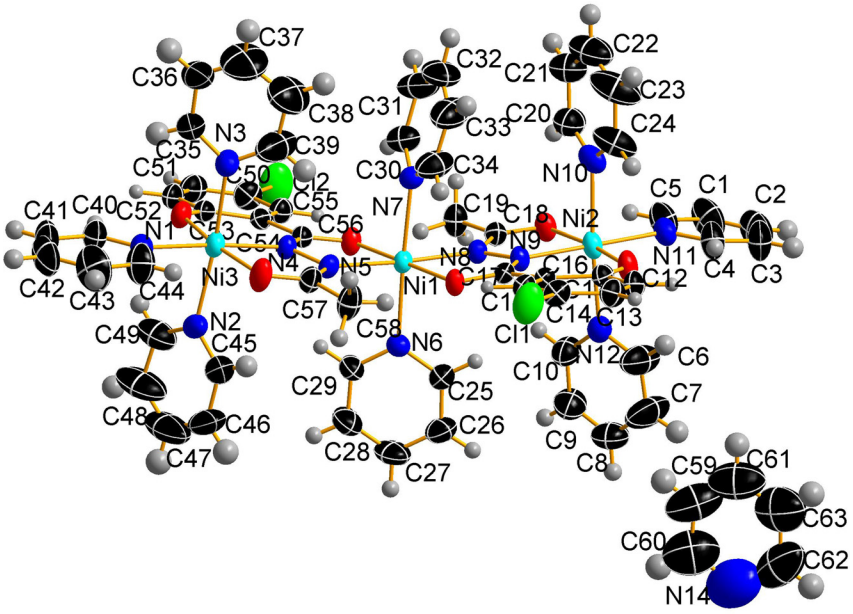
Liguo Yang*, Xin Wang, Dan Luo, Nana Liu and Dayong Tian

The crystal structure of bis(μ$_2$-5-chloro-2-oxido-*N*-(1-oxidoethylidene) benzohydrazonato-κ^5*N*,*O*,*O*′:*N*′,*O*″) hexkis(pyridine-κ^1*N*)trinickel(II) - pyridine (1/1), $C_{63}H_{57}Cl_2N_{13}Ni_3O_6$



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Abstract

$C_{63}H_{57}Cl_2N_{13}Ni_3O_6$, monoclinic, $P2_1/c$, a = 16.136(4) Å, b = 16.432(4) Å, c = 23.881(6) Å, β = 101.900(3)°, V = 6196(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0461, $wR_{ref}(F^2)$ = 0.1357, T = 298 K [1–3].

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.06 × 0.04 × 0.02 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.05 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	72,238, 10,897, 0.053
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 8298
$N(param)_{refined}$:	786
Programs:	Bruker [1], SHELX [2, 3]

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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.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.30718 (2)	0.39503 (3)	0.28225 (2)	0.03055 (12)
Ni2	0.59164 (3)	0.40468 (3)	0.39023 (2)	0.03796 (14)
Ni3	0.02977 (3)	0.33339 (3)	0.17469 (2)	0.03905 (14)
O1	−0.03985 (14)	0.30837 (16)	0.23295 (11)	0.0453 (6)
O2	0.11658 (16)	0.36264 (18)	0.12628 (10)	0.0520 (7)
O3	0.21115 (14)	0.37930 (15)	0.32435 (10)	0.0393 (6)
O4	0.40322 (13)	0.41154 (15)	0.24046 (9)	0.0360 (5)
O5	0.50154 (14)	0.39447 (15)	0.43821 (10)	0.0406 (6)
O6	0.66494 (14)	0.41634 (17)	0.33259 (11)	0.0466 (6)
N1	−0.07082 (19)	0.3139 (2)	0.10421 (14)	0.0486 (8)
N2	−0.0134 (2)	0.4601 (2)	0.17227 (16)	0.0583 (10)
N3	0.0633 (2)	0.2044 (2)	0.16906 (15)	0.0516 (8)
N4	0.13045 (16)	0.35747 (17)	0.23514 (12)	0.0334 (6)
N5	0.20385 (16)	0.37956 (17)	0.21484 (12)	0.0344 (6)
N6	0.28788 (18)	0.52543 (17)	0.28177 (12)	0.0387 (7)
N7	0.33262 (19)	0.26500 (18)	0.28403 (13)	0.0413 (7)
N8	0.41164 (16)	0.40238 (17)	0.35037 (11)	0.0326 (6)
N9	0.48748 (16)	0.40517 (17)	0.32985 (12)	0.0338 (6)
N10	0.6033 (2)	0.2706 (2)	0.38994 (13)	0.0510 (8)
N11	0.69262 (19)	0.40791 (19)	0.46179 (14)	0.0462 (8)
N12	0.58868 (19)	0.5387 (2)	0.39976 (13)	0.0458 (8)
N14	0.7383 (9)	0.9771 (6)	0.5261 (4)	0.172 (4)
Cl1	0.57028 (8)	0.38651 (9)	0.08203 (5)	0.0736 (4)
Cl2	0.04575 (9)	0.34987 (11)	0.48288 (5)	0.0868 (4)
C1	0.7353 (4)	0.4230 (4)	0.5622 (2)	0.0870 (17)
H1	0.7207	0.4226	0.5979	0.104*
C2	0.8150 (4)	0.4379 (4)	0.5575 (3)	0.098 (2)
H2	0.8563	0.4496	0.5899	0.118*
C3	0.8353 (3)	0.4355 (4)	0.5046 (3)	0.101 (2)
H3	0.8907	0.4443	0.5004	0.122*
C4	0.7715 (3)	0.4198 (3)	0.4575 (2)	0.0710 (14)
H4	0.7850	0.4176	0.4215	0.085*
C5	0.6755 (3)	0.4085 (3)	0.51376 (18)	0.0643 (12)
H5	0.6201	0.3986	0.5174	0.077*
C6	0.6535 (4)	0.5834 (3)	0.3923 (3)	0.097 (2)
H6	0.6998	0.5567	0.3832	0.116*
C7	0.6572 (4)	0.6663 (4)	0.3971 (4)	0.118 (3)
H7	0.7054	0.6944	0.3923	0.142*
C8	0.5890 (4)	0.7075 (3)	0.4090 (2)	0.0741 (14)
H8	0.5878	0.7641	0.4103	0.089*
C9	0.5239 (3)	0.6622 (3)	0.4186 (2)	0.0715 (14)
H9	0.4771	0.6873	0.4282	0.086*
C10	0.5265 (3)	0.5789 (3)	0.4141 (2)	0.0612 (12)
H10	0.4809	0.5493	0.4217	0.073*
C11	0.6387 (2)	0.4115 (2)	0.27738 (15)	0.0368 (8)
C12	0.7005 (2)	0.4125 (2)	0.24263 (17)	0.0431 (9)
H12	0.7571	0.4181	0.2605	0.052*
C13	0.6807 (2)	0.4056 (2)	0.18399 (17)	0.0459 (9)
H13	0.7232	0.4068	0.1629	0.055*
C14	0.5969 (2)	0.3968 (2)	0.15679 (15)	0.0421 (9)
C15	0.5341 (2)	0.3977 (2)	0.18755 (15)	0.0379 (8)
H15	0.4780	0.3929	0.1683	0.045*
C16	0.5519 (2)	0.4055 (2)	0.24723 (14)	0.0326 (7)
C17	0.4765 (2)	0.40798 (19)	0.27399 (14)	0.0316 (7)
C18	0.4272 (2)	0.3947 (2)	0.40645 (14)	0.0341 (8)

Table 2: (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C19	0.3542 (2)	0.3838 (3)	0.43533 (16)	0.0482 (10)
H19A	0.3551	0.3295	0.4504	0.072*
H19B	0.3022	0.3924	0.4082	0.072*
H19C	0.3585	0.4223	0.4660	0.072*
C20	0.5614 (3)	0.2236 (3)	0.4204 (2)	0.0700 (13)
H20	0.5267	0.2490	0.4417	0.084*
C21	0.5665 (4)	0.1400 (3)	0.4222 (3)	0.0897 (17)
H21	0.5367	0.1100	0.4446	0.108*
C22	0.6163 (5)	0.1021 (4)	0.3905 (3)	0.099 (2)
H22	0.6199	0.0456	0.3899	0.119*
C23	0.6608 (5)	0.1486 (4)	0.3595 (2)	0.102 (2)
H23	0.6962	0.1243	0.3382	0.122*
C24	0.6525 (4)	0.2325 (3)	0.3603 (2)	0.0794 (16)
H24	0.6829	0.2636	0.3390	0.095*
C25	0.3531 (3)	0.5769 (2)	0.29261 (18)	0.0513 (10)
H25	0.4076	0.5555	0.3002	0.062*
C26	0.3437 (3)	0.6602 (3)	0.2931 (2)	0.0628 (12)
H26	0.3908	0.6940	0.3013	0.075*
C27	0.2636 (3)	0.6920 (3)	0.2812 (2)	0.0688 (13)
H27	0.2554	0.7480	0.2804	0.083*
C28	0.1960 (3)	0.6401 (3)	0.2704 (2)	0.0679 (13)
H28	0.1410	0.6602	0.2629	0.081*
C29	0.2107 (2)	0.5574 (2)	0.27089 (18)	0.0508 (10)
H29	0.1644	0.5225	0.2632	0.061*
C30	0.3130 (3)	0.2185 (3)	0.3245 (2)	0.0643 (12)
H30	0.2784	0.2397	0.3476	0.077*
C31	0.3417 (4)	0.1395 (3)	0.3338 (2)	0.0885 (18)
H31	0.3275	0.1085	0.3630	0.106*
C32	0.3913 (4)	0.1077 (3)	0.2993 (3)	0.0870 (17)
H32	0.4099	0.0540	0.3038	0.104*
C33	0.4126 (4)	0.1549 (3)	0.2590 (3)	0.096 (2)
H33	0.4480	0.1353	0.2359	0.115*
C34	0.3816 (3)	0.2328 (3)	0.2523 (3)	0.0768 (15)
H34	0.3961	0.2647	0.2236	0.092*
C35	0.0100 (4)	0.1449 (3)	0.1628 (4)	0.128 (3)
H35	−0.0464	0.1573	0.1623	0.154*
C36	0.0304 (5)	0.0634 (4)	0.1565 (4)	0.148 (4)
H36	−0.0119	0.0240	0.1506	0.177*
C37	0.1084 (6)	0.0431 (4)	0.1591 (3)	0.125 (3)
H37	0.1223	−0.0089	0.1487	0.150*
C38	0.1715 (5)	0.1009 (4)	0.1779 (4)	0.117 (2)
H38	0.2284	0.0868	0.1890	0.140*
C39	0.1437 (4)	0.1809 (4)	0.1789 (4)	0.123 (3)
H39	0.1849	0.2213	0.1871	0.148*
C40	−0.1490 (2)	0.2981 (3)	0.1111 (2)	0.0599 (11)
H40	−0.1584	0.2933	0.1481	0.072*
C41	−0.2159 (3)	0.2888 (3)	0.0663 (3)	0.0801 (16)
H41	−0.2697	0.2776	0.0728	0.096*
C42	−0.2033 (4)	0.2960 (4)	0.0122 (3)	0.0891 (19)
H42	−0.2481	0.2903	−0.0190	0.107*
C43	−0.1228 (4)	0.3118 (4)	0.0043 (2)	0.099 (2)
H43	−0.1120	0.3165	−0.0323	0.118*
C44	−0.0589 (3)	0.3205 (3)	0.0515 (2)	0.0742 (14)
H44	−0.0046	0.3315	0.0461	0.089*
C45	0.0266 (4)	0.5210 (3)	0.1542 (3)	0.108 (2)
H45	0.0755	0.5104	0.1406	0.129*

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C46	−0.0022 (6)	0.6024 (4)	0.1548 (4)	0.148 (4)
H46	0.0286	0.6445	0.1429	0.178*
C47	−0.0733 (7)	0.6182 (5)	0.1723 (4)	0.151 (5)
H47	−0.0931	0.6713	0.1721	0.181*
C48	−0.1167 (6)	0.5569 (4)	0.1905 (3)	0.117 (3)
H48	−0.1672	0.5665	0.2025	0.141*
C49	−0.0836 (4)	0.4796 (3)	0.1906 (2)	0.0814 (16)
H49	−0.1124	0.4377	0.2046	0.098*
C50	0.0205 (3)	0.3395 (3)	0.40822 (17)	0.0511 (10)
C51	−0.0608 (3)	0.3196 (2)	0.38023 (19)	0.0528 (10)
H51	−0.1033	0.3119	0.4008	0.063*
C52	−0.0779 (2)	0.3113 (2)	0.32200 (18)	0.0460 (9)
H52	−0.1331	0.2985	0.3038	0.055*
C53	−0.0167 (2)	0.3211 (2)	0.28761 (16)	0.0375 (8)
C54	0.0666 (2)	0.3437 (2)	0.31787 (15)	0.0347 (8)
C55	0.0827 (2)	0.3518 (2)	0.37748 (16)	0.0419 (9)
H55	0.1369	0.3658	0.3968	0.050*
C56	0.1409 (2)	0.3606 (2)	0.29093 (15)	0.0324 (7)
C57	0.1883 (2)	0.3806 (2)	0.15869 (15)	0.0406 (8)
C58	0.2588 (2)	0.4047 (3)	0.13024 (17)	0.0580 (12)
H58A	0.2693	0.3617	0.1055	0.087*
H58B	0.3090	0.4148	0.1588	0.087*
H58C	0.2432	0.4532	0.1082	0.087*
C59	0.6863 (8)	0.8488 (6)	0.5177 (4)	0.142 (4)
H59	0.6393	0.8148	0.5138	0.171*
C60	0.6740 (8)	0.9273 (7)	0.5182 (4)	0.151 (4)
H60	0.6192	0.9478	0.5129	0.182*
C61	0.7589 (9)	0.8161 (6)	0.5223 (4)	0.136 (3)
H61	0.7640	0.7597	0.5220	0.163*
C62	0.8171 (9)	0.9487 (8)	0.5301 (4)	0.151 (4)
H62	0.8636	0.9832	0.5343	0.181*
C63	0.8258 (8)	0.8616 (7)	0.5275 (3)	0.148 (4)
H63	0.8788	0.8382	0.5295	0.178*

Source of material

The educt *N′*-acetyl-5-chloro-2-hydroxybenzohydrazide (LH_3), intended to be the bridging ligand in its deprotonated form was synthesized according to reference [4]. A mixture of LH_3 (0.196 g, 1 mmol) and nickel acetate (0.162 g, 1 mmol) and a few drops of a NaOH solution in 10 ml methanol was stirred at room temperature for 1 h. The mixture was filtered to remove impurties, and then left at room temperature. After a few days, red blocks of the ligand were formed. Yield (0.23 g, 60%).

Experimental details

H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5 U_{eq}(C) [3].

Comment

Pentadentate ligands have been synthesized in recent years [5]. Pentadentate ligands can react with the transition metals and rare earth metals [6, 7]. A lot of the ring structure containing complexes and metallacrown complexes have been synthesized. In recent years, our group synthesized several pentadentate ligands, the ligand L/LH_3 is one of them. The new ligand reacts with the transition metals [8].

As shown in the Figure, the title compound crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. The bond lengths of Ni–O are 2.030, 2.000, 2.035, 2.003 and 2.049 Å, the bond lengths of Ni–N are 2.081, 2.091, 2.165, 2.174, 1.976, 2.105, 2.211, 2.215, 1.978, 2.108, 2.193 and 2.198 Å, respectively, the bond lengths of Ni–N from the pyridine molecule is longer than the bond lengths of Ni–N from the anionic ligands, which are similar with the reference [8]. The trinuclear complex is almost centrosymmetric but this symmetry is not supported by the crystallographic findings. The Ni complex is formed by two chelated ligands three nickel ions and eight pyridine molecules. We can see that each nickel ion resides in a slightly distorted octahedral coordination environment, consisting of three pyridine N, a phenolate O, a carbonyl oxido O and an imine-type nitrogen of L, which construct the five-membered and six-membered rings with each nickel atom.

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

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