Crystal structure of bis[bisaqua-bis(2,2′-bipyridine)nickel(II)]-(9,10-dioxo-9,10-anthracene-2,6-disulfonate) dinitrate dihydrate, $[Ni(H_2O)_2(C_{10}H_8N_2)_2]_2[C_{14}H_6S_2O_8][NO_3]_2 \cdot 2H_2O$

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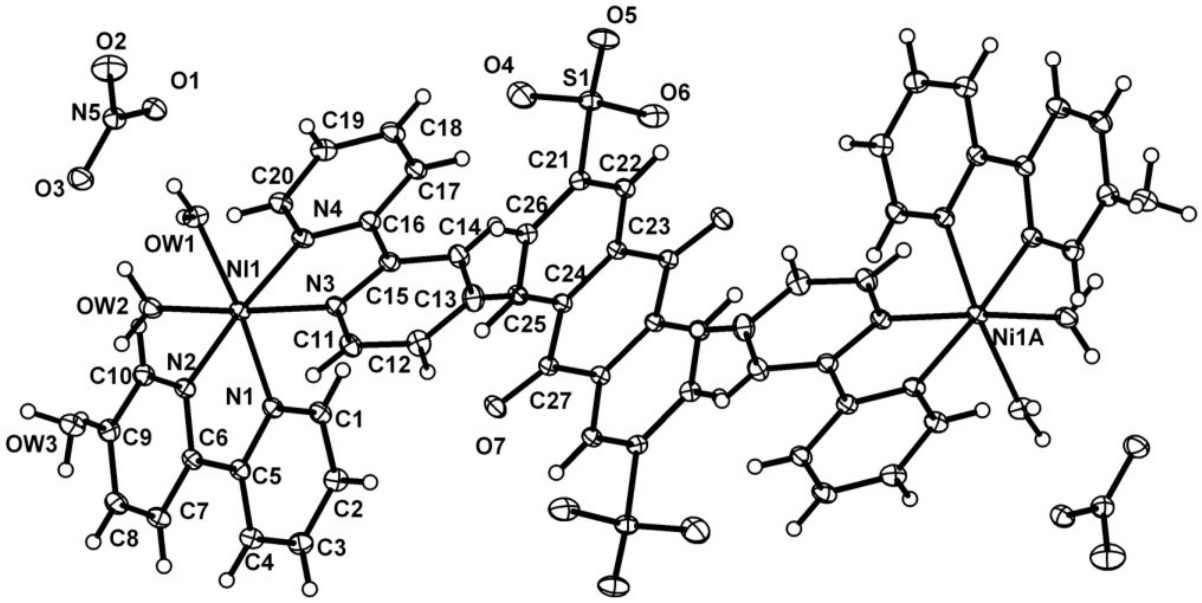

Abstract

$C_{54}H_{50}N_{10}Ni_2O_{20}S_2$, monoclinic, $P12_1/c1$ (no. 14), a = 9.6994(2) Å, b = 25.2194(4) Å, c = 11.2571(2) Å, β = 93.788(2)°, V = 2747.6 Å^3, Z = 2, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.161, T = 298 K.

Source of material

A mixture of 0.29 g of $Ni(NO_3)_2 \cdot 6H_2O$(1 mmol), 0.16 g of 2,2′-bipyridine (1 mmol), 0.31 g of sodium salt of 9,10-dioxoanthracene-2,6-disulfonic acid (1 mmol), and 15 mL of deionized water were sealed into a bomb equipped with a Teflon liner (25 mL) and heated at 373 K for 3 days. Blue rod-like crystals of the title compound were obtained after the mixture was cooled to room temperature (yield 69 % based on Ni).

Elemental analysis — found: C, 34.39 %; H, 3.35 %; N, 10.27 %; calculated for $C_{54}H_{50}N_{10}Ni_2O_{20}S_2$: C, 43.50 %; H, 3.38 %; N, 10.33 %.

Experimental details

The C-bound H atoms were geometrically placed (d(C—H) = 0.93 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The O-bound H atoms were located by difference maps and constrained to ride on their parent O atoms.

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Discussion

Studies of metal sulfonates have shown that the use of bisfunctional or multifunctional anionic units, such as disulfonates can lead to a number of new materials with layered frameworks or open-framework structures [1-3]. Direct use of two types of ligands in the preparation, such as the carboxylic acid or the sulfonic acids with 2,2′-bipy, 4,4′-bipy, or 1,10-phenanththroline has been found to be another useful method to build hybrid materials [3-6].

The title compound possesses a discrete structure. The unit cell of the title compound contains two Ni^{2+} ions, one 2,6-ADS anion, four 2,2′-bipy ligands, two nitrate ions and four aqua ligands. Each Ni atom is coordinated by four nitrogen atoms of two crystallographically independent 2,2′-bipy ligands, and two oxygen atoms of two aqua ligands. The Ni—N distances range from 2.061(2) Å to 2.077(2) Å, comparable to those reported for other nickel complexes [5,6]; d(Ni—O) of 2.082(2) Å and 2.092(2) Å are in agreement with those found in comparable structures [7]. The angles subtended at Ni(II) atom by cis pairs of ligating atoms cover the range 79.31(8)° - 97.26(8)°, and the angles subtended by the trans pairs are in the range 172.37(8)° to 175.09(8)°. Thus, the coordination geometry around Ni(II) can be described as a distorted $Ni[O_2N_4]$ octahedron. The two aqua ligands are in the *cis* positions. The 2,2′-bipy ligand binds in a chelate fashion to the metal ion and its two pyridine rings are affected by distortion. The dihedral angles between the pyridine rings containing N3 and N4, N1 and N2 are 5.9° and 5.8°, respec-

tively. The 2,6-ADS anion does not participate in the coordination of Ni(II) atom, and has an inversion centre at the midpoint of the central C—C bond. In the comparable structure of $[Cd(bipy)_2(H_2O)](2,6\text{-ADS}) \cdot H_2O$, the 2,6-ADS aions adopts an O-monodentate mode [8]. The hexa-coordinated Ni(II) complexes in the title compound are bridged by hydrogen bonds formed by the coordinated water molecules and the sulfonate oxygen atoms and form a dimeric unit. The dimeric units are extended into an infinite chain along [110] by aromatic interaction between the parallel neighboring pyriding rings with a face-to-face distance of 3.38 Å. Adjacent chains are linked to a 3D packing structure by hydrogen bonds between the lattice water molecules and sulfonate oxygen atoms.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.29 × 0.33 × 0.38 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	23.41 cm^{-1}
Diffractometer, scan mode:	CrysAlis CCD, κ geometry, ω
$2\theta_{max}$:	134.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11499, 4892
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4442
$N(param)_{refined}$:	404
Programs:	SHELXS-97, SHELXL-97, SHELXTL [9]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.4133	0.6521	1.1352	0.060
H(1B)	4*e*	0.3250	0.6084	1.1626	0.040
H(2A)	4*e*	0.0011	0.6516	1.0328	0.060
H(2B)	4*e*	0.0757	0.6192	1.1102	0.060
H(3A)	4*e*	–0.2088	0.6890	1.0597	0.050
H(3B)	4*e*	–0.1931	0.7136	0.9588	0.070
H(1)	4*e*	0.1001	0.5721	0.7325	0.041
H(2)	4*e*	–0.0463	0.5907	0.5689	0.046
H(3)	4*e*	–0.1257	0.6769	0.5373	0.047
H(4)	4*e*	–0.0452	0.7433	0.6682	0.044
H(7)	4*e*	0.0608	0.8023	0.7813	0.044
H(8)	4*e*	0.1732	0.8604	0.9155	0.047
H(9)	4*e*	0.3202	0.8262	1.0692	0.043
H(10)	4*e*	0.3499	0.7361	1.0839	0.040
H(11)	4*e*	0.4629	0.7039	0.8264	0.044
H(12)	4*e*	0.6446	0.6913	0.7081	0.051
H(13)	4*e*	0.7156	0.6053	0.6694	0.052
H(14)	4*e*	0.5996	0.5343	0.7479	0.045
H(17)	4*e*	0.4879	0.4724	0.8339	0.042
H(18)	4*e*	0.3509	0.4094	0.9207	0.046
H(19)	4*e*	0.1560	0.4379	1.0146	0.048
H(20)	4*e*	0.1072	0.5274	1.0202	0.041
H(22)	4*e*	0.5497	0.3717	0.5869	0.035
H(25)	4*e*	0.1764	0.4867	0.5975	0.036
H(26)	4*e*	0.1593	0.4008	0.6685	0.037

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	4*e*	0.24431(4)	0.63421(2)	0.94746(4)	0.0273(3)	0.0228(3)	0.0340(3)	0.0005(2)	–0.0009(2)	–0.0003(1)
S(1)	4*e*	0.34401(6)	0.31280(2)	0.69428(5)	0.0353(4)	0.0244(3)	0.0378(4)	–0.0044(2)	–0.0024(3)	0.0043(2)
OW(1)	4*e*	0.3581(2)	0.62806(7)	1.1113(2)	0.042(1)	0.034(1)	0.037(1)	–0.0088(8)	–0.0055(8)	0.0029(7)
OW(2)	4*e*	0.0648(2)	0.62870(7)	1.0384(2)	0.031(1)	0.039(1)	0.046(1)	0.0061(8)	0.0064(8)	0.0082(8)
OW(3)	4*e*	–0.1699(2)	0.6854(1)	0.9952(2)	0.054(1)	0.062(2)	0.054(1)	0.025(1)	0.003(1)	0.009(1)
N(1)	4*e*	0.1189(2)	0.64515(8)	0.7933(2)	0.029(1)	0.027(1)	0.035(1)	0.0004(8)	–0.0004(8)	–0.0020(8)
N(2)	4*e*	0.2278(2)	0.71568(8)	0.9453(2)	0.029(1)	0.027(1)	0.034(1)	0.0002(8)	0.0006(8)	0.0001(8)
N(3)	4*e*	0.4199(2)	0.62895(8)	0.8531(2)	0.029(1)	0.026(1)	0.036(1)	0.0007(8)	–0.0007(8)	–0.0020(8)
N(4)	4*e*	0.2647(2)	0.55247(8)	0.9344(2)	0.029(1)	0.026(1)	0.036(1)	–0.0005(8)	–0.0049(8)	0.0007(8)
N(5)	4*e*	0.1463(2)	0.54072(9)	1.2746(2)	0.038(1)	0.033(1)	0.039(1)	–0.0026(9)	0.0006(9)	0.0007(9)
O(1)	4*e*	0.2697(2)	0.54885(7)	1.2508(2)	0.035(1)	0.037(1)	0.049(1)	0.0015(8)	0.0035(8)	0.0043(8)
O(2)	4*e*	0.1150(3)	0.4990(1)	1.3227(2)	0.065(2)	0.047(1)	0.079(2)	–0.019(1)	0.000(1)	0.022(1)
O(3)	4*e*	0.0574(2)	0.5757(1)	1.2492(2)	0.040(1)	0.063(1)	0.055(1)	0.017(1)	0.0100(9)	0.016(1)
O(4)	4*e*	0.2305(3)	0.31397(9)	0.7716(2)	0.062(2)	0.046(1)	0.079(2)	0.003(1)	0.028(1)	0.023(1)
O(5)	4*e*	0.4765(2)	0.30227(8)	0.7554(2)	0.047(1)	0.033(1)	0.062(1)	–0.0065(9)	–0.0169(9)	0.0102(9)
O(6)	4*e*	0.3164(3)	0.27887(8)	0.5925(2)	0.071(2)	0.031(1)	0.055(1)	–0.007(1)	–0.019(1)	–0.0006(9)
O(7)	4*e*	0.2956(2)	0.56958(7)	0.5294(2)	0.037(1)	0.029(1)	0.052(1)	0.0079(8)	0.0137(8)	0.0054(8)
C(1)	4*e*	0.0718(3)	0.6069(1)	0.7184(2)	0.033(1)	0.028(1)	0.042(1)	–0.000(1)	–0.001(1)	–0.004(1)
C(2)	4*e*	–0.0174(3)	0.6177(1)	0.6210(2)	0.037(1)	0.036(1)	0.041(1)	–0.006(1)	–0.005(1)	–0.003(1)
C(3)	4*e*	–0.0635(3)	0.6690(1)	0.6013(2)	0.034(1)	0.044(2)	0.040(1)	–0.002(1)	–0.005(1)	0.002(1)
C(4)	4*e*	–0.0152(3)	0.7085(1)	0.6790(2)	0.035(1)	0.033(1)	0.042(1)	0.001(1)	–0.002(1)	0.002(1)
C(5)	4*e*	0.0782(3)	0.6956(1)	0.7728(2)	0.032(1)	0.027(1)	0.035(1)	0.001(1)	0.003(1)	–0.001(1)
C(6)	4*e*	0.1423(3)	0.7354(1)	0.8561(2)	0.029(1)	0.026(1)	0.037(1)	0.001(1)	0.0044(9)	0.001(1)
C(7)	4*e*	0.1200(3)	0.7894(1)	0.8431(2)	0.036(1)	0.027(1)	0.046(2)	0.001(1)	–0.002(1)	0.002(1)
C(8)	4*e*	0.1868(3)	0.8240(1)	0.9230(3)	0.045(2)	0.024(1)	0.047(2)	0.001(1)	0.003(1)	–0.001(1)
C(9)	4*e*	0.2742(3)	0.8037(1)	1.0144(2)	0.038(1)	0.030(1)	0.038(1)	–0.003(1)	0.001(1)	–0.003(1)
C(10)	4*e*	0.2915(3)	0.7496(1)	1.0224(2)	0.036(1)	0.030(1)	0.035(1)	–0.001(1)	0.000(1)	–0.0022(9)
C(11)	4*e*	0.4897(3)	0.6695(1)	0.8091(3)	0.037(1)	0.028(1)	0.046(1)	–0.001(1)	0.005(1)	–0.003(1)
C(12)	4*e*	0.5996(3)	0.6623(1)	0.7390(3)	0.038(2)	0.038(2)	0.052(2)	–0.007(1)	0.009(1)	–0.002(1)
C(13)	4*e*	0.6413(3)	0.6112(1)	0.7158(3)	0.036(2)	0.046(2)	0.049(2)	–0.003(1)	0.010(1)	–0.007(1)
C(14)	4*e*	0.5717(3)	0.5689(1)	0.7620(2)	0.032(1)	0.038(1)	0.041(1)	0.004(1)	0.001(1)	–0.007(1)
C(15)	4*e*	0.4595(3)	0.5786(1)	0.8297(2)	0.031(1)	0.029(1)	0.032(1)	0.002(1)	–0.0050(9)	–0.0017(9)
C(16)	4*e*	0.3772(3)	0.5360(1)	0.8800(2)	0.030(1)	0.029(1)	0.032(1)	0.000(1)	–0.0045(9)	–0.0025(9)
C(17)	4*e*	0.4107(3)	0.4829(1)	0.8728(2)	0.039(1)	0.030(1)	0.036(1)	0.007(1)	–0.005(1)	–0.004(1)
C(18)	4*e*	0.3289(3)	0.4453(1)	0.9239(2)	0.045(2)	0.024(1)	0.045(1)	0.002(1)	–0.008(1)	–0.003(1)
C(19)	4*e*	0.2132(3)	0.4622(1)	0.9799(3)	0.043(2)	0.031(1)	0.044(1)	–0.007(1)	–0.007(1)	0.003(1)
C(20)	4*e*	0.1848(3)	0.5160(1)	0.9830(2)	0.035(1)	0.025(1)	0.043(1)	–0.004(1)	–0.002(1)	0.000(1)
C(21)	4*e*	0.3543(3)	0.37853(9)	0.6364(2)	0.033(1)	0.025(1)	0.028(1)	–0.003(1)	–0.0023(9)	0.0002(9)
C(22)	4*e*	0.4754(3)	0.3949(1)	0.5891(2)	0.030(1)	0.025(1)	0.033(1)	0.0019(9)	0.0001(9)	–0.0010(9)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(23)	4*e*	0.4857(2)	0.44633(9)	0.5446(2)	0.027(1)	0.025(1)	0.031(1)	0.0014(9)	0.0004(9)	0.0007(9)
C(24)	4*e*	0.3742(3)	0.48146(9)	0.5497(2)	0.029(1)	0.026(1)	0.030(1)	0.0019(9)	0.0005(9)	0.0005(9)
C(25)	4*e*	0.2515(3)	0.4638(1)	0.5957(2)	0.028(1)	0.028(1)	0.034(1)	0.003(1)	0.0029(9)	0.001(1)
C(26)	4*e*	0.2411(3)	0.4125(1)	0.6386(2)	0.030(1)	0.029(1)	0.032(1)	–0.003(1)	0.0006(9)	0.0000(9)
C(27)	4*e*	0.3853(3)	0.5373(1)	0.5112(2)	0.032(1)	0.026(1)	0.030(1)	0.002(1)	0.0027(9)	0.0014(9)

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