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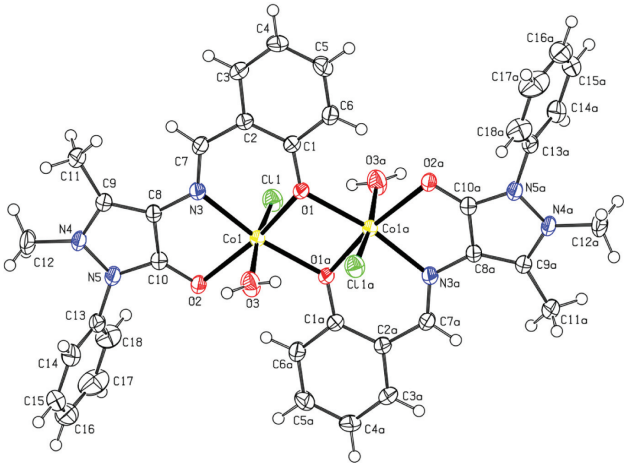
Crystal structure of diaqua-dichlorido-bis(μ$_2$-2-(((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)imino)methyl)phenolato-κ^4*O*:*O*,*N*,*O*′) dicobalt(II), $C_{36}H_{36}Cl_2N_6O_6Co_2$



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Abstract

$C_{36}H_{36}Cl_2N_6O_6Co_2$, triclinic, $P\bar{1}$ (no. 2), $a = 7.4399(9)$ Å, $b = 9.5362(11)$ Å, $c = 13.1754(15)$ Å, $\alpha = 73.589(2)°$, $\beta = 84.396(2)°$, $\gamma = 74.709(2)°$, $V = 864.68(17)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0306$, $wR_{ref}(F^2) = 0.1068$, $T = 298(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.10 × 0.10 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.17 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.0°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7072, 3723, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3231
$N(param)_{refined}$:	243
Programs:	Bruker [1], SHELX [2, 3]

Source of material

The title compound was synthesized by mixing 0.154 g (0.5 mmol) 4-(2-hydroxybenzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one) (HL5), 0.601 g (2.5 mmol) $CoCl_2{\cdot}H_2O$, 9 mL absolute methanol, 0.5 mL dichloromethane and 0.5 mL trithylamine in a 25 mL polytetrafluoroethylene reactor. Then the reactor was placed in an oven at 90 °C. After 7 days, amaranth tabular crystals were obtained with 80.91% yield. Elemental analysis calculated for $C_{36}H_{36}Cl_2N_6O_6Co_2$: C 51.58, H 4.69, O 11.46, N 9.86%; found C 51.63, H 4.64, O 11.35, N 10.03%. IR spectrum (cm^{-1}, KBr pellet): 3421(*s*), 3334(*s*), 1612(*s*), 1536(*m*), 1492(*m*), 1436(*m*), 1390(*m*), 1288(*m*), 1039(w), 902(w), 761(*m*), 574(w).

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

A reaction which is difficult to occur at normal temperature can synthesize certain materials having special properties by using a high-temperature aqueous solution or a solvent as a reaction medium [4]. The transition metal Schiff base complex can also be synthesized by solvothermal methods. After decades of efforts, it was discovered that the transition metal Schiff base complex has unique biological activity, and research in this field has gradually become active [5, 6]. Schiff base complexes have been widely, systematically and deeply explored by theory and application for their physical properties, coordination chemistry and physiological activities [7].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.57715(4)	0.90182(3)	0.91716(2)	0.02184(12)
C1	0.5425(3)	0.7457(3)	1.15178(18)	0.0224(5)
C2	0.6033(3)	0.5999(3)	1.13353(19)	0.0241(5)
C3	0.5969(4)	0.4720(3)	1.2189(2)	0.0310(5)
H3	0.6347	0.3769	1.2068	0.037*
C4	0.5372(4)	0.4830(3)	1.3189(2)	0.0343(6)
H4	0.5337	0.3972	1.3737	0.041*
C5	0.4821(4)	0.6252(3)	1.3360(2)	0.0374(6)
H5	0.4427	0.6342	1.4036	0.045*
C6	0.4842(4)	0.7529(3)	1.2557(2)	0.0325(6)
H6	0.4464	0.8465	1.2702	0.039*
C7	0.6767(3)	0.5685(3)	1.03451(19)	0.0264(5)
H7	0.7149	0.4678	1.0336	0.032*
C8	0.7702(3)	0.6335(3)	0.85369(18)	0.0235(5)
C9	0.8704(3)	0.5060(3)	0.82495(19)	0.0252(5)
C10	0.7474(3)	0.7572(3)	0.76184(19)	0.0255(5)
C11	0.9301(4)	0.3450(3)	0.8869(2)	0.0355(6)
H11A	0.8403	0.2924	0.8799	0.053*
H11B	0.9391	0.3398	0.9601	0.053*
H11C	1.0495	0.2991	0.8605	0.053*
C12	0.9794(5)	0.4499(3)	0.6508(2)	0.0452(7)
H12A	1.1023	0.4580	0.6247	0.068*
H12B	0.8973	0.4802	0.5924	0.068*
H12C	0.9834	0.3473	0.6891	0.068*
C13	0.8636(4)	0.7790(3)	0.57385(19)	0.0291(5)
C14	1.0445(4)	0.7862(3)	0.5394(2)	0.0391(6)
H14	1.1428	0.7398	0.5856	0.047*
C15	1.0775(5)	0.8623(4)	0.4367(3)	0.0499(8)
H15	1.1985	0.8672	0.4139	0.060*
C16	0.9341(6)	0.9312(4)	0.3674(2)	0.0551(9)
H16	0.9581	0.9812	0.2979	0.066*
C17	0.7524(6)	0.9255(4)	0.4020(3)	0.0567(9)
H17	0.6542	0.9736	0.3559	0.068*
C18	0.7183(5)	0.8482(4)	0.5050(2)	0.0431(7)
H18	0.5974	0.8430	0.5278	0.052*
Cl1	0.26885(9)	0.87593(8)	0.88696(5)	0.03302(16)
N3	0.6936(3)	0.6686(2)	0.94707(15)	0.0231(4)
N4	0.9118(3)	0.5467(2)	0.72054(17)	0.0315(5)
N5	0.8291(3)	0.7001(2)	0.68013(17)	0.0318(5)
O1	0.5404(2)	0.87214(18)	1.07690(13)	0.0239(3)
O2	0.6689(3)	0.89351(19)	0.75584(13)	0.0296(4)
O3	0.8275(3)	0.9675(2)	0.92313(18)	0.0390(5)
H3A	0.947(3)	0.932(4)	0.913(3)	0.059*
H3B	0.822(5)	1.007(4)	0.972(2)	0.059*

But there are few reports on the structural characterization of 4-aminoantipyrine derived metal complexes.

Each Co(II) atom is coordinated by one water molecule, a chlorido ligand and three atoms from two different L5 ligands (see the figure). In the complex, the metal Co(II) center adopts a distorted octahedral coordination. The chlorido ligand and the oxygen atom from the water molecule are respectively at the top of the cone of the distorted octahedron. Two different oxygen atoms, the nitrogen atom in the imine and the carbonyl oxygen atom in the pyrazole ring are in the equatorial plane of the distorted octahedron. Each ligand coordinates with two metal centers to form a μ_2-bridge mode. The Co—O bond length is 2.0436(16)−2.1848(17) Å, which is longer than that reported in [8]; Co(1)—Cl(1) bond length is 2.4521(7) Å, Co—N bond length is 2.099(2) Å. The lengths of the two Co—N bonds are similar to the length reported in the literatures [9, 10]. Two Co (II) atoms and two oxygen atoms form a Co_2O_2 parallelogram. The distance of Co1—Co1a is 3.206(4) Å, and O1—O1a is 2.662(4) Å. The bond angle of O1—Co1—O1a is 79.41(3)°, that of Co1—O1—Co1a is 100.59(3)°. Each dinuclear cobalt could form a structurally stable six-membered ring with a hydroxyl oxygen atom, an imine nitrogen atom and three carbon atoms. It also formed a five-membered ring with a carbonyl atom, an imine nitrogen atom and two carbon atoms in the pyrazole ring. The remaining bond length and bond angle are in the normal range.

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