Crystal structure of bis[(3,3′-dimethoxy-2,2′-1,3-propylene)dioxybis(nitrilomethylidyne)diphenolato]-bis(acetato-O^1,O^2)-bis(ethanol-O)trinickel(II) — ethanol — acetone (1:2:1.06), $Ni_3(C_{19}H_{20}N_2O_6)_2(C_2H_5OH)_2(C_2H_3O_2)_2 \cdot 2C_2H_5OH \cdot 1.06C_3H_6O$

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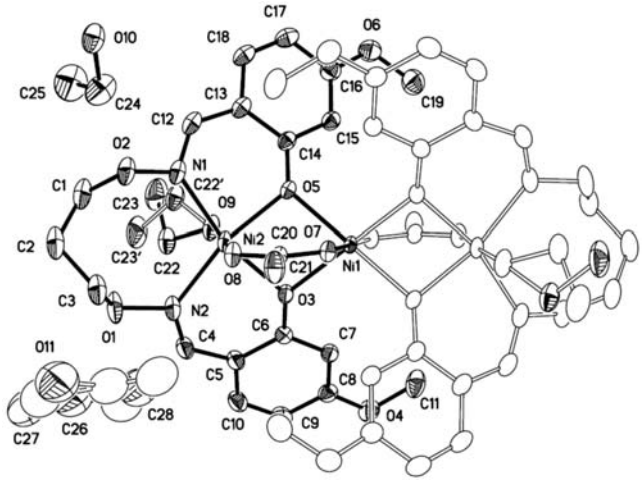

Abstract

$C_{53.18}H_{76.38}N_4Ni_3O_{21.06}$, triclinic, $P\bar{1}$ (no. 2), a = 11.557(2) Å, b = 11.913(2) Å, c = 12.136(2) Å, α = 70.175(3)°, β = 71.716(2)°, γ = 85.930(3)°, V = 1491.3 Å^3, Z = 1, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.106, T = 298 K.

Source of material

A solution of nickel(II) acetate tetrahydrate (8.1 mg, 0.03 mmol) in ethanol (4 ml) was added dropwise to a solution of 3,3′-dimethoxy-2,2′-[(1,3-propylene)dioxybis(nitrilomethylidyne)]-diphenol (12.1 mg, 0.03 mmol) in acetone (30 ml). The color of the mixed solution turned to pale-green immediately, then the mixture was stirred for 1 h at room temperature. Finally, the solution was filtered, and the filtrate was allowed to stand at room temperature for about one week. When the solvent was partially evaporated, several green block-shaped single crystals suitable for X-ray crystallographic analysis were obtained.

Experimental details

All H atoms were positioned geometrically with d(C—H) = 0.93 - 0.98 Å, and refined as riding with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). The aceton molecule and the ethyl group of an ethanol molecule are disordered with occupancies of 0.532(6) and 0.56(2) : 0.44(2), respectively.

Discussion

Transition metal complexes with *N*,*N*′-disalicylideneethylenediamine (salen) ligand or its derivatives are extensively investigated, because these complexes have played a seminal role in the development of modern coordination chemistry. They can also be used in the design and construction of new magnetic materials and model of the metal center of enzymes. Although some advance has been made in the studies of salen-Ni(II) complexes [1-3], it still seems there could be new and specific applications for such a unique group of compounds. To change the structures or improve the functions of the resulted complexes, chemical modifications of the elemental salen-type ligand, e.g., introduction of some functional groups or appropriate substitution of some parts, are effective and inevitable. In particular, replacement of some atoms of the ligand with other elements often changes its properties drastically [4,5]. If an *O*-alkyloxime moiety (–CH=N–O–$(CH_2)_n$–O–N=CH–) is used instead of the imine moiety, the larger electronegativity of oxygen atoms is expected to strongly affect the electronic properties of N_2O_2 coordination sphere, which can lead to different and novel properties and structures of the resulted complexes [6,7]. Recently, we studied trinuclear complexes of cobalt [8,9].

The crystal structure contains a linear trinuclear array of three Ni(II) ions coupled by both doubly μ-phenoxo oxygen atoms of $(C_{19}H_{20}N_2O_6)^{2-}$ units and simultaneously two acetate anions in the *syn-syn* bridging mode. The hexa-coordinated Ni(II) ions of the cluster have a slightly distorted octahedral coordination. The terminal nickel(II) ions (Ni2 and Ni2′) are located in the N_2O_2 coordination sphere of $(C_{19}H_{20}N_2O_6)^{2-}$ unit. One oxygen atom O8 from the μ-acetato bridge and one oxygen atom O9 from the ethanol molecule are also coordinating Ni2. Consequently, the dihedral angle between the coordination plane of O5–Ni2–N1 and that of O3–Ni2–N2 is about 6.88(2)°, indicating slight distortion from the square planar toward octahedral geometry. In addition, the coordination sphere of the central nickel(II) ion (Ni1) is completed by quadruple μ-phenoxo oxygen atoms from two $(C_{19}H_{20}N_2O_6)^{2-}$ moieties and double μ-acetato oxygen atoms which adopt a familiar μ-O–C–O fashion. All the six oxygen atoms coordinating Ni1 constitute octahedral environment. On the other hand, the distance d(Ni1—O7) = 2.102(2) Å is longer than that of d(Ni1—O5) = 2.058(2) Å, indicating a weak steric effect. Similar elongations of M—O bonds have also been observed in dimer $[M(salen)]_2$ [10]. The Ni2—N2 bond (2.098(4) Å) is slightly longer than Ni2—N1 bond (2.085(4) Å), which is attrib-

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uted to the ethanol molecule coordinating the terminal nickel(II) ions resulting in the larger steric hindrance. Furthermore, the distance of Ni1—Ni2 (3.102 Å) is significantly longer than all the Ni—O and Ni—N bonds (2.084 to 2.134 Å) and indicates a weak intermetal interaction, which is similar to those previously reported salen-type clusters of {[Ni(Salpr)NC_5H_5]$_2$-(μOAc)$_2$Ni} [11]. The unit cell contains two lattice ethanol molecules. There are complicated hydrogen bonding interactions. The O10–H10 group of the two lattice ethanol molecule is hydrogen-bonded to the oxygen atom O7 of the bridged acetic ions, while the C21–H21B group of the bridged acetic ions and the O9–H9 group of the coordinating ethanol molecule is hydrogen-bonded to its oxygen atom O10.

In addition, analysis of the crystal packing of the cluster shows that a two-dimensional (2D) hydrogen-bonding supramolecular networks were formed through four pairs of intermolecular C–H···O interactions, C2–H2A···O1 and C2–H2B···O4, which formed through the –CH group of the O-alkyl chain of the $(C_{19}H_{20}N_2O_6)^{2-}$ moieties with the oxime oxygen atom O1 and the oxygen atoms O4 of the methoxy group, respectively.

Table 1. Data collection and handling.

Crystal:	green block, size 0.40 × 0.49 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.14 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7797, 5178
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3970
$N(param)_{refined}$:	406
Programs:	SHELXS-97, SHELXL-97 [12]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(9)	2*i*		0.6140	0.6442	0.1523	0.075
H(10)	2*i*		0.4386	0.5456	0.2312	0.081
H(1A)	2*i*		0.9758	0.7319	0.0585	0.079
H(1B)	2*i*		1.1142	0.7037	0.0396	0.079
H(2A)	2*i*		1.1266	0.8246	0.1534	0.079
H(2B)	2*i*		1.0875	0.8993	0.0376	0.079
H(3A)	2*i*		0.9197	0.8042	0.2757	0.078
H(3B)	2*i*		0.9660	0.9389	0.2156	0.078
H(4)	2*i*		0.6777	0.9750	0.1364	0.056
H(7)	2*i*		0.3141	0.6674	0.4319	0.041
H(9A)	2*i*		0.2754	0.9901	0.1986	0.066
H(10A)	2*i*		0.4809	1.0233	0.1311	0.064
H(11A)	2*i*		0.1305	0.6388	0.4056	0.106
H(11B)	2*i*		0.0096	0.7004	0.4530	0.106
H(11C)	2*i*		0.1102	0.6818	0.5186	0.106
H(12)	2*i*		0.9859	0.4419	0.2057	0.057
H(15)	2*i*		0.5246	0.2951	0.4003	0.045
H(17)	2*i*		0.7891	0.1210	0.2253	0.069
H(18)	2*i*		0.9263	0.2678	0.1844	0.064
H(19A)	2*i*		0.4294	0.1146	0.4771	0.118
H(19B)	2*i*		0.3966	0.0380	0.4077	0.118
H(19C)	2*i*		0.4060	0.1777	0.3502	0.118
H(21A)	2*i*		0.8225	0.5498	0.6592	0.085
H(21B)	2*i*		0.7018	0.6055	0.7176	0.085
H(21C)	2*i*		0.8074	0.6880	0.6102	0.085
H(22A)	2*i*	0.56	0.8005	0.7777	0.0011	0.067
H(22B)	2*i*	0.56	0.6695	0.7811	–0.0133	0.067
H(23A)	2*i*	0.56	0.8185	0.5922	–0.0442	0.165
H(23B)	2*i*	0.56	0.8301	0.7104	–0.1560	0.165
H(23C)	2*i*	0.56	0.7071	0.6341	–0.0937	0.165
H(22C)	2*i*	0.44	0.8438	0.6064	0.0081	0.068
H(22D)	2*i*	0.44	0.7241	0.5832	–0.0179	0.068
H(23D)	2*i*	0.44	0.6999	0.7870	–0.0870	0.149
H(23E)	2*i*	0.44	0.8233	0.7524	–0.1665	0.149
H(23F)	2*i*	0.44	0.8226	0.8076	–0.0660	0.149
H(24A)	2*i*		0.3942	0.7278	0.1228	0.095
H(24B)	2*i*		0.3062	0.6230	0.1439	0.095
H(25A)	2*i*		0.5023	0.7135	–0.0650	0.157
H(25B)	2*i*		0.3661	0.7432	–0.0564	0.157
H(25C)	2*i*		0.4093	0.6130	–0.0439	0.157
H(27A)	2*i*	0.532	1.1373	0.1362	0.3216	0.223
H(27B)	2*i*	0.532	1.0032	0.1783	0.3391	0.223
H(27C)	2*i*	0.532	1.0428	0.0683	0.2948	0.223
H(28A)	2*i*	0.532	0.8559	–0.0008	0.4266	0.128
H(28B)	2*i*	0.532	0.8517	–0.0099	0.5597	0.128
H(28C)	2*i*	0.532	0.9256	–0.1012	0.4997	0.128

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	1*h*		½	½	½	0.0213(3)	0.0304(3)	0.0203(3)	–0.0015(2)	–0.0017(2)	–0.0043(2)
Ni(2)	2*i*		0.72343(4)	0.64438(4)	0.29094(4)	0.0248(2)	0.0405(3)	0.0248(2)	–0.0054(2)	–0.0013(2)	–0.0030(2)
N(1)	2*i*		0.8914(3)	0.5712(3)	0.2337(3)	0.023(2)	0.062(2)	0.037(2)	–0.005(1)	–0.002(1)	–0.012(2)
N(2)	2*i*		0.7442(3)	0.8305(3)	0.2109(3)	0.032(2)	0.047(2)	0.040(2)	–0.012(1)	–0.007(1)	0.001(1)
O(1)	2*i*		0.8570(3)	0.8953(3)	0.1364(3)	0.040(2)	0.071(2)	0.068(2)	–0.024(1)	–0.014(2)	0.026(2)
O(2)	2*i*		1.0080(2)	0.6253(3)	0.2110(2)	0.029(1)	0.075(2)	0.051(2)	–0.009(1)	–0.008(1)	–0.010(1)
O(3)	2*i*		0.5462(2)	0.6708(2)	0.3728(2)	0.024(1)	0.033(1)	0.031(1)	0.0000(9)	–0.006(1)	–0.001(1)
O(4)	2*i*		0.1509(2)	0.8125(3)	0.3600(3)	0.037(2)	0.066(2)	0.062(2)	0.014(1)	–0.018(1)	–0.011(2)
O(5)	2*i*		0.6539(2)	0.4739(2)	0.3701(2)	0.028(1)	0.037(1)	0.028(1)	–0.001(1)	0.0025(9)	–0.010(1)
O(6)	2*i*		0.5652(3)	0.1039(3)	0.3356(3)	0.067(2)	0.053(2)	0.078(2)	–0.000(2)	–0.014(2)	–0.035(2)
O(7)	2*i*		0.6137(2)	0.5330(2)	0.5918(2)	0.028(1)	0.040(1)	0.026(1)	–0.005(1)	–0.006(1)	–0.008(1)
O(8)	2*i*		0.7684(2)	0.6471(2)	0.4390(2)	0.033(1)	0.053(2)	0.029(1)	–0.010(1)	–0.005(1)	–0.005(1)
O(9)	2*i*		0.6887(2)	0.6448(2)	0.1287(2)	0.036(1)	0.075(2)	0.028(1)	–0.009(1)	–0.003(1)	–0.008(1)
O(10)	2*i*		0.4680(2)	0.5713(2)	0.1561(2)	0.047(2)	0.074(2)	0.031(1)	–0.005(1)	–0.009(1)	–0.006(1)
C(1)	2*i*		1.0407(4)	0.7218(4)	0.0955(4)	0.040(2)	0.101(4)	0.038(2)	–0.019(2)	0.001(2)	–0.008(2)
C(2)	2*i*		1.0618(4)	0.8352(4)	0.1162(4)	0.044(3)	0.080(3)	0.053(3)	–0.026(2)	–0.015(2)	0.010(2)
C(3)	2*i*		0.9486(4)	0.8693(4)	0.1983(4)	0.048(3)	0.068(3)	0.069(3)	–0.023(2)	–0.017(2)	–0.004(2)
C(4)	2*i*		0.6561(4)	0.8970(3)	0.1890(3)	0.050(2)	0.035(2)	0.044(2)	–0.010(2)	–0.011(2)	0.001(2)
C(5)	2*i*		0.5282(3)	0.8652(3)	0.2362(3)	0.040(2)	0.031(2)	0.044(2)	–0.002(2)	–0.013(2)	–0.007(2)
C(6)	2*i*		0.4762(3)	0.7556(3)	0.3281(3)	0.036(2)	0.030(2)	0.028(2)	0.000(1)	–0.011(2)	–0.008(1)
C(7)	2*i*		0.3491(3)	0.7384(3)	0.3707(3)	0.032(2)	0.036(2)	0.031(2)	0.002(2)	–0.009(2)	–0.007(1)

Table 3. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(8)	2*i*		0.2748(3)	0.8243(3)	0.3239(3)	0.037(2)	0.046(2)	0.048(2)	0.010(2)	–0.014(2)	–0.019(2)
C(9)	2*i*		0.3252(4)	0.9324(3)	0.2315(4)	0.056(3)	0.039(2)	0.067(3)	0.013(2)	–0.028(2)	–0.008(2)
C(10)	2*i*		0.4478(4)	0.9510(3)	0.1911(4)	0.057(3)	0.032(2)	0.060(3)	–0.002(2)	–0.020(2)	0.001(2)
C(11)	2*i*		0.0958(4)	0.6992(4)	0.4409(4)	0.034(2)	0.089(4)	0.064(3)	0.003(2)	–0.010(2)	0.001(3)
C(12)	2*i*		0.9059(3)	0.4647(4)	0.2304(3)	0.029(2)	0.073(3)	0.038(2)	0.008(2)	–0.004(2)	–0.024(2)
C(13)	2*i*		0.8116(3)	0.3765(3)	0.2608(3)	0.034(2)	0.057(2)	0.033(2)	0.006(2)	–0.007(2)	–0.019(2)
C(14)	2*i*		0.6885(3)	0.3844(3)	0.3280(3)	0.035(2)	0.041(2)	0.022(2)	0.005(2)	–0.006(1)	–0.007(1)
C(15)	2*i*		0.6054(3)	0.2917(3)	0.3550(3)	0.037(2)	0.041(2)	0.032(2)	0.003(2)	–0.007(2)	–0.012(2)
C(16)	2*i*		0.6417(4)	0.1951(3)	0.3154(3)	0.056(2)	0.044(2)	0.041(2)	0.006(2)	–0.014(2)	–0.018(2)
C(17)	2*i*		0.7640(4)	0.1865(4)	0.2508(4)	0.060(3)	0.062(3)	0.062(3)	0.021(2)	–0.020(2)	–0.039(2)
C(18)	2*i*		0.8449(4)	0.2746(4)	0.2261(4)	0.041(2)	0.072(3)	0.051(2)	0.014(2)	–0.007(2)	–0.035(2)
C(19)	2*i*		0.4390(4)	0.1090(4)	0.3977(5)	0.068(3)	0.067(3)	0.100(4)	–0.016(3)	–0.008(3)	–0.038(3)
C(20)	2*i*		0.7119(3)	0.5962(3)	0.5500(3)	0.028(2)	0.039(2)	0.032(2)	0.001(2)	–0.008(2)	–0.009(2)
C(21)	2*i*		0.7658(4)	0.6112(4)	0.6427(3)	0.050(3)	0.078(3)	0.038(2)	–0.024(2)	–0.013(2)	–0.010(2)
C(22)	2*i*	0.56(2)	0.7336(8)	0.729(1)	0.0069(8)	0.046(5)	0.083(9)	0.027(5)	–0.019(5)	–0.006(4)	–0.005(4)
C(23)	2*i*	0.56	0.776(1)	0.660(2)	–0.079(1)	0.105(9)	0.18(2)	0.040(8)	–0.03(1)	0.013(6)	–0.05(1)
C(22')	2*i*	0.44	0.765(1)	0.637(2)	0.005(1)	0.047(6)	0.08(1)	0.041(8)	0.003(6)	–0.012(5)	–0.015(6)
C(23')	2*i*	0.44	0.779(2)	0.756(2)	–0.087(2)	0.09(1)	0.11(1)	0.06(1)	–0.02(1)	–0.011(8)	0.02(1)
C(24)	2*i*		0.3895(5)	0.6551(5)	0.1049(4)	0.073(3)	0.109(4)	0.049(3)	0.020(3)	–0.020(2)	–0.018(3)
C(25)	2*i*		0.4193(6)	0.6836(6)	–0.0260(5)	0.108(5)	0.128(5)	0.064(3)	0.009(4)	–0.041(3)	–0.004(3)
C(26)	2*i*		1.026(2)	0.044(1)	0.441(2)	0.11(1)	0.09(1)	0.13(1)	0.05(1)	–0.03(1)	–0.043(8)
C(27)	2*i*	0.532(6)	1.054(1)	0.110(2)	0.346(2)	0.08(1)	0.15(2)	0.13(1)	0.026(9)	0.005(9)	0.01(1)
C(28)	2*i*	0.532	0.902(3)	–0.020(3)	0.484(4)	0.07(1)	0.09(1)	0.10(2)	0.01(1)	–0.02(1)	–0.05(1)
O(11)	2*i*	0.532	1.094(3)	0.003(3)	0.533(3)	0.14(2)	0.14(2)	0.14(2)	0.01(1)	–0.01(1)	–0.02(1)

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