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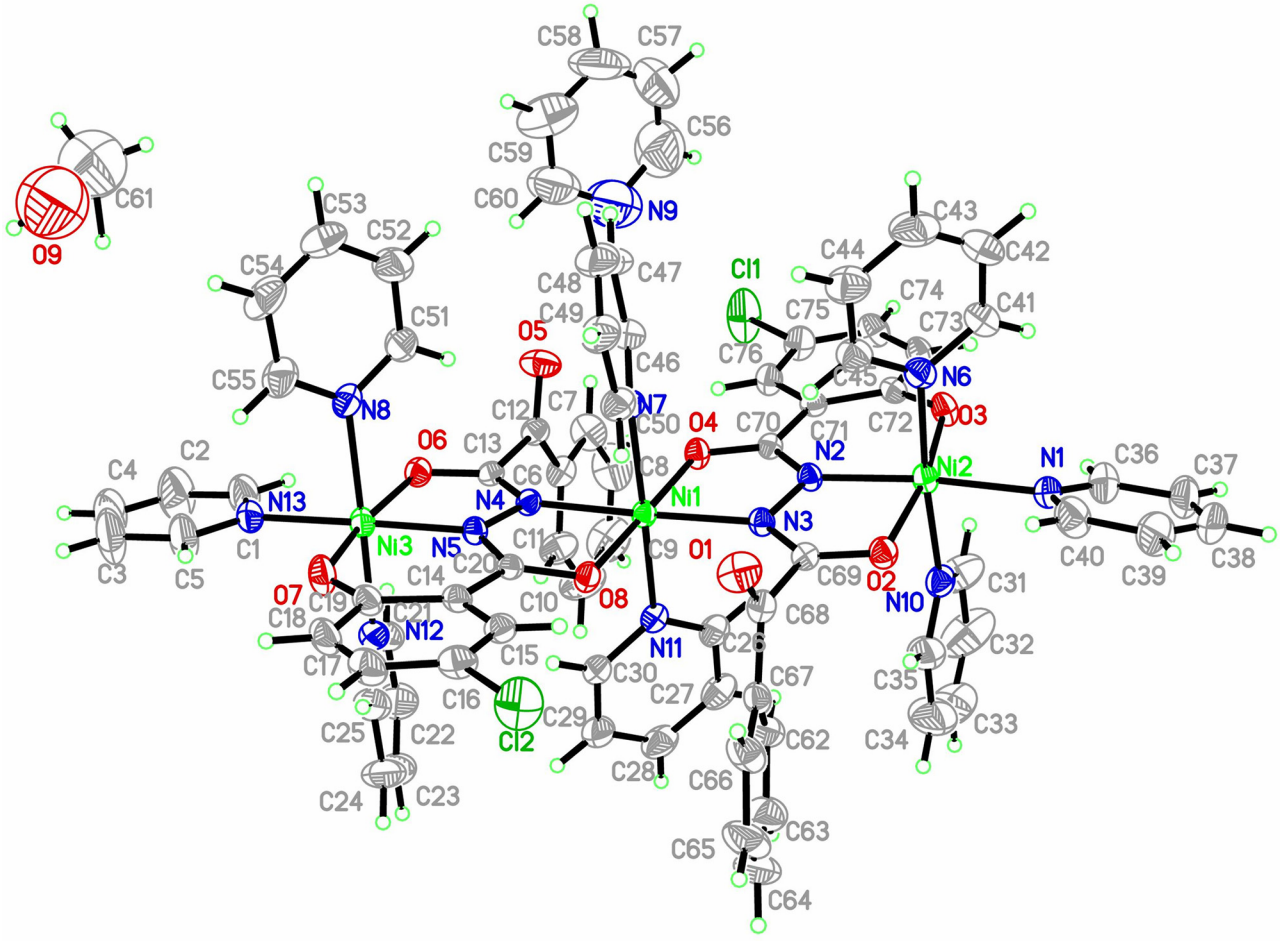
Crystal structure of bis(μ$_2$-5-chloro-2-oxido-*N*-(1-oxido-2-oxo-2-phenylethylidene)-benzohydrazonato-κ^5*N*,*O*,*O*′:*N*′,*O*″)-oktakis(pyridine-κ^1*N*)trinickel(II) – methanol – pyridine (1/1/1) $C_{76}H_{65}N_{13}Cl_2Ni_3O_9$



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Abstract

$C_{76}H_{65}N_{13}Cl_2Ni_3O_9$, monoclinic, $P2_1/n$, a = 15.937(4) Å, b = 16.805(4) Å, c = 27.463(7) Å, β = 94.613(3)°, V = 7332(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0490, $wR_{ref}(F^2)$ = 0.1596, T = 298 K.

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The crystal 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 1: Data collection and handling.

Crystal:	Red block
Size:	0.17 × 0.12 × 0.08 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.90 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	27.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	78367, 16866, 0.041
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 11675
$N(param)_{refined}$:	928
Programs:	Bruker programs [1], SHELX [2, 3]

Source of material

The ligand was synthesized from the reaction of benzoyl hydrazine (100 mg, 0.60 mmol) and benzoate (50 mg, 0.60 mmol) according to the procedure reported earlier [4]. Yield (0.020 g, 60%).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5\ U_{eq}(C)$.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.57840 (2)	0.26476 (2)	0.38038 (2)	0.03263 (10)
Cl1	0.48043 (7)	0.31827 (11)	0.12749 (4)	0.1068 (5)
O1	0.76547 (18)	0.32019 (16)	0.48243 (9)	0.0661 (7)
N1	0.96745 (16)	0.34201 (16)	0.30767 (10)	0.0451 (6)
C1	0.1390 (2)	0.1977 (3)	0.41881 (16)	0.0776 (13)
H1	0.1611	0.2011	0.3885	0.093*
Ni2	0.83732 (2)	0.32671 (2)	0.31229 (2)	0.03728 (11)
Cl2	0.67252 (8)	0.26969 (9)	0.63572 (4)	0.0850 (4)
O2	0.84896 (12)	0.29712 (13)	0.38655 (7)	0.0428 (5)
N2	0.71812 (14)	0.30550 (14)	0.32390 (8)	0.0331 (5)
C2	0.0556 (3)	0.1781 (4)	0.4200 (2)	0.114 (2)
H2	0.0228	0.1673	0.3912	0.137*
Ni3	0.31677 (2)	0.23389 (2)	0.45099 (2)	0.04128 (11)
O3	0.80597 (13)	0.35326 (14)	0.24237 (7)	0.0461 (5)
N3	0.70463 (14)	0.28382 (14)	0.37274 (8)	0.0339 (5)
C3	0.0221 (3)	0.1747 (4)	0.4632 (2)	0.111 (2)
H3	−0.0344	0.1623	0.4648	0.133*
O4	0.57639 (12)	0.28586 (13)	0.30787 (7)	0.0392 (5)
N4	0.45166 (14)	0.25054 (13)	0.38845 (8)	0.0324 (5)
C4	0.0716 (3)	0.1894 (5)	0.5039 (2)	0.119 (2)
H4	0.0497	0.1877	0.5343	0.142*
O5	0.36931 (19)	0.32895 (15)	0.29200 (9)	0.0650 (7)
N5	0.43664 (15)	0.24795 (14)	0.43871 (8)	0.0343 (5)
C5	0.1562 (3)	0.2071 (4)	0.50020 (16)	0.0871 (15)
H5	0.1907	0.2159	0.5287	0.105*
O6	0.30644 (12)	0.23896 (13)	0.37511 (7)	0.0411 (5)
N6	0.82958 (17)	0.45276 (16)	0.33275 (9)	0.0457 (6)
C6	0.38798 (19)	0.1942 (2)	0.27219 (11)	0.0457 (7)
N7	0.56249 (16)	0.39070 (15)	0.39421 (9)	0.0426 (6)
O7	0.34524 (15)	0.23180 (16)	0.52280 (8)	0.0568 (6)
C7	0.3755 (3)	0.2069 (3)	0.22198 (13)	0.0672 (10)
H7	0.3625	0.2577	0.2102	0.081*
N8	0.29200 (17)	0.36276 (17)	0.45093 (10)	0.0494 (6)
O8	0.58011 (12)	0.24454 (12)	0.45332 (7)	0.0383 (4)
C8	0.3822 (3)	0.1455 (4)	0.18979 (16)	0.0930 (16)
H8	0.3746	0.1548	0.1563	0.112*
N9	0.3786 (6)	0.4744 (5)	0.2181 (3)	0.179 (3)
C9	0.4000 (4)	0.0706 (4)	0.2069 (2)	0.1001 (17)
H9	0.4039	0.0290	0.1849	0.120*
O9	0.0262 (5)	0.5537 (5)	0.5280 (3)	0.236 (3)
H9C	−0.0109	0.5227	0.5348	0.354*
C10	0.4123 (3)	0.0556 (3)	0.2565 (2)	0.0926 (16)
H10	0.4240	0.0043	0.2678	0.111*
N10	0.85686 (16)	0.20157 (17)	0.29187 (11)	0.0488 (6)
C11	0.4071 (3)	0.1184 (2)	0.28947 (15)	0.0647 (10)
H11	0.4164	0.1093	0.3229	0.078*
N11	0.59065 (15)	0.13856 (15)	0.36634 (9)	0.0396 (5)
C13	0.38073 (18)	0.24715 (16)	0.36093 (10)	0.0344 (6)
N13	0.18932 (17)	0.21193 (18)	0.45791 (11)	0.0528 (7)
C12	0.38180 (19)	0.26154 (19)	0.30631 (11)	0.0401 (6)
N12	0.33098 (17)	0.10332 (17)	0.44434 (11)	0.0515 (7)
C14	0.49781 (19)	0.24723 (17)	0.52215 (10)	0.0373 (6)
C15	0.5734 (2)	0.25677 (18)	0.55108 (11)	0.0421 (7)
H15	0.6234	0.2619	0.5361	0.051*
C16	0.5754 (2)	0.2587 (2)	0.60129 (11)	0.0501 (8)
C17	0.5022 (3)	0.2505 (2)	0.62461 (12)	0.0575 (9)
H17	0.5038	0.2514	0.6585	0.069*
C18	0.4274 (2)	0.2410 (2)	0.59724 (12)	0.0556 (9)
H18	0.3788	0.2347	0.6134	0.067*
C19	0.4200 (2)	0.24027 (19)	0.54488 (11)	0.0444 (7)
C20	0.50583 (17)	0.24621 (16)	0.46825 (10)	0.0324 (6)
C21	0.3062 (3)	0.0655 (2)	0.40349 (16)	0.0654 (10)
H21	0.2793	0.0946	0.3780	0.078*
C22	0.3183 (3)	−0.0146 (3)	0.3967 (2)	0.0858 (14)
H22	0.3005	−0.0386	0.3671	0.103*
C23	0.3563 (3)	−0.0583 (3)	0.4337 (2)	0.0906 (15)
H23	0.3641	−0.1128	0.4302	0.109*
C24	0.3825 (3)	−0.0208 (3)	0.4759 (2)	0.0881 (15)
H24	0.4096	−0.0493	0.5016	0.106*
C25	0.3687 (2)	0.0604 (2)	0.48046 (17)	0.0698 (11)
H25	0.3864	0.0856	0.5097	0.084*
C26	0.6347 (2)	0.1100 (2)	0.33113 (12)	0.0502 (8)
H26	0.6642	0.1459	0.3131	0.060*
C28	0.5955 (2)	−0.0235 (2)	0.34638 (17)	0.0701 (11)
H28	0.5965	−0.0776	0.3394	0.084*
C27	0.6393 (3)	0.0302 (2)	0.31987 (14)	0.0643 (10)
H27	0.6711	0.0129	0.2950	0.077*
C29	0.5509 (2)	0.0051 (2)	0.38314 (17)	0.0696 (11)
H29	0.5214	−0.0295	0.4020	0.083*
C30	0.5501 (2)	0.0852 (2)	0.39186 (13)	0.0511 (8)
H30	0.5195	0.1036	0.4170	0.061*
C31	0.8508 (3)	0.1767 (3)	0.24590 (17)	0.0850 (14)
H31	0.8391	0.2142	0.2213	0.102*
C32	0.8609 (4)	0.0983 (4)	0.2324 (3)	0.120 (2)
H32	0.8575	0.0832	0.1998	0.144*
C33	0.8760 (4)	0.0434 (3)	0.2693 (3)	0.126 (3)

Table 2: (continued)

	x	y	z	U_{iso}*/U_{eq}
H33	0.8814	−0.0103	0.2619	0.151*
C34	0.8830 (4)	0.0677 (3)	0.3155 (3)	0.116 (2)
H34	0.8952	0.0316	0.3408	0.139*
C35	0.8721 (3)	0.1462 (2)	0.32525 (18)	0.0758 (12)
H35	0.8757	0.1618	0.3578	0.091*
C36	1.0032 (2)	0.3342 (2)	0.26566 (14)	0.0617 (10)
H36	0.9686	0.3255	0.2373	0.074*
C37	1.0884 (3)	0.3383 (3)	0.2622 (2)	0.0800 (13)
H37	1.1108	0.3331	0.2321	0.096*
C38	1.1401 (3)	0.3503 (3)	0.3040 (2)	0.0881 (15)
H38	1.1982	0.3528	0.3028	0.106*
C39	1.1046 (3)	0.3585 (3)	0.3471 (2)	0.0884 (15)
H39	1.1382	0.3668	0.3759	0.106*
C40	1.0182 (2)	0.3544 (3)	0.34761 (15)	0.0693 (11)
H40	0.9946	0.3605	0.3773	0.083*
C41	0.8741 (3)	0.5083 (2)	0.31126 (15)	0.0631 (10)
H41	0.9101	0.4917	0.2882	0.076*
C42	0.8700 (3)	0.5882 (3)	0.3212 (2)	0.0851 (14)
H42	0.9019	0.6245	0.3050	0.102*
C43	0.8184 (3)	0.6134 (3)	0.3553 (2)	0.0866 (14)
H43	0.8147	0.6671	0.3631	0.104*
C44	0.7716 (3)	0.5574 (3)	0.37818 (16)	0.0736 (11)
H44	0.7356	0.5728	0.4015	0.088*
C45	0.7791 (2)	0.4789 (2)	0.36584 (13)	0.0563 (9)
H45	0.7473	0.4417	0.3814	0.068*
C46	0.5251 (2)	0.4385 (2)	0.36033 (13)	0.0553 (8)
H46	0.5102	0.4180	0.3294	0.066*
C47	0.5078 (3)	0.5176 (2)	0.36945 (17)	0.0719 (11)
H47	0.4816	0.5495	0.3451	0.086*
C48	0.5297 (3)	0.5479 (2)	0.41478 (19)	0.0774 (12)
H48	0.5178	0.6006	0.4218	0.093*
C49	0.5694 (3)	0.5000 (2)	0.45000 (16)	0.0655 (10)
H49	0.5852	0.5197	0.4811	0.079*
C50	0.5850 (2)	0.4229 (2)	0.43813 (13)	0.0516 (8)
H50	0.6128	0.3907	0.4618	0.062*
C51	0.3181 (3)	0.4109 (2)	0.41701 (15)	0.0650 (10)
H51	0.3510	0.3892	0.3939	0.078*
C52	0.2999 (3)	0.4900 (2)	0.41382 (17)	0.0758 (12)
H52	0.3197	0.5207	0.3890	0.091*
C53	0.2526 (3)	0.5238 (3)	0.44738 (18)	0.0796 (13)
H53	0.2387	0.5775	0.4457	0.096*
C54	0.2257 (3)	0.4763 (3)	0.48373 (18)	0.0875 (15)
H54	0.1941	0.4973	0.5077	0.105*
C55	0.2468 (3)	0.3967 (3)	0.48392 (14)	0.0717 (11)
H55	0.2284	0.3648	0.5086	0.086*
C56	0.4011 (6)	0.5255 (8)	0.1837 (3)	0.164 (3)
H56	0.4207	0.5064	0.1549	0.197*
C57	0.3952 (6)	0.6013 (9)	0.1908 (4)	0.194 (6)
H57	0.4259	0.6365	0.1731	0.233*
C58	0.3503 (7)	0.6263 (5)	0.2202 (6)	0.201 (6)
H58	0.3326	0.6790	0.2180	0.242*
C59	0.3244 (5)	0.5803 (5)	0.2566 (3)	0.143 (3)
H59	0.2993	0.6025	0.2828	0.171*
C60	0.3359 (6)	0.5039 (5)	0.2537 (3)	0.151 (3)
H60	0.3142	0.4700	0.2763	0.181*
C61	0.0062 (7)	0.5620 (7)	0.4726 (4)	0.222 (4)

Table 2: (continued)

	x	y	z	U_{iso}*/U_{eq}
H61A	−0.0425	0.5953	0.4665	0.334*
H61B	−0.0045	0.5109	0.4578	0.334*
H61C	0.0536	0.5863	0.4590	0.334*
C62	0.7834 (2)	0.1190 (2)	0.44030 (13)	0.0563 (9)
H62	0.7638	0.1269	0.4078	0.068*
C63	0.8043 (3)	0.0431 (3)	0.45651 (18)	0.0789 (12)
H63	0.7980	0.0002	0.4351	0.095*
C64	0.8340 (3)	0.0312 (3)	0.5037 (2)	0.0934 (16)
H64	0.8495	−0.0197	0.5143	0.112*
C65	0.8413 (3)	0.0930 (3)	0.53541 (18)	0.0909 (16)
H65	0.8609	0.0841	0.5678	0.109*
C66	0.8198 (2)	0.1692 (3)	0.52009 (13)	0.0666 (11)
H66	0.8244	0.2112	0.5422	0.080*
C67	0.79125 (18)	0.1828 (2)	0.47167 (11)	0.0436 (7)
C68	0.77291 (18)	0.26548 (19)	0.45476 (10)	0.0407 (7)
C69	0.77531 (17)	0.28291 (17)	0.40020 (10)	0.0341 (6)
C70	0.64904 (17)	0.30409 (17)	0.29423 (9)	0.0330 (6)
C71	0.65591 (18)	0.32185 (17)	0.24138 (9)	0.0344 (6)
C72	0.73149 (18)	0.34339 (17)	0.21996 (10)	0.0370 (6)
C73	0.7230 (2)	0.3544 (2)	0.16815 (11)	0.0469 (7)
H73	0.7710	0.3669	0.1525	0.056*
C74	0.6486 (2)	0.3475 (2)	0.14038 (11)	0.0544 (9)
H74	0.6462	0.3559	0.1068	0.065*
C75	0.5769 (2)	0.3279 (2)	0.16269 (11)	0.0553 (9)
C76	0.5805 (2)	0.3146 (2)	0.21218 (10)	0.0455 (7)
H76	0.5317	0.3006	0.2265	0.055*

The N-bound H atoms were located in a difference Fourier map but were refined with a distance restraint of N—H = 0.88 ± 0.01 Å, and with U_{iso}(H) set to 1.2 U_{equiv}(N) [1–3].

Discussion

Aldooxime and acyl compounds both containing multiple O and N atoms can participate in coordination, so the coordination ability of them are very strong, then they can show diversity in their coordination forms. A part of the multinuclear complexes have been one of the research hotspots in recent years [4–7]. A lot of multinuclear metal complexes with aldooxime and acyl compounds have been reported. In this paper, a three nuclear Ni complex is reported.

The title complex is composed of three Ni atoms, two acylhydrazine ligands, nine pyridines and one methanol molecule. It is the first trinuclear Ni complex with this specific salycilate ligand. The coordination geometry of three Ni atoms is octahedral. The Ni1 atoms is bound to two carbonyl oxygens, two hydrazine nitrogens of two ligands and two nitrogens of pyridines. The bond lengths of Ni1–O are 2.020 and 2.029 Å, which are similar to the corresponding values

of the reference [7–10]. For the Ni2 and Ni3 atoms, the octahedral geometry is realized with one carbonyl oxygen atom, one phenolate oxygen atom, one hydrazine nitrogen of ligand and three pyridine nitrogen atoms. The average bond distances of Ni–N and Ni–O for Ni2 and Ni3 are 2.123 and 2.039 Å, which is shorter than the distances of Ni1 atoms. This difference may be attributed to the difference in stereochemistry between the central and terminal Ni atoms. The neighboring Ni–Ni interatomic distances are 4.766 and 4.780 Å, respectively [10].

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

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