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Crystal structure of (dimethylformamide- κO)(perchlorato- $\kappa^2 O, O'$){ μ_2 -6,6'-((1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(4-bromo-2-methoxyphenolate)- $\kappa^8 N, N', O: O, O': O', O'', O'''$ }sodium(I)nickel(II), $C_{25}H_{23}Br_2ClN_3NaNiO_9$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.21 × 0.15 × 0.11 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.58 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	27.7°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16821, 6678, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3992
$N(\text{param})_{\text{refined}}$:	393
Programs:	Bruker programs [1], SHELX [2], OLEX2 [3]

and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

The Schiff-base ligand was synthesized by condensation of 1,2-diaminobenzene and 5-bromo-3-methoxy-2-hydroxybenzaldehyde with the molar ratio 1:2 in ethanol. The synthesis of the title complex was carried out by reacting $Ni(ClO_4)_2 \cdot 6H_2O$, CH_3COONa and the schiff-base ligand (1:2:1, molar ratio) in DMF. Stirring was continued for half an hour at room temperature. The mixture was filtered and the filtrate was evaporated in air without disturbed. After 1 month, block red-brown crystals suitable were obtained with a yield about 55%.

Experimental details

A terminal methyl group was refined with disorder model and SADI and RIGU restrains to get better models. U_{iso} values of hydrogen atoms were set to $1.2U_{\text{eq}}$ or $1.5U_{\text{eq}}$ of the parent atoms.

Comment

Because not only of their interesting structures, but also more important of the great potential applications in many fields, the Schiff-base ligand based complexes have all along attracted much attention [4–6]. Among which, the complexes containing paramagnetic transition ion(s) based-on the salen types of quasi-planar chelate ligands have been widely studied in the molecular magnetism field owing to

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Abstract

$C_{25}H_{23}Br_2ClN_3NaNiO_9$, monoclinic, $P2_1/n$ (no. 14), $a = 15.595(4)$ Å, $b = 10.993(3)$ Å, $c = 18.660(5)$ Å, $\beta = 114.536(4)^\circ$, $V = 2910.2(14)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0390$, $wR_{\text{ref}}(F^2) = 0.0998$, $T = 293$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.02437(3)	0.22736(4)	0.99954(2)	0.03812(12)
Na1	0.10600(10)	0.26663(12)	0.85809(8)	0.0530(4)
Br1	−0.26624(3)	0.74480(4)	0.78779(2)	0.06748(15)
Br2	0.35619(3)	−0.28026(4)	1.09436(3)	0.07031(15)
Cl1	0.26998(7)	0.43203(9)	0.85196(6)	0.0574(3)
O1	0.00350(16)	0.3294(2)	0.91574(12)	0.0438(5)
O2	−0.00289(17)	0.4422(2)	0.79237(13)	0.0530(6)
O3	0.11197(16)	0.1584(2)	0.96945(12)	0.0458(6)
O4	0.23071(18)	0.1020(2)	0.91047(14)	0.0569(7)
O5	0.0323(2)	0.1807(3)	0.73615(16)	0.0753(8)
O6	0.2134(2)	0.3506(3)	0.79185(18)	0.0982(11)
O7	0.2606(3)	0.5497(3)	0.8201(2)	0.0994(11)
O8	0.3643(2)	0.3931(4)	0.88111(19)	0.1063(12)
O9	0.2350(2)	0.4291(3)	0.91208(15)	0.0778(9)
N1	−0.06207(19)	0.3021(2)	1.02925(15)	0.0389(6)
N2	0.04339(19)	0.1175(2)	1.08009(14)	0.0399(6)
N3	0.0000(2)	0.1853(3)	0.60707(19)	0.0711(10)
C1	−0.0691(2)	0.2457(3)	1.09520(19)	0.0403(8)
C2	−0.0118(2)	0.1446(3)	1.12281(18)	0.0439(8)
C3	−0.0127(3)	0.0792(3)	1.1860(2)	0.0558(10)
H3	0.025065	0.010644	1.204327	0.067*
C4	−0.0696(3)	0.1164(4)	1.2211(2)	0.0616(11)
H4	−0.070255	0.073049	1.263671	0.074*
C5	−0.1255(3)	0.2170(4)	1.1941(2)	0.0588(10)
H5	−0.163191	0.241538	1.219215	0.071*
C6	−0.1274(3)	0.2826(3)	1.1306(2)	0.0513(9)
H6	−0.166577	0.349885	1.111953	0.062*
C7	−0.1143(2)	0.4569(3)	0.92802(18)	0.0405(8)
C8	−0.0560(2)	0.4193(3)	0.89152(18)	0.0387(8)
C9	−0.0624(2)	0.4836(3)	0.82363(18)	0.0401(8)
C10	−0.1235(2)	0.5788(3)	0.79397(19)	0.0465(9)
H10	−0.126927	0.620074	0.749331	0.056*
C11	−0.1806(2)	0.6133(3)	0.8317(2)	0.0482(9)
C12	−0.1767(2)	0.5562(3)	0.8973(2)	0.0476(9)
H12	−0.214622	0.581871	0.921918	0.057*
C13	−0.1128(2)	0.3965(3)	0.99617(19)	0.0446(8)
H13	−0.151455	0.427435	1.018706	0.053*
C14	−0.0123(3)	0.4925(4)	0.7190(2)	0.0643(11)
H14A	−0.074827	0.477303	0.679757	0.096*
H14B	0.032826	0.455333	0.703260	0.096*
H14C	−0.001363	0.578573	0.724724	0.096*
C15	0.1602(2)	−0.0068(3)	1.06129(18)	0.0394(8)
C16	0.1648(2)	0.0645(3)	1.00023(18)	0.0384(7)
C17	0.2304(2)	0.0283(3)	0.96927(19)	0.0446(8)
C18	0.2862(2)	−0.0717(3)	0.9976(2)	0.0483(9)
H18	0.329241	−0.093723	0.977246	0.058*
C19	0.2781(2)	−0.1406(3)	1.05700(19)	0.0454(8)
C20	0.2178(2)	−0.1105(3)	1.08900(19)	0.0455(8)
H20	0.214185	−0.157660	1.129021	0.055*
C21	0.0999(2)	0.0252(3)	1.09780(18)	0.0442(8)
H21	0.100945	−0.024969	1.138307	0.053*
C22	0.2917(3)	0.0701(4)	0.8731(2)	0.0736(13)
H22A	0.356165	0.073614	0.911092	0.110*
H22B	0.282484	0.126302	0.831147	0.110*
H22C	0.277343	−0.010774	0.852189	0.110*

Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C23	0.0547(3)	0.1919(4)	0.6815(3)	0.0648(11)
H23	0.118089	0.206822	0.694459	0.078*
C24 ^a	−0.0876(10)	0.123(2)	0.5919(11)	0.148(11)
H24A ^a	−0.088489	0.046218	0.566743	0.222*
H24B ^a	−0.139629	0.171695	0.558037	0.222*
H24C ^a	−0.092693	0.108735	0.640724	0.222*
C25	0.0348(4)	0.2003(5)	0.5464(3)	0.1039(18)
H25A	0.009378	0.273696	0.517460	0.156*
H25B	0.015678	0.132048	0.511217	0.156*
H25C	0.102366	0.205234	0.570549	0.156*
C24A ^a	−0.1020(8)	0.195(3)	0.5768(12)	0.142(11)
H24D ^a	−0.130286	0.121621	0.548696	0.212*
H24E ^a	−0.123318	0.263070	0.541864	0.212*
H24F ^a	−0.119808	0.205367	0.619862	0.212*

^aOccupancy: 0.5.

their interesting magnetic properties [7–9]. For example new sandwich-type heterometallic Zn^{II}–Ln^{III} clusters based on a methoxy substituted salicylamide salen-like ligand [Zn₂Er₃(HL)₂(H₂L)₂(OH)₂(NO₃)₃] (NO₃)_{2.2}CH₃OH(Zn₂Er₃), [Zn₂Yb₃(HL)₂(H₂L)₂(OH)₂(NO₃)₃] (NO₃)_{2.2}CH₃OH (Zn₂Yb₃), H₃L = 1-(2-hydroxy-4-methoxy-benzamido)-2-(2-hydroxy-3-methoxy-benzylideneamino)-ethane were reported. The magnetic susceptibility measurements shows that Zn₂Er₃ displays anti-ferromagnetic interactions with zero field slow magnetization relaxation diagnostic of single-molecule-magnet [10]. The Ghosh group reported three trinuclear hetero-metallic complexes with a reduced salen type Schiff base ligand and further investigated their magnetic properties [11].

Herein, we report the synthesis and crystal structure of a heterometallic NiNa complex, which can maybe act as a suitable assemble segment to prepare multimetallic molecule-based magnetic material.

The Ni ion is four-coordinated by a N₂O₂ unit from the Schiff-base ligand, forming a square planar geometry. The Ni–O and Ni–N bond lengths are almost equal to each other with the average value of 1.841 Å and 1.852 Å, respectively. The mean deviation of the plane formed by NiN₂O₂ is only 0.01(2) Å, indicating that these five atoms are in a perfect plane. The coordination sphere of the Na ion is a distorted pentagonal bipyramid, in which the five equatorial positions are from a O₄ unit of the Schiff-base ligand and one O atom of ClO₄[−] ion and the axial ones occupied by one O atom of the coordinated DMF molecule and one O atom of ClO₄[−] ion. The distances between the Na atom and the seven O atoms are with slight difference within a narrow range from 2.287(4) to 2.627(4) Å. Additionally, this complex forms a supramolecular three-dimensional structure based on weak intermolecular C–H···O and C–H···Cl interactions.

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