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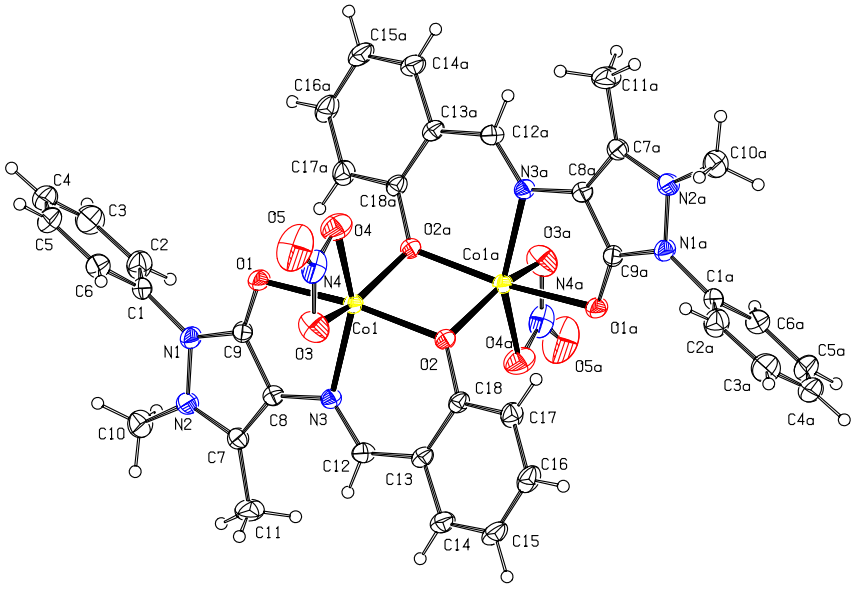
Crystal structure of bis(μ_2-2-(1,5-dimethyl–3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)imino)methyl)phenolato-κ^4O:*O*,*N*,*O*′)-(nitrato-κ^2O,*O*′) dicobalt(II), $C_{36}H_{32}Co_2N_8O_4$



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Abstract

$C_{36}H_{32}Co_2N_8O_4$, monoclinic, $P2_1/c$ (no. 14), a = 12.2971(12) Å, b = 13.1008(13) Å, c = 11.0864(11) Å, β = 99.174(2)°, V = 1763.2(3) Å^3, Z = 2, $R_{gt}(F)$ = 0.0277, $wR_{ref}(F^2)$ = 0.0818, T = 296 K.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.23 × 0.20 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.01 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13,853, 4251, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3598
$N(param)_{refined}$:	255
Programs:	Bruker [1], SHELX [2, 3]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

HL_5 0.1540 g (0.5 mmol), $Co(NO_3)_2{\cdot}6H_2O$ 0.7349 g (2.5 mmol), anhydrous methanol 9 mL, dichloromethane 0.5 mL,

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.62733 (2)	0.49420 (2)	0.03284 (2)	0.02769 (8)
N1	0.83352 (11)	0.60072 (11)	0.33622 (12)	0.0350 (3)
N2	0.83443 (12)	0.53740 (12)	0.43705 (12)	0.0370 (3)
N3	0.65348 (10)	0.41238 (9)	0.19570 (11)	0.0275 (3)
N4	0.73744 (14)	0.45552 (16)	−0.14059 (15)	0.0521 (4)
O1	0.75400 (10)	0.59022 (9)	0.13030 (10)	0.0372 (3)
O2	0.49563 (9)	0.40153 (8)	−0.02309 (10)	0.0317 (2)
O3	0.73572 (13)	0.39368 (13)	−0.05481 (15)	0.0601(4)
O4	0.68012 (14)	0.53470 (13)	−0.13715 (13)	0.0579 (4)
O5	0.79039 (17)	0.4399 (2)	−0.22199 (17)	0.0957 (7)
C1	0.89906 (13)	0.69120 (13)	0.33974 (15)	0.0340 (3)
C2	0.87307 (17)	0.77547 (15)	0.4049 (2)	0.0497 (5)
H2	0.8113	0.7749	0.4436	0.060*
C3	0.9403 (2)	0.86040 (17)	0.4117 (2)	0.0630 (6)
H3	0.9245	0.9170	0.4564	0.076*
C4	1.0306 (2)	0.86166 (18)	0.3525 (2)	0.0640 (7)
H4	1.0760	0.9188	0.3584	0.077*
C5	1.05365 (17)	0.77921 (19)	0.2853 (2)	0.0596 (6)
H5	1.1137	0.7814	0.2438	0.072*
C6	0.98820 (15)	0.69218 (15)	0.27830 (18)	0.0439 (4)
H6	1.0042	0.6358	0.2332	0.053*
C7	0.76947 (13)	0.45554 (13)	0.40388 (14)	0.0320 (3)
C8	0.72797 (12)	0.46507 (12)	0.28135 (14)	0.0287 (3)
C9	0.77013 (12)	0.55635 (12)	0.23791 (14)	0.0294 (3)
C10	0.88853 (17)	0.56792 (17)	0.55778 (16)	0.0491 (5)
H10A	0.8437	0.6171	0.5912	0.074*
H10B	0.9588	0.5976	0.5518	0.074*
H10C	0.8988	0.5092	0.6101	0.074*
C11	0.75018 (19)	0.37489 (16)	0.49268 (17)	0.0504 (5)
H11A	0.7847	0.3126	0.4734	0.076*
H11B	0.6724	0.3639	0.4881	0.076*
H11C	0.7809	0.3961	0.5738	0.076*
C12	0.61221 (13)	0.32417 (12)	0.21450 (15)	0.0330 (3)
H12	0.6321	0.2952	0.2914	0.040*
C13	0.53746 (13)	0.26695 (11)	0.12531 (15)	0.0306 (3)
C14	0.51813 (15)	0.16504 (12)	0.15742 (17)	0.0387 (4)
H14	0.5485	0.1413	0.2345	0.046*
C15	0.45562 (15)	0.10017 (13)	0.07747 (19)	0.0442 (4)
H15	0.4446	0.0329	0.0996	0.053*
C16	0.40901 (16)	0.13617 (13)	−0.03692 (19)	0.0448 (4)
H16	0.3681	0.0922	−0.0924	0.054*
C17	0.42278 (14)	0.23641 (13)	−0.06917 (17)	0.0388 (4)
H17	0.3895	0.2594	−0.1455	0.047*
C18	0.48610 (12)	0.30439 (12)	0.01110 (14)	0.0299 (3)

triethylamine 0.5 mL were placed in a reaction kettle, pH was adjusted to 7, shaken and sealed in an oven at 90 °C, and green needle crystals grew after seven days with a yield of 80.63 %.

2 Comment

In the field of scientific research, there is a significant increase in interest in the design of metal compounds as drugs and diagnostic agents [4]. Schiff base metal complexes are of wide interest for their use in optoelectronic materials, magnetic materials, analytical chemistry, and biology due to their specific properties [5], especially in medicine [6]. Among them, Co(II) Schiff bases have excellent DNA binding/cleavage, antibacterial, anticancer and antioxidant inhibitory properties that may help in developing innovative therapeutic strategies for the treatment of various diseases [7]. The 4-aminoantipyrine (Ampyrone) is an antipyrine derivative with an amino group at the C-4 position that has a large range of biological activities [8], and these derivatives have been used as ligands to develop multifunctional transition metal complexes with potential biological applications [9]. Based on some of our previously published Zn [10] and Co [11] metal complexes with 4-aminoantipyrine Schiff base ligands, we fitted 4-aminoantipyrine condensed o-hydroxybenzaldehyde (HL_5) as a ligand and synthesized a novel reactivity and solubility of the reactants by using a solvothermal method in a sealed vessel by heating to produce an increase in self-pressure [12]. The synthesis of a new type of mononuclear Co(II) complex was carried out to lay some theoretical foundation for the study of the synthesis of metal complexes from 4-aminoantipyrine Schiff base ligands.

The title complex is a binuclear Co(II) coordination consisting of one compound. Each Co(II) center is coordinated by two salicylaldehyde oxygen atoms, imino nitrogen atoms and carbonyl oxygen atoms in the ligand HL_5; plus the oxygen atoms of the nitrato ligand. The metal Co center adopts a distorted octahedral coordination configuration, and the ligand atoms come from two oxygen atoms in two HL_5 ligand molecules, two oxygen atoms in one NO_3^-, one nitrogen atom in imine and carbonyl oxygen atom in pyrazole ring in HL_5 ligand molecule; one hydroxy oxygen atom in HL_5 ligand molecule and carbonyl oxygen atom in pyrazole ring are in the cone of the distorted octahedron, respectively. The two oxygen atoms in one NO_3^- ion and the nitrogen atom in the imine of one HL_5 ligand molecule and the hydroxyl oxygen atom in another HL_5 ligand molecule are in the equatorial plane of the distorted octahedron; each HL_5 ligand molecule is coordinated to two metal centers, forming a μ_2-bridging mode, and NO_3^- is coordinated to the metal center in a bidentate coordination (O(4)–Co(1)–O(3) bond angle of 58.29(7)°), and this coordination mode is also more common in similar complexes.

The Co–O bond lengths are 2.0282(12) and 2.2064(16) Å and the Co–N bond length is 2.0806(13) Å. The two Co–N bonds are

of equal length, similar to that reported in the literature at [13, 14]. Each two Co (II) atoms and two oxygen atoms form a Co_2O_2 parallelogram with a Co1–Co1a spacing of 3.104(4) Å, an O2–O2a spacing of 2.630(3) Å, an O2a–Co1–O2 bond angle of 80.55(4)°, and a Co1–O2–Co1a bond angle of 99.45(5)° (Symmetrical codes: #1 $-x+1, -y+1, -z+1$); the rest of the bond lengths and bond angles are within the normal range.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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