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Crystal structure of dimethanol-dichlorido-bis(μ_2 -2-(((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)imino)methyl)phenolato- $\kappa^4 O:O,O',N$)dinickel (II), $C_{20}H_{24}ClNiN_3O_4$

Abstract

$C_{20}H_{24}ClNiN_3O_4$, monoclinic, $P2_1/c$ (no. 14), $a = 10.3831(7)$ Å, $b = 17.0139(12)$ Å, $c = 12.2649(9)$ Å, $\beta = 102.6230(10)^\circ$, $V = 2114.3(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0318$, $wR_{ref}(F^2) = 0.1066$, $T = 298(2)$ K.

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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.

Source of material

The title compound was synthesized by mixing 0.154 g (0.5 mmol) (4E)-4-(2-hydroxybenzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one (LH), 0.6064 g (2.5 mmol) $NiCl_2 \cdot H_2O$, 9 mL absolute methanol, 0.5 mL dichloromethane and 0.5 mL triethylamine in a 25 mL polytetrafluoroethylene-lined reactor. Then the reactor was placed in an oven at 90 °C. After seven days, green needle crystals separated out with 80.60% yield. **Elemental Analysis** Data (%), measured/theoretical: C, 51.71/51.66; H, 5.21/5.27; N, 9.03/8.98. **IR** spectrum (cm^{-1} , KBr pellet): 3423(s), 3332(s), 1624(s), 1591(s), 1539(m), 1496(m),

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Table 1: Data collection and handling.

Crystal:	Green needle
Size:	0.10 × 0.10 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.08 mm ⁻¹
Diffractometer, scan mode: θ_{max} , completeness:	27.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	15523, 4610, 0.026
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3909
$N(param)_{refined}$:	276
Programs:	Bruker [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Ni1	0.55092 (2)	0.91538 (2)	0.03408 (2)	0.02728 (11)
C1	0.8363 (2)	0.70927 (13)	0.26612 (18)	0.0336 (5)
C2	0.9438 (3)	0.66454 (16)	0.2565 (2)	0.0506 (6)
H2	0.9429	0.6356	0.1921	0.061*
C3	1.0544 (3)	0.6634 (2)	0.3452 (3)	0.0645 (9)
H3	1.1276	0.6333	0.3398	0.077*
C4	1.0556 (3)	0.7059 (2)	0.4390 (3)	0.0722 (10)
H4	1.1297	0.7048	0.4975	0.087*
C5	0.9485 (3)	0.7503 (2)	0.4482 (2)	0.0650 (9)
H5	0.9504	0.7793	0.5128	0.078*
C6	0.8367 (3)	0.75216 (16)	0.3614 (2)	0.0441 (6)
H6	0.7635	0.7819	0.3676	0.053*
C7	0.5913 (2)	0.67067 (12)	0.01814 (18)	0.0333 (5)
C8	0.5836 (2)	0.75125 (12)	0.02114 (17)	0.0303 (4)
C9	0.6662 (2)	0.77761 (12)	0.12177 (18)	0.0323 (4)
C10	0.5184 (3)	0.61269 (14)	−0.0632 (2)	0.0505 (7)
H10A	0.5536	0.5611	−0.0441	0.076*
H10B	0.5281	0.6260	−0.1370	0.076*
H10C	0.4266	0.6135	−0.0608	0.076*
C11	0.6684 (3)	0.57173 (14)	0.1674 (2)	0.0496 (6)
H11A	0.5823	0.5687	0.1839	0.074*
H11B	0.7343	0.5693	0.2357	0.074*
H11C	0.6800	0.5285	0.1201	0.074*
C12	0.4523 (2)	0.79991 (13)	−0.14835 (18)	0.0336 (5)
H12	0.4491	0.7490	−0.1764	0.040*
C13	0.3825 (2)	0.86047 (12)	−0.22113 (17)	0.0306 (4)
C14	0.3174 (3)	0.83425 (14)	−0.32878 (19)	0.0415 (5)
H14	0.3244	0.7816	−0.3473	0.050*
C15	0.2452 (3)	0.88356 (15)	−0.4060 (2)	0.0485 (6)
H15	0.2049	0.8653	−0.4767	0.058*
C16	0.2327 (3)	0.96181 (15)	−0.3772 (2)	0.0474 (6)
H16	0.1821	0.9958	−0.4287	0.057*
C17	0.2941 (2)	0.98965 (13)	−0.27332 (18)	0.0373 (5)
H17	0.2838	1.0422	−0.2563	0.045*
C18	0.37198 (19)	0.94089 (12)	−0.19233 (16)	0.0264 (4)
C19	0.8346 (3)	0.9550 (2)	0.0061 (3)	0.0606 (8)
H19A	0.8376	0.9869	0.0711	0.091*
H19B	0.8826	0.9806	−0.0425	0.091*
H19C	0.8738	0.9048	0.0282	0.091*
Cl1	0.38041 (6)	0.88730 (4)	0.13587 (5)	0.04530 (16)
N1	0.7226 (2)	0.71252 (10)	0.17782 (15)	0.0368 (4)
N2	0.6812 (2)	0.64593 (10)	0.11016 (15)	0.0369 (4)
N3	0.51804 (17)	0.81115 (10)	−0.04814 (14)	0.0295 (4)
O1	0.68866 (16)	0.84778 (9)	0.15263 (13)	0.0403 (4)
O2	0.42909 (14)	0.97077 (8)	−0.09405 (11)	0.0281 (3)
O3	0.70015 (15)	0.94432 (10)	−0.05165 (13)	0.0384 (4)
H3A	0.6679	0.9870	−0.0736	0.058*
C20 ^a	0.942 (2)	0.0665 (19)	0.6923 (15)	0.116 (3)
H20A ^a	0.9294	0.1184	0.6611	0.175*
H20B ^a	0.9035	0.0287	0.6363	0.175*
H20C ^a	1.0342	0.0560	0.7174	0.175*
O4 ^a	0.8804 (14)	0.0611 (13)	0.7818 (11)	0.1230 (17)
H4 ^a	0.8277	0.0973	0.7789	0.184*
O4 ^b	0.8071 (4)	0.1097 (4)	0.6906 (3)	0.1230 (17)
H4A ^b	0.7620	0.0977	0.7353	0.184*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C20 ^b	0.9311 (6)	0.1144 (5)	0.7427 (6)	0.116 (3)
H20D ^b	0.9488	0.1660	0.7741	0.175*
H20E ^b	0.9864	0.1046	0.6909	0.175*
H20F ^b	0.9490	0.0760	0.8014	0.175*

^aOccupancy: 0.233(5), ^bOccupancy: 0.767(5).

1439(*m*), 1397(*m*), 1285(*m*), 1037(*w*), 901(*w*), 762(*m*), 571(*w*).

Experimental details

Comment

Nickel, as an essential trace element in organisms participates in the composition and metabolism of many enzymes in the human body, thus promoting iron absorption, the growth of red blood cells and the synthesis of amino acids [4, 5]. Schiff base complexes have a series of excellent properties, such as bactericidal, antiviral and magnetic properties, and have a wide application prospect in bioengineering and material research [6–10]. Because of its rich spatial topology, binuclear metal complexes can be used as artificial nuclease and have a good catalytic hydrolysis mechanism but there are few reports on the structural characterization of 4-aminoantipyrine derivative ligands and metal complexes. Therefore, it is of great significance to study the synthesis and structure of such metal complexes.

Each Ni(II) in the dinuclear title is coordinated by a methanol molecule, a chlorine atom and three atoms from two different L[−] ligands (a salicylidene hydroxyl oxygen atom, an imino nitrogen atom, and a carbonyl oxygen atom). In the complex, the Ni(II) center adopts a distorted octahedral coordination (see the Figure). The chlorine atom and the oxygen atom from the methanol molecule are respectively above and underneath the plane defined by the Ni atoms and the bridging ligands. Two different hydroxyl 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 molecule coordinates two metal centers. The Ni–O bond length is 2.0222(13)–2.1385(15) Å, which is slightly longer than that reported in [11]; Ni(1)–Cl(1) bond length is 2.4263(7) Å, which is longer than that reported in [12]; Ni–N bond length is 2.0317(17) Å. The distance of Ni1–Ni1a is 3.118(17) Å, and O2–O2a is 2.645(17) Å. The bond angle of O2–Ni1–O2a is 80.61(6)°, Ni1–O2–Ni1a is 99.39(6)°. Each

dinuclear Ni 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 lengths and bond angles are in the normal range [13].

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