions, above and below the mirror plane, and were allowed for by placing six H atoms with equivalent half-occupancies.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

This study was supported financially by the Research Centre of Ondokuz Mayıs University (project No. F-366).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3032). Services for accessing these data are described at the back of the journal.

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