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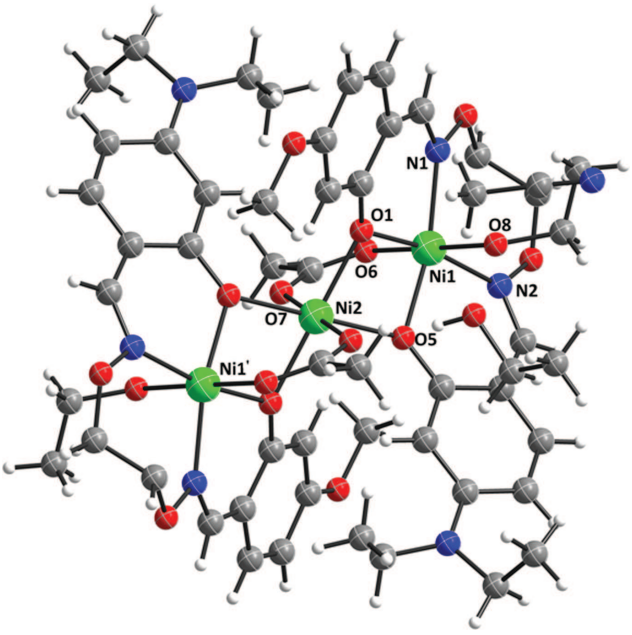
Synthesis and crystal structure of bis(μ_2-acetato-κ^2*O*:*O*′)-di(ethanol)-bis{μ_2-5-(*N*,*N*′-diethylamine)-5′-methoxyl-2,2′-[ethylenediyldioxybis(nitrilomethylidyne)]diphenolato-κ^6*O*:*O*,*N*,*N*,*O*′:*O*′}trinickel(II) – ethanol – acetonitrile (1/2/2), $C_{58}H_{86}Ni_3N_8O_{18}$



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Abstract

$C_{58}H_{86}Ni_3N_8O_{18}$, triclinic, $P\bar{1}$ (no. 2), $a = 11.4561(8)$ Å, $b = 13.1859(8)$ Å, $c = 13.5063(11)$ Å, $\alpha = 109.620(7)°$, $\beta = 101.234(7)°$, $\gamma = 114.469(6)°$, $V = 1611.1(2)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0518$, $wR_{ref}(F^2) = 0.1315$, $T = 173.69(10)$ K.

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The crystal structure is shown in the figure. Not coordinated solvent molecules are omitted for clarity. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Block, clear light green
Size:	0.29 × 0.26 × 0.25 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.94 mm^{-1}
Diffractometer, scan mode:	SuperNova, φ and ω-scans
θ_{max}, completeness:	26°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11648, 6323, 0.038
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4833
$N(param)_{refined}$:	415
Programs:	CrysAlis^{PRO} [1], SHELX [2], OLEX2 [3]

Source of materials

Source of the ligand H_2L: 4-(*N*,*N*′-diethylamino)salicylaldehyde (386.5 mg, 2.00 mmol) in ethanol (50 mL) was slowly added to a solution of 1,2-bis(aminooxy)ethane (276.5 mg, 3.00 mmol) in ethanol (80 mL) over 2.5 h. The solution was heated at 50–55 °C for 5 h. The solution was concentrated by reduced pressure distillation. The mixture was subjected to column chromatography with chloroform:ethyl acetate = 10:1 gave 439.6 mg of 2-[*O*-(1-ethyloxyamide)]oxime-5-(*N*,*N*′-diethylamino)phenol. A solution of 4-methoxysalicylaldehyde (242.8 mg, 1.6 mmol) in ethanol (20 mL) was slowly added to 2-[*O*-(1-ethyloxyamide)]oxime-5-(*N*,*N*′-diethylamino)phenol (439.6 mg, 1.59 mmol) in ethanol solution (10 mL) over 2 h, and stirred for about 6 h. Then distilled under reduced pressure, filtered, washed by ethanol/hexane (1:4). The product was dried under vacuum and we obtained 551.6 mg of the yellow solid di(5-(*N*,*N*′-diethylamine)-5′-methoxyl-2,2′-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol. Yield 72.8%, m.p. 365–366 K. Elemental analysis – Anal. Calcd. for $C_{21}H_{22}N_3O_5$: C, 63.63%; H, 5.59%; N, 10.60%. Found: C, 63.78%; H, 5.30%; N, 10.32%.

Source of the Ni(II) title complex: An ethanol solution (3.0 mL) of nickel acetate tetrahydrate (3.76 mg, 0.015 mmol) was added to an acetonitrile solution (2.0 mL) of H_2L: di(5-(*N*,*N*′-diethylamine)-5′-methoxyl-2,2′-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol) (4.01 mg, 0.010 mmol) at room temperature, the color of the mixing solution turned

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

Atom	x	y	z	U_{iso}*/U_{eq}
Ni1	0.03052(4)	−0.15206(4)	−0.21417(4)	0.02595(14)
Ni2	0.0000	0.0000	0.0000	0.02082(16)
O1	−0.1186(2)	−0.1644(2)	−0.15110(19)	0.0259(5)
O2	−0.5813(3)	−0.2589(2)	−0.1940(3)	0.0464(7)
O3	−0.0605(3)	−0.4318(2)	−0.3784(3)	0.0514(8)
O4	0.2507(3)	−0.1686(3)	−0.3223(3)	0.0594(9)
O5	0.1185(2)	0.0299(2)	−0.09753(19)	0.0245(5)
O6	0.1367(2)	−0.1797(2)	−0.0958(2)	0.0299(6)
O7	0.0999(2)	−0.0842(2)	0.05586(19)	0.0252(5)
O8	−0.0779(3)	−0.1268(3)	−0.3402(2)	0.0394(6)
H8	−0.105(4)	−0.075(3)	−0.3191(18)	0.059*
N1	−0.0984(3)	−0.3461(3)	−0.3188(3)	0.0336(7)
N2	0.1941(3)	−0.0975(3)	−0.2666(3)	0.0357(8)
N3	0.2959(3)	0.4663(3)	0.0074(3)	0.0379(8)
C1	−0.2539(4)	−0.2398(3)	−0.2070(3)	0.0278(8)
C2	−0.3449(3)	−0.2059(3)	−0.1701(3)	0.0294(8)
H2	−0.3087	−0.1278	−0.1082	0.035*
C3	−0.4874(4)	−0.2870(3)	−0.2245(3)	0.0355(9)
C4	−0.5447(4)	−0.4053(4)	−0.3159(4)	0.0450(10)
H4	−0.6407	−0.4603	−0.3513	0.054*
C5	−0.4576(4)	−0.4393(4)	−0.3529(4)	0.0439(10)
H5	−0.4960	−0.5187	−0.4137	0.053*
C6	−0.3117(4)	−0.3587(3)	−0.3025(3)	0.0323(8)
C7	−0.2295(4)	−0.4069(3)	−0.3456(3)	0.0363(9)
H7	−0.2776	−0.4917	−0.3987	0.044*
C8	−0.5289(4)	−0.1397(4)	−0.0998(4)	0.0525(12)
H8A	−0.4747	−0.0739	−0.1161	0.079*
H8B	−0.4713	−0.1326	−0.0328	0.079*
H8C	−0.6052	−0.1323	−0.0871	0.079*
C9	0.0869(4)	−0.3747(4)	−0.3418(4)	0.0414(10)
H9A	0.1095	−0.4402	−0.3594	0.050*
H9B	0.1295	−0.3225	−0.2596	0.050*
C10	0.1469(5)	−0.2956(4)	−0.3969(4)	0.0529(12)
H10A	0.1858	−0.3338	−0.4442	0.063*
H10B	0.0716	−0.2979	−0.4470	0.063*
C11	0.2667(4)	0.0155(3)	−0.2511(3)	0.0345(9)
H11	0.3304	0.0287	−0.2858	0.041*
C12	0.2612(3)	0.1229(3)	−0.1870(3)	0.0284(8)
C13	0.1936(3)	0.1306(3)	−0.1083(3)	0.0243(7)
C14	0.2087(3)	0.2461(3)	−0.0443(3)	0.0251(7)
H14	0.1684	0.2527	0.0093	0.030*
C15	0.2821(4)	0.3527(3)	−0.0571(3)	0.0295(8)
C16	0.3427(4)	0.3416(3)	−0.1389(3)	0.0362(9)
H16	0.3880	0.4098	−0.1520	0.043*
C17	0.3344(4)	0.2314(3)	−0.1980(3)	0.0354(9)
H17	0.3793	0.2274	−0.2484	0.042*
C18	0.3268(4)	0.5616(4)	−0.0317(4)	0.0438(10)
H18A	0.4084	0.5775	−0.0500	0.053*
H18B	0.3486	0.6396	0.0297	0.053*
C19	0.2072(5)	0.5226(4)	−0.1355(4)	0.0560(12)
H19A	0.1928	0.4517	−0.1994	0.084*
H19B	0.2287	0.5915	−0.1529	0.084*
H19C	0.1241	0.5000	−0.1201	0.084*
C20	0.2769(5)	0.4939(4)	0.1132(4)	0.0574(13)
H20A	0.3495	0.5797	0.1685	0.069*
H20B	0.2887	0.4386	0.1412	0.069*
C21	0.1434(6)	0.4806(6)	0.1070(6)	0.0865(19)
H21A	0.0704	0.3954	0.0540	0.130*
H21B	0.1315	0.5369	0.0818	0.130*
H21C	0.1397	0.5005	0.1811	0.130*
C22	0.1504(3)	−0.1451(3)	0.0058(3)	0.0257(7)
C23	0.2338(4)	−0.1791(4)	0.0752(4)	0.0414(10)
H23A	0.2901	−0.1100	0.1508	0.062*
H23B	0.2928	−0.1966	0.0396	0.062*
H23C	0.1717	−0.2523	0.0791	0.062*
C24	−0.0806(6)	−0.1472(6)	−0.4523(4)	0.0724(15)
H24A[a]	−0.0859	−0.0810	−0.4655	0.087*
H24B[a]	0.0061	−0.1408	−0.4552	0.087*
H24C[b]	−0.0116	−0.0684	−0.4456	0.087*
H24D[b]	−0.0514	−0.2072	−0.4786	0.087*
C25[a]	−0.1906(10)	−0.2629(8)	−0.5392(8)	0.081(3)
H25A[a]	−0.1931	−0.2660	−0.6117	0.121*
H25B[a]	−0.2764	−0.2738	−0.5324	0.121*
H25C[a]	−0.1785	−0.3289	−0.5337	0.121*
C25'[b]	−0.199(2)	−0.1880(18)	−0.5314(15)	0.088(6)
H25D[b]	−0.2737	−0.2515	−0.5250	0.131*
H25E[b]	−0.1969	−0.2233	−0.6053	0.131*
H25F[b]	−0.2136	−0.1192	−0.5216	0.131*
O9	−0.1397(3)	0.0493(2)	−0.2707(2)	0.0392(6)
H9	−0.1179	0.0631	−0.2039	0.059*
C26	−0.1497(5)	0.1725(5)	−0.3645(5)	0.0691(15)
H26A	−0.1873	0.1000	−0.4369	0.104*
H26B	−0.0949	0.2474	−0.3696	0.104*
H26C	−0.2244	0.1758	−0.3445	0.104*
C27	−0.0603(4)	0.1637(4)	−0.2756(4)	0.0456(10)
H27A	0.0182	0.1650	−0.2935	0.055*
H27B	−0.0244	0.2355	−0.2020	0.055*
N4	−0.5069(7)	−0.1576(7)	−0.6136(6)	0.128(3)
C28	−0.4842(6)	−0.1468(6)	−0.4177(5)	0.0879(19)
H28A	−0.5002	−0.2253	−0.4205	0.132*
H28B	−0.5508	−0.1291	−0.3950	0.132*
H28C	−0.3918	−0.0805	−0.3636	0.132*
C29	−0.4986(6)	−0.1547(6)	−0.5274(6)	0.0824(19)

Occupancies: [a] = 0.65, [b] = 0.35.

to light green immediately. After the mixture was stirred for 1 h and then the mixture was filtered. The resulting filtrate was left undisturbed for about 1 week to form clear light green block-like crystals suitable for X-ray crystallographic analysis. Yield: 76.9%. Elemental analysis – Anal. Calcd. for $C_{58}H_{86}Ni_3N_8O_{18}$: C, 51.24%; H, 6.38%; N, 8.24; Ni, 12.95%. Found: C, 51.30%; H, 6.04%; N, 8.06%; Ni, 12.86%.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. U_{iso} parameters were set by the SHELX program [2] system according to the functional group present.

Discussion

Salen-type compounds and their transition metal complexes have been investigated for decades with a focus on

modified ligand systems in the last years [4–7], and their metal complexes have a very wide range of applications, such as catalytic activities [8], electrochemical fields [9, 10], optical and magnetic materials [11–14], biological activities [15–17] and supramolecular architectures [18–20].

X-ray crystallographical analysis reveals that the title compound crystallizes in the triclinic space group $P\bar{1}$, with the trinuclear complex located at an inversion center. The title complex consists of three Ni(II) atoms, two completely deprotonated $(L)^{2-}$ units, two μ_2-acetate ions, two coordinated ethanol molecules, two crystalling acetonitrile and ethanol molecules, and forms a 2:3 ligand to metal stoichiometry (*cf*. the figure). The three Ni(II) atoms are all hexa-coordinated, and the coordination environments of the two terminal Ni(II) atoms (Ni1 and Ni1′) in the title compound are different from that of the central Ni(II) atom (Ni2). The terminal Ni1 (or Ni1′) atom is located at the *cis*-N_2O_2 coordination site (N1, N4, O1 and O5), and its axial positions are occupied by one μ_2-acetate oxygen atom (O6) and one coordinated ethanol oxygen atom (O8), and form a slightly distorted octahedral geometry. The central Ni2 atom coordinates to four phenolic oxygen atoms (O1, O5, O1′ and O5′), located in the inversion center of the title compound, and its axial positions are occupied by μ_2-acetate oxygen atoms (O7 and O7′) indicating that the central Ni2 atom forms a slightly distorted octahedral geometry. In addition, two μ_2-acetate ions take the familiar M—O—C—O—*M* configuration bridging center Ni2 and terminal Ni1 (or Ni1′) atoms.

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