Crystal structure of bis(diethylenetriamino)nickel(II) dinitrate, $[\text{Ni}(\text{dien})_2](\text{NO}_3)_2$

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Abstract

$\text{C}_8\text{H}_{26}\text{N}_8\text{NiO}_6$, monoclinic, $P12_1/c1$ (No. 14), $a = 13.351(2)$ Å, $b = 8.931(1)$ Å, $c = 14.207(2)$ Å, $\beta = 92.61(1)^\circ$, $V = 1692.3$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.030$, $wR_{\text{ref}}(F^2) = 0.072$, $T = 296$ K.

Source of material

An alcohol solution (5 ml) of dien (2 mmol, 206 mg) was added to an aqua-alcohol solution (1: 1 v/v, 5 ml) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 291 mg). The resulting purple solution was stood still in air to evaporate about half of the solvents. Large blue prism crystals of $\text{C}_8\text{H}_{26}\text{N}_8\text{NiO}_6$ were collected by filtration, washed with alcohol and dried with CaCl_2 in vacuum (yield 35%). Analysis: found: C, 24.28%; H, 6.90%; N, 28.35%; calc. for $\text{C}_8\text{H}_{26}\text{N}_8\text{NiO}_6$: C, 24.70%; H, 6.74%; N, 28.80%.

Discussion

Since nickel is present in the active sites of several important classes of metalloproteins, and its potent application in the design and construction of new magnetic materials, study on nickel complexes is of great interest in various aspects of chemistry [1–4]. Molecular magnetism is one of the most active fields in modern inorganic chemistry, and materials exhibiting different magnetic properties have been the focus of many contemporary experimental and theoretical studies. A mononuclear nickel(II) complex with diethylenetriamine is reported here.

The crystal structure of the title complex shows that it comprises of a discrete mononuclear $[\text{Ni}(\text{dien})_2]^{2+}$ cation and two nitrate anions. In each cation, the nickel(II) atom is coordinated by six nitrogen atoms from two dien molecules. The average Ni—N bond distances

(2.148 Å for nickel(II) and primary nitrogens, and 2.086 Å for nickel(II) and secondary nitrogen atoms) are comparable to those in the complexes we reported previously [3,4]. The nickel(II) atom has a greatly distorted octahedral environment with N1, N3, N4 and N6 (the four primary nitrogen atoms) constituting the equatorial plane and the two secondary nitrogen atoms (N2 and N5) occupying the two axial positions. One ($\angle \text{N5–Ni–N2} = 178.72(8)^\circ$) of the three diagonal angles is close to 180° , and the other two diagonals ($\angle \text{N6–Ni–N4} = 162.44(8)^\circ$ and $\angle \text{N1–Ni–N3} = 162.54(8)^\circ$) deviate from 180° , indicating that the coordination around the nickel(II) atom is a largely distorted octahedron. In order to minimize the steric effects, two dien molecules in the $[\text{Ni}(\text{dien})_2]^{2+}$ cation are nearly perpendicular to each other. All the nitrogen atoms in dien molecules and four of the six oxygen atoms in the two nitrate anions participate in the formation of H-bonds (from 2.953(3) Å to 3.187(3) Å), which join the complex into a three-dimensional structure.

Table 1. Data collection and handling.

Crystal:	blue prism, size $0.26 \times 0.40 \times 0.52$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	11.89 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	3441, 2979
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2351
$N(\text{param})_{\text{refined}}$:	209
Program:	SHELXTL [4]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.7485	0.1484	0.2497	0.051
H(1B)	4e	0.8526	0.1230	0.2816	0.051
H(2N)	4e	0.6700	−0.1273	0.4067	0.045
H(3A)	4e	0.7680	0.1099	0.6157	0.047
H(3B)	4e	0.6626	0.1437	0.5932	0.047
H(4A)	4e	0.9133	0.0974	0.5350	0.047
H(4B)	4e	0.9423	0.0979	0.4373	0.047
H(5N)	4e	0.7826	0.3902	0.3788	0.045
H(6A)	4e	0.5754	0.1324	0.3442	0.047
H(6B)	4e	0.5572	0.1508	0.4440	0.047
H(1C)	4e	0.8245	−0.0938	0.2174	0.064
H(1D)	4e	0.7106	−0.0869	0.2405	0.064
H(2C)	4e	0.7865	−0.2650	0.3397	0.060
H(2D)	4e	0.8696	−0.1496	0.3739	0.060
H(3C)	4e	0.8228	−0.1562	0.5403	0.062
H(3D)	4e	0.7333	−0.2693	0.5237	0.062

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Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(4C)	4e	0.6190	−0.0890	0.5709	0.064
H(4D)	4e	0.7031	−0.1055	0.6514	0.064
H(5C)	4e	0.9614	0.3360	0.4302	0.059
H(5D)	4e	0.9822	0.3144	0.5391	0.059
H(6C)	4e	0.8189	0.3757	0.5695	0.056

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(6D)	4e	0.8581	0.5020	0.5033	0.056
H(7C)	4e	0.6628	0.5288	0.4366	0.059
H(7D)	4e	0.6446	0.4078	0.5145	0.059
H(8C)	4e	0.5208	0.3770	0.3965	0.061
H(8D)	4e	0.6012	0.3694	0.3192	0.061

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ni	4e	0.74897(2)	0.12645(3)	0.43229(2)	0.0255(2)	0.0304(2)	0.0315(2)	0.0001(1)	0.0016(1)	−0.0009(1)
O(1)	4e	0.5704(2)	0.6962(3)	0.2894(1)	0.051(1)	0.088(2)	0.062(1)	0.011(1)	0.021(1)	−0.009(1)
O(2)	4e	0.4163(1)	0.6658(2)	0.3236(1)	0.044(1)	0.080(2)	0.058(1)	−0.016(1)	−0.0040(9)	−0.008(1)
O(3)	4e	0.5123(1)	0.8113(3)	0.4073(2)	0.048(1)	0.101(2)	0.065(1)	−0.015(1)	0.007(1)	−0.039(1)
O(4)	4e	0.9587(2)	−0.0252(3)	0.6600(2)	0.075(2)	0.160(3)	0.046(1)	0.028(2)	0.021(1)	−0.011(2)
O(5)	4e	0.8574(2)	0.0708(3)	0.7512(2)	0.061(1)	0.135(2)	0.070(2)	0.041(2)	−0.002(1)	−0.033(2)
O(6)	4e	0.9846(2)	−0.0492(3)	0.8064(2)	0.102(2)	0.139(2)	0.066(2)	0.031(2)	−0.019(2)	0.027(2)
N(1)	4e	0.7889(2)	0.0935(2)	0.2886(1)	0.040(1)	0.050(1)	0.037(1)	0.001(1)	0.0041(9)	−0.001(1)
N(2)	4e	0.7345(1)	−0.1058(2)	0.4255(1)	0.035(1)	0.034(1)	0.044(1)	−0.0015(9)	−0.0020(9)	−0.003(1)
N(3)	4e	0.7148(2)	0.0866(2)	0.5773(1)	0.035(1)	0.048(1)	0.036(1)	0.004(1)	0.0032(9)	0.002(1)
N(4)	4e	0.9036(1)	0.1434(2)	0.4790(1)	0.031(1)	0.046(1)	0.040(1)	0.003(1)	0.0019(9)	−0.001(1)
N(5)	4e	0.7624(1)	0.3592(2)	0.4359(1)	0.040(1)	0.035(1)	0.037(1)	−0.002(1)	−0.0006(9)	0.001(1)
N(6)	4e	0.5961(1)	0.1802(2)	0.3974(2)	0.032(1)	0.042(1)	0.043(1)	−0.0011(9)	−0.0005(9)	−0.000(1)
N(7)	4e	0.5003(2)	0.7240(3)	0.3394(2)	0.039(1)	0.053(1)	0.039(1)	0.005(1)	−0.000(1)	0.002(1)
N(8)	4e	0.9339(2)	−0.0023(3)	0.7394(2)	0.040(1)	0.064(2)	0.038(1)	0.003(1)	0.005(1)	−0.000(1)
C(1)	4e	0.7782(2)	−0.0671(3)	0.2653(2)	0.058(2)	0.059(2)	0.044(2)	−0.002(2)	0.009(1)	−0.019(1)
C(2)	4e	0.7998(2)	−0.1601(3)	0.3528(2)	0.045(2)	0.038(2)	0.066(2)	0.007(1)	0.004(1)	−0.017(1)
C(3)	4e	0.7523(2)	−0.1646(3)	0.5214(2)	0.060(2)	0.035(2)	0.059(2)	−0.005(1)	−0.010(1)	0.009(1)
C(4)	4e	0.6897(2)	−0.0735(3)	0.5868(2)	0.057(2)	0.061(2)	0.043(2)	−0.015(2)	0.004(1)	0.010(1)
C(5)	4e	0.9323(2)	0.3025(3)	0.4879(2)	0.036(2)	0.056(2)	0.056(2)	−0.012(1)	−0.004(1)	−0.005(1)
C(6)	4e	0.8415(2)	0.3965(3)	0.5069(2)	0.050(2)	0.040(2)	0.050(2)	−0.010(1)	−0.005(1)	−0.007(1)
C(7)	4e	0.6627(2)	0.4222(3)	0.4497(2)	0.050(2)	0.035(1)	0.062(2)	0.009(1)	−0.002(1)	−0.005(1)
C(8)	4e	0.5881(2)	0.3441(3)	0.3839(2)	0.044(2)	0.046(2)	0.063(2)	0.015(1)	−0.010(1)	−0.002(1)

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