Wang Xin, Yang Liguo*, Dong Yizhuo, Ye Yanlin and Wang Yifan

The crystal structure of bis(μ_2-5-chloro-2-oxido-*N*-(1-oxidopropylidene)benzohydrazonato-κ^5*N*,*O*,*O*′:*N*′,*O*′′)-octakis(pyridine-κ^1*N*)trinickel(II) $C_{60}H_{56}Cl_2N_{12}Ni_3O_6$

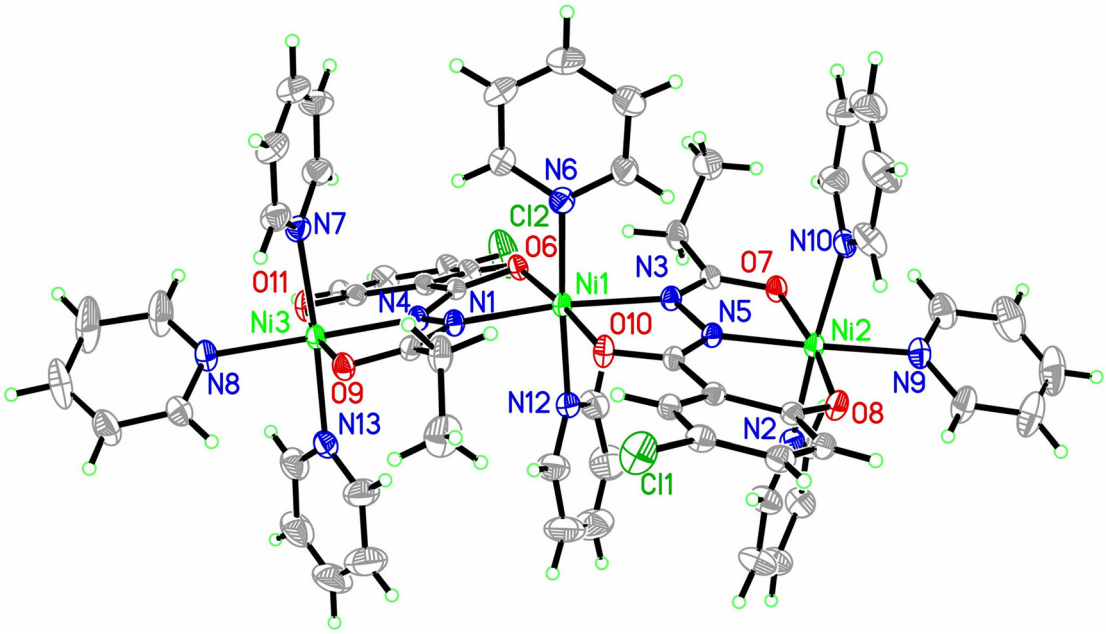

Figure 1: The crystal structure of complex 1.

https://doi.org/10.1515/ncrs-2022-0023
Received January 16, 2022; accepted April 5, 2022;
published online April 25, 2022

Abstract

$C_{60}H_{56}Cl_2N_{12}Ni_3O_6$, triclinic, $P\bar{1}$ (no. 2), a = 12.684(5) Å, b = 12.827(5) Å, c = 19.100(7) Å, α = 84.641(4)°, β = 81.178(4)°, γ = 85.471(4)°, V = 3050.7(19) Å^3, Z = 2, $R_{gt}(F)$ = 0.0267, $wR_{ref}(F^2)$ = 0.0735, T = 298 K.

CCDC no.: 2164555

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 1: Data collection and handling.

Crystal:	Red block
Size:	0.16 × 0.10 × 0.08 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.06 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}:	36,535, 10710, 0.018
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 9545
$N(param)_{refined}$:	750
Programs:	Bruker [1], SHELX [2, 3]

Source of material

The ligand was synthesized from the reaction of 5-chloride-Salicylate hydrazazine (80 mg, 0.60 mmol) and methyl

***Corresponding author: Yang Liguo**, College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P. R. China, E-mail: lgyang@ayit.edu.cn.
https://orcid.org/0000-0003-4899-8298
Wang Xin, Dong Yizhuo, Ye Yanlin and Wang Yifan, College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P. R. China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.76551 (2)	0.46264 (2)	0.23100 (2)	0.02833 (6)
Ni2	0.45812 (2)	0.26706 (2)	0.31169 (2)	0.03122 (7)
Ni3	1.01724 (2)	0.72588 (2)	0.20044 (2)	0.03256 (7)
Cl1	0.88114 (5)	0.13772 (5)	0.53246 (3)	0.06341 (17)
Cl2	0.59538 (7)	0.85341 (6)	−0.01967 (5)	0.0953 (3)
N1	0.89806 (11)	0.54340 (11)	0.23924 (8)	0.0308 (3)
N2	0.38247 (12)	0.40627 (12)	0.35996 (8)	0.0367 (3)
N3	0.62356 (11)	0.38829 (11)	0.23214 (7)	0.0297 (3)
N4	0.89672 (11)	0.63883 (11)	0.19541 (7)	0.0293 (3)
N5	0.60039 (11)	0.32498 (11)	0.29694 (7)	0.0289 (3)
N6	0.85804 (12)	0.34286 (12)	0.17275 (8)	0.0372 (3)
N7	1.12266 (12)	0.62260 (13)	0.13038 (8)	0.0401 (4)
N8	1.15139 (13)	0.80751 (13)	0.20925 (9)	0.0438 (4)
N9	0.30416 (13)	0.21186 (13)	0.32035 (9)	0.0441 (4)
N10	0.52311 (13)	0.12369 (12)	0.26087 (9)	0.0405 (4)
N12	0.66354 (13)	0.58058 (13)	0.28825 (9)	0.0409 (4)
N13	0.92531 (14)	0.82797 (14)	0.27546 (10)	0.0474 (4)
O6	0.76995 (10)	0.56861 (9)	0.14347 (6)	0.0320 (3)
O7	0.45727 (9)	0.34612 (10)	0.21283 (6)	0.0349 (3)
O8	0.48111 (10)	0.20025 (11)	0.40821 (7)	0.0393 (3)
O9	1.03615 (10)	0.61286 (10)	0.28161 (6)	0.0361 (3)
O10	0.76214 (10)	0.36722 (10)	0.32171 (7)	0.0386 (3)
O11	0.98113 (11)	0.82310 (11)	0.11870 (7)	0.0429 (3)
C1	0.57234 (14)	0.19073 (13)	0.43283 (9)	0.0309 (4)
C2	0.66584 (14)	0.24471 (13)	0.40306 (9)	0.0292 (4)
C3	0.58119 (16)	0.12104 (14)	0.49447 (9)	0.0364 (4)
H3	0.5217	0.0853	0.5152	0.044*
C4	0.76175 (15)	0.15820 (15)	0.49530 (10)	0.0373 (4)
C5	0.73030 (15)	0.75367 (14)	0.06627 (10)	0.0366 (4)
H5	0.6836	0.7001	0.0723	0.044*
C6	0.82972 (13)	0.64325 (13)	0.14900 (9)	0.0273 (3)
C7	0.54547 (14)	0.39128 (13)	0.19358 (9)	0.0313 (4)
C8	0.67302 (16)	0.10383 (15)	0.52503 (10)	0.0396 (4)
H8	0.6757	0.0567	0.5649	0.048*
C9	0.67648 (13)	0.31774 (13)	0.33722 (9)	0.0289 (4)
C10	0.86523 (16)	0.91447 (14)	0.04736 (10)	0.0385 (4)
H10	0.9098	0.9699	0.0409	0.046*
C11	0.81982 (14)	0.74210 (13)	0.10171 (9)	0.0288 (4)
C12	0.89252 (14)	0.82477 (14)	0.09182 (9)	0.0319 (4)
C13	0.56197 (17)	0.44861 (17)	0.12060 (10)	0.0434 (5)
H13A	0.6302	0.4802	0.1132	0.052*
H13B	0.5064	0.5046	0.1177	0.052*
C14	0.97325 (14)	0.53890 (14)	0.28056 (9)	0.0326 (4)
C15	0.98858 (17)	0.44021 (17)	0.32848 (11)	0.0479 (5)
H15A	1.0616	0.4113	0.3175	0.058*
H15B	0.9416	0.3888	0.3189	0.058*
C16	0.81866 (19)	0.24940 (17)	0.17101 (13)	0.0571 (6)
H16	0.7505	0.2384	0.1952	0.069*
C17	0.24588 (18)	0.54586 (18)	0.36465 (13)	0.0536 (6)
H17	0.1904	0.5823	0.3442	0.064*
C18	0.30218 (16)	0.46192 (16)	0.33357 (11)	0.0452 (5)
H18	0.2831	0.4428	0.2917	0.054*
C19	0.77668 (18)	0.92415 (16)	0.01328 (11)	0.0465 (5)
H19	0.7621	0.9844	−0.0156	0.056*
C20	1.25779 (18)	0.4809 (2)	0.11957 (13)	0.0583 (6)

Table 2: (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
H20	1.3094	0.4380	0.1400	0.070*
C21	0.40948 (18)	0.43660 (18)	0.41901 (12)	0.0509 (5)
H21	0.4664	0.4001	0.4378	0.061*
C22	0.3571 (2)	0.5196 (2)	0.45379 (13)	0.0649 (7)
H22	0.3782	0.5381	0.4952	0.078*
C23	1.10556 (18)	0.60958 (19)	0.06449 (11)	0.0516 (5)
H23	1.0537	0.6534	0.0450	0.062*
C24	0.70962 (17)	0.84219 (16)	0.02279 (11)	0.0465 (5)
C25	1.1618 (2)	0.5336 (2)	0.02395 (13)	0.0663 (7)
H25	1.1478	0.5268	−0.0217	0.080*
C26	1.19850 (16)	0.55869 (18)	0.15619 (11)	0.0497 (5)
H26	1.2121	0.5672	0.2017	0.060*
C27	0.8735 (2)	0.1693 (2)	0.13546 (16)	0.0757 (8)
H27	0.8427	0.1058	0.1356	0.091*
C28	0.2732 (2)	0.57477 (19)	0.42637 (13)	0.0602 (6)
H28	0.2359	0.6304	0.4492	0.072*
C29	0.5598 (2)	0.3764 (2)	0.06248 (12)	0.0665 (7)
H29A	0.6190	0.3249	0.0622	0.100*
H29B	0.5650	0.4168	0.0173	0.100*
H29C	0.4941	0.3419	0.0711	0.100*
C30	1.2386 (2)	0.4687 (2)	0.05214 (14)	0.0650 (7)
H30	1.2771	0.4170	0.0259	0.078*
C31	0.95561 (17)	0.35554 (18)	0.13756 (11)	0.0502 (5)
H31	0.9849	0.4197	0.1377	0.060*
C32	0.9740 (2)	0.1837 (2)	0.09972 (16)	0.0770 (8)
H32	1.0129	0.1304	0.0753	0.092*
C33	1.0156 (2)	0.2781 (2)	0.10076 (14)	0.0691 (7)
H33	1.0837	0.2904	0.0769	0.083*
C34	0.9656 (2)	0.4590 (3)	0.40697 (13)	0.0797 (9)
H34A	1.0043	0.5167	0.4156	0.120*
H34B	0.9876	0.3970	0.4347	0.120*
H34C	0.8904	0.4750	0.4202	0.120*
C35	0.8807 (2)	0.7914 (2)	0.33917 (14)	0.0722 (7)
H35	0.8869	0.7195	0.3513	0.087*
C36	0.6724 (2)	0.6025 (2)	0.35342 (12)	0.0614 (6)
H36	0.7297	0.5713	0.3745	0.074*
C37	0.5406 (2)	0.12204 (18)	0.18996 (12)	0.0566 (6)
H37	0.5175	0.1808	0.1627	0.068*
C38	1.17862 (18)	0.82120 (18)	0.27182 (12)	0.0519 (5)
H38	1.1381	0.7912	0.3123	0.062*
C39	0.6092 (2)	−0.0485 (2)	0.26670 (17)	0.0745 (7)
H39	0.6322	−0.1068	0.2945	0.089*
C40	0.6272 (2)	−0.0472 (2)	0.19423 (18)	0.0754 (8)
H40	0.6635	−0.1038	0.1720	0.090*
C41	0.58030 (18)	0.62648 (17)	0.25975 (13)	0.0545 (6)
H41	0.5741	0.6133	0.2135	0.065*
C42	0.2543 (2)	0.2084 (2)	0.26458 (15)	0.0649 (7)
H42	0.2898	0.2274	0.2194	0.078*
C43	0.25135 (19)	0.1825 (2)	0.38400 (14)	0.0639 (7)
H43	0.2855	0.1840	0.4236	0.077*
C44	1.3221 (2)	0.9219 (2)	0.2214 (2)	0.0878 (10)
H44	1.3778	0.9629	0.2256	0.105*
C45	1.2627 (2)	0.8768 (2)	0.28046 (16)	0.0722 (8)
H45	1.2790	0.8838	0.3256	0.087*
C46	0.5559 (2)	0.03831 (17)	0.29872 (14)	0.0591 (6)
H46	0.5431	0.0363	0.3481	0.071*

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C47	0.5033 (2)	0.6921 (2)	0.29470 (18)	0.0809 (9)
H47	0.4455	0.7208	0.2731	0.097*
C48	0.0987 (2)	0.1478 (3)	0.3376 (2)	0.0997 (12)
H48	0.0292	0.1267	0.3433	0.120*
C49	0.5909 (2)	0.0386 (2)	0.15531 (16)	0.0746 (8)
H49	0.6000	0.0407	0.1060	0.090*
C50	0.8604 (2)	1.0001 (2)	0.3060 (2)	0.0828 (9)
H50	0.8547	1.0717	0.2929	0.099*
C51	0.9145 (2)	0.93162 (19)	0.25926 (15)	0.0623 (6)
H51	0.9448	0.9587	0.2145	0.075*
C52	0.5989 (3)	0.6706 (3)	0.39175 (15)	0.0884 (10)
H52	0.6080	0.6860	0.4370	0.106*
C53	0.8251 (3)	0.8555 (3)	0.38886 (17)	0.0985 (11)
H53	0.7949	0.8271	0.4333	0.118*
C54	0.8156 (3)	0.9613 (3)	0.3714 (2)	0.0948 (11)
H54	0.7790	1.0061	0.4038	0.114*
C55	0.1497 (2)	0.1501 (3)	0.3941 (2)	0.0905 (10)
H55	0.1161	0.1299	0.4396	0.109*
C56	0.1508 (3)	0.1771 (3)	0.2717 (2)	0.0951 (11)
H56	0.1172	0.1761	0.2318	0.114*
C57	0.5132 (3)	0.7140 (3)	0.3613 (2)	0.0941 (11)
H57	0.4621	0.7583	0.3860	0.113*
C58	1.2111 (2)	0.8490 (3)	0.15190 (15)	0.0834 (10)
H58	1.1935	0.8398	0.1075	0.100*
C59	1.2984 (3)	0.9056 (3)	0.15538 (19)	0.1081 (14)
H59	1.3401	0.9319	0.1141	0.130*
C60	0.75782 (14)	0.22719 (14)	0.43608 (9)	0.0331 (4)
H60	0.8179	0.2633	0.4173	0.040*

propionate (50 mg, 0.60 mmol) according to the procedure reported earlier [4]. Yield (0.012 g, 70%).

Experimental details

The 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).

Comment

Ligand choice plays a crucial role in the course of exploring polynuclear heterometallic complexes with the desired properties. For this purpose, various ligands have been developed. Among the wealth of ligands used in the preparation of such complexes, a prominent position is occupied by multidentate Schiff base ligands. Many ligands can form multinuclear metal complexes, but Schiff-based ligands are better applicants as they own versatile structures. Depending on the structures of their metal complexes with Schiff base ligands they are similar with that of some biological systems. So the Schiff base ligand is important for the development of coordination chemistry. In the following account, we synthesized a new Schiff base strating material: (*E*)-5-chloro-2-hydroxy-N-((*E*)-1-hydroxypropylidene)benzohydrazonic acid. The similar complexes have been reported [4–7].

As shown in Figure 1, the title compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The title complex is composed of three Ni atoms, two Schiff base ligans and six pyridines. It is the first trinuclear Ni complex with the 5-chloro-2-oxido-*N*-(1-oxidopropylidene)benzohydrazonato ligand. The coordination geometry of the three Ni atoms is octahedral. The Ni1 atoms is bound to two oxygens, two nitrogens of two ligands and two nitrogens atoms of pyridine ligands. The bond lengths of Ni1–O are 2.0228 and 2.0504 Å, the bond length of Ni1–N are 2.0764, 2.0993, 2.1471 and 2.1734 Å, which are similar to the corresponding values of the reference. For two equivalent Ni2 and Ni3 atoms, the octahedral geometry is realized with oxygen, nitrogen, and pyridine nitrogen atoms. The average bond distances of Ni–N and Ni–O for Ni2 and Ni3 are 2.1147, 2.1144, 2.0357 and 2.0209 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 4.764 and 4.780 Å, respectively, which are longer than those in related complexes [8, 9].

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This study was supported by the Nature Science Foundation of Henan Province (202300410010), and the foundation of Anyang Institute of Technology (YPY2020025).

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

References

1. Sheldrick G. M. *SMART* and *SAINT* for Windows NT Software Reference Manuals (version 5.0); Bruker Analytical X-Ray Systems: Madison, WI, 1997.
2. Sheldrick G. M. *SADABS*, A Software for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, 1997.
3. Sheldrick G. M. *SHELXL* Reference Manual (version 5.1); Bruker Analytical X-Ray Systems: Madison, WI, 1997.
4. Lin S., Yang M. X., Liu S. X. Three novel trinuclear zinc(II)/nickel(II) complexes with pentadentate ligands N-nitrogenzoylsalicylhydrazidate. *Polyhedron* 2007, *26*, 4793–4798.

5. Yang M. X., Lin S., Chen L. J., Liu S. X. Synthesis and crystal structure of the trinuclear nickel(II) complex with Schiff base ligand N-butylsalicylhydrazide. *Chin. J. Inorg. Chem.* 2003, *19*, 433–436.
6. Wu Q. J., Chen X. H., Cai B. Q., Wu D. Synthesis and crystal structure of trinuclear nickel(II) complex with N-acetylsalicyhydrazide and imidazole ligands. *Chin. J. Inorg. Chem.* 2012, *28*, 2650–2654.
7. Yang L. G., Wang X., Luo D., Liu N. N., Tian D. Y. The crystal structure of bis(5-chloro-2-oxido-*N*-(1-oxidoethylidene)benzohydrazonato) hexkis(pyridine)trinickel(II)-pyridine, $C_{63}H_{57}Cl_2N_{13}Ni_3O_6$. *Z. Kristallogr. NCS* 2021, *236*, 487–490.
8. Chen X. H., Liu S. X. Syntheses and crystal structures of two nickel complexes with *N*-substituted-salicyl ligand. *Chin. J. Inorg. Chem.* 2005, *21*, 15–260.
9. Yang M. X., Lin S. Bis(dimethylformamide-2κ*O*)dipyridine-1κ*N*,3κ*N*-bis(2′-salicylbenzohydrazidato)-1κ^3*O*,*N*, *O*′:2κ^2*N*,*O*″; 2κ^2*N*, *O*″:3κ^3*O*,*N*,*O*′-trinickel(II) dimethylformamide disolvate hemihydrate. *Acta Crystallogr.* 2005, *E61*, m1095–m1096.