Crystal structure of aqua-trans-bis(dimethyl sulfoxide-κO)(pyridine-2,6-dicarboxylato-κ²O²,N,O⁶)nickel(II)

Chen Liu, Ashley C. Felts, Daisuke Takahashi, Wynnry Kinden and Khalil A. Abboud

In the title complex, [Ni(C₂H₃NO₄)(C₂H₆OS)₂(H₂O)], the Ni²⁺ cation is situated on a twofold rotation axis and exhibits a distorted octahedral NO₅ coordination environment defined by a tridentate pyridine-2,6-dicarboxylic acid dianion (dpa²⁻), two dimethyl sulfoxide (DMSO) molecules, and a water molecule. In the crystal, the complex molecules are linked by O—H···N and C—H···O hydrogen bonds into a three-dimensional network whereby DMSO molecules from neighboring complexes overlap to form layers parallel to (001), alternating with layers of Ni²⁺-dpa²⁻ moieties. The title complex is isotypic with its cobalt(II) analogue.

1. Chemical context

Crystal engineering plays an important role in the research of molecule-based functional materials by providing an effective approach towards the rational design and preparation of compounds with special structural features (Robin & Fromm, 2006; Cook et al., 2013; Wang et al., 2013). The crystallization of coordination polymers involves both the formation of a local coordination geometry and the propagation and packing of extended polymeric structures in the three-dimensional space. The competition among various types of intermolecular interactions plays a critical role in this process and is strongly influenced by synthetic conditions such as the choice of solvent, temperature, and the molecular features of the starting materials (Li & Du, 2011; Du et al., 2013). Although much has been learned about how the synthetic conditions affect intermolecular interactions and the final crystal structures, the targeted synthesis of a coordination polymer with a particular crystal structure is still a challenge. We recently reported an Ni²⁺-containing one-dimensional coordination polymer based on the tridentate 2,6-pyridine dicarboxylic acid dianion (dpa²⁻) and bridging pyrazine molecules that was prepared by using DMSO as the solvent (Liu et al., 2016). The one-dimensional polymeric structure exhibits π-π interactions that were not previously observed when water was used as the solvent under the same preparation conditions. In order to explore the bridging effect of substituted pyrazine, we have repeated this preparation using 2-chloropyrazine to replace pyrazine under the same synthetic conditions. We report herein the synthesis and crystal structure of the resulting title compound for which incorporation of 2-chloropyrazine was not observed.
2. Structural commentary

The title complex crystallizes in the monoclinic space group C\(2/c\) with half of the molecule in the asymmetric unit, the other half being generated by twofold rotation symmetry. The tridentate 2,6-pyridine dicarboxylic acid dianion coordinates to the Ni\(II\) cation in a meridional fashion via the pyridine nitrogen atom and two carboxylate oxygen atoms (Fig. 1). The reactant 2-chloropyrazine is not found in the structure of the title complex. Instead, the Ni\(II\) cation is further coordinated by two trans-positioned DMSO molecules and a water molecule through their oxygen atoms. Water molecules may have been produced as a result of the reaction between 2,6-pyridine dicarboxylic acid and nickel carbonate. The two Ni1—O1\textsubscript{dpa} bonds have the same length 2.1130 (7) \(\text{Å}\) and the two Ni1—O4\textsubscript{DMSO} bonds have the same length [2.0934 (7) \(\text{Å}\)]. The Ni1—N1 bond length is 1.9613 (12) \(\text{Å}\) and the Ni1—O3 water bond length is 2.0040 (11) \(\text{Å}\), both being significantly shorter than the other four bonds, resulting in a distorted octahedral NO5 coordination environment of the Ni\(II\) cation. These bond lengths are very similar to those observed in the pyrazine-bridged one-dimensional structure reported previously (Liu et al., 2016).

3. Supramolecular features

In the crystal, the mononuclear complexes are linked via an extensive network of C—H···O hydrogen bonds where the hydrogen-bond donors are the C—H groups of DMSO molecules and the O—H groups of the coordinating water molecules (Fig. 2). These hydrogen bonds are mediated by extensive C—H···O and C—H···O hydrogen bonds (Table 1). The crystal packing of the title compound is shown in Fig. 2.

![Figure 1](image1.png)

**Figure 1**
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Unlabeled atoms are related by the symmetry transformation \(-x, y, \frac{1}{2} - z\).

![Figure 2](image2.png)

**Figure 2**
The crystal packing of the title compound, showing hydrogen bonds as dashed lines.

Table 1

| Bond          | D—H   | A | D—A   | A | D···A  | A | D···H  | A |
|---------------|-------|---|-------|---|--------|---|-------|---|
| O3—H3···O2\(a\) | 0.790 (17) | 1.867 (17) | 2.6555 (10) | 176.3 (18) |
| C5—H5···O2\(a\) | 0.98  | 2.58 | 3.3650 (14) | 137 |
| C6—H6A···O2\(ii\) | 0.98  | 2.62 | 3.3504 (13) | 132 |
| C6—H6B···O4\(iii\) | 0.98  | 2.38 | 3.3302 (14) | 162 |

Symmetry codes: (i) \(-x, \frac{1}{2} + y, \frac{1}{2} + z\); (ii) \(-x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z\); (iii) \(-x + \frac{1}{2} + y, \frac{1}{2} - z\).
water molecules and the hydrogen-bond acceptors are the non-coordinating O2 atoms of the 2,6-pyridine dicarboxylic acid dianion and the O4 atoms of the DMSO molecules (Table 1, Fig. 2). In the crystal packing, layers of the NiII–acid dianion and the O4 atoms of the DMSO molecules alternating with layers of DMSO molecules and one or more 2,6-pyridine dicarboxylic non-coordinating O2 atoms of the 2,6-pyridine dicarboxylic acid dianion coordinating to a metal ion.

5. Synthesis and crystallization

Anhydrous NiCO3 (0.33 mmol, 39.56 mg), 2,6-pyridine dicarboxylic acid (0.33 mmol, 55.71 mg), and 2-chloropyrazine (0.50 mmol, 57.26 mg) were mixed in 10 ml dimethyl sulfoxide under stirring for 30 minutes. The resulting mixture was placed in a stainless steel autoclave. The autoclave was then sealed and heated to 373 K for 24 h and cooled to room temperature at a rate of 0.1 K per minute. The resulting green crystals were collected by filtration (yield 30.0%). Selected IR bands (KBr, cm⁻¹): 3134.9 (O—H), 1613.1 (C=O), 1365.8 (C—O), 999.6 (S=O).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The title complex is located on a twofold rotation axis, thus half of it occupies the asymmetric unit. The coordinating water molecule lies on the symmetry axis which requires one hydrogen atom to be located while the other is related by symmetry. This hydrogen atom was obtained from a difference-Fourier map and was refined freely. The other hydrogen atoms were positioned geometrically (C—H = 0.93/1.00 Å) and allowed to ride with Uiso(H) = 1.2/1.5 Ueq(C). Methyl hydrogen atoms were allowed to rotate but not to tip.

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Computing details

Data collection: APEX2 (Bruker, 2014); cell refinement: SAINT (Bruker, 2014); data reduction: SAINT (Bruker, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015b); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 2008); software used to prepare material for publication: publCIF (Westrip, 2010).

Aqua-trans-bis(dimethyl sulfoxide-κO)(pyridine-2,6-dicarboxylato-κ³O²,N,O⁶)nickel(II)

Crystal data

[Ni(C₇H₃NO₄)(C₂H₆OS)₂(H₂O)]

Mr = 398.08

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 9953 reflections
θ = 2.0–28.0°
µ = 1.53 mm⁻¹
T = 100 K

Monoclinic, C2/c

a = 9.8767 (5) Å

b = 11.4597 (5) Å

c = 14.3166 (7) Å

β = 104.4577 (7)°

V = 1569.09 (13) Å³

Z = 4

Data collection

Bruker APEXII DUO CCD
diffractometer

Radiation source: fine-focus sealed tube

phi and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2014)

Tmin = 0.678, Tmax = 0.910

18746 measured reflections

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.016

wR(F²) = 0.043

S = 1.06

1936 reflections

108 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo²) + (0.0225P)² + 1.5829P]

where P = (Fo² + 2Fc²)/3

(Δ/σ)max = 0.001

Δρmax = 0.46 e Å⁻³

Δρmin = −0.24 e Å⁻³
Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. All H atoms were positioned geometrically (C—H = 0.93/1.00 Å) and allowed to ride with $U_{	ext{iso}}$(H) = 1.2/1.5$U_{	ext{eq}}$(C). Methyl ones were allowed to rotate around the corresponding C—C. The Ni complex is located on a 2-fold rotational axis of symmetry thus half of it occupies the asymmetric unit. The coordinated water molecule lies on the symmetry axis which requires one proton to be located while the other is related by the symmetry. The water proton was obtained from a Difference Fourier map and refined freely.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

|    | x     | y     | z     | $U_{	ext{iso}}^*/U_{	ext{eq}}$ |
|----|-------|-------|-------|-------------------------------|
| Ni1| 0.0000| 0.32387(2)| 0.2500| 0.00867(6) |
| S1 | 0.08818(3)| 0.40008(2)| 0.46249(2)| 0.01346(7) |
| O1 | 0.16898(7)| 0.28806(6)| 0.18844(5)| 0.01235(14) |
| O2 | 0.29613(8)| 0.13796(7)| 0.15626(6)| 0.01647(15) |
| O3 | 0.0000| 0.49874(10)| 0.2500| 0.0186(2) |
| H3 | 0.0626(17)| 0.5376(15)| 0.2789(12)| 0.033(4)* |
| O4 | 0.13764(8)| 0.32772(6)| 0.38736(5)| 0.01257(14) |
| N1 | 0.0000| 0.15272(10)| 0.2500| 0.0095(2) |
| C1 | 0.0000| −0.08533(12)| 0.2500| 0.0151(3) |
| H1A| 0.0000| −0.1682| 0.2500| 0.016* |
| C2 | 0.10055(10)| −0.02463(9)| 0.21553(7)| 0.01328(18) |
| H2A| 0.1691| −0.0650| 0.1919| 0.016* |
| C3 | 0.09697(10)| 0.09684(8)| 0.21703(7)| 0.01026(17) |
| C4 | 0.19693(10)| 0.18040(9)| 0.18444(7)| 0.01114(18) |
| C5 | 0.24415(12)| 0.46192(10)| 0.53687(8)| 0.0204(2) |
| H5A| 0.2213| 0.5058| 0.5897| 0.031* |
| H5B| 0.2865| 0.5145| 0.4982| 0.031* |
| H5C| 0.3102| 0.3994| 0.5636| 0.031* |
| C6 | 0.04879(12)| 0.29765(11)| 0.54609(8)| 0.0213(2) |
| H6A| 0.0278| 0.3397| 0.6004| 0.032* |
| H6B| 0.1294| 0.2463| 0.5699| 0.032* |
| H6C| −0.0324| 0.2508| 0.5138| 0.032* |

Atomic displacement parameters ($\AA^2$)

|    | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|----|----------|----------|----------|----------|----------|----------|
| Ni1 | 0.00926(9) | 0.00735(9) | 0.00927(9) | 0.000 | 0.00206(6) | 0.000 |
| S1 | 0.01554(12) | 0.01458(12) | 0.00942(12) | 0.00621(9) | 0.00155(9) | −0.00145(8) |
| O1 | 0.0122(3) | 0.0109(3) | 0.0147(3) | −0.0010(3) | 0.0048(3) | −0.0004(3) |
| O2 | 0.0138(3) | 0.0181(4) | 0.0196(4) | 0.0040(3) | 0.0081(3) | 0.0023(3) |
| O3 | 0.0178(5) | 0.0085(5) | 0.0237(6) | 0.000 | −0.0057(4) | 0.000 |
| O4 | 0.0131(3) | 0.0143(3) | 0.0099(3) | 0.0037(3) | 0.0021(3) | −0.0030(2) |
| N1 | 0.0102(5) | 0.0094(5) | 0.0083(5) | 0.000 | 0.0011(4) | 0.000 |
| C1 | 0.0189(7) | 0.0091(6) | 0.0170(7) | 0.000 | 0.0038(5) | 0.000 |
| C2 | 0.0143(4) | 0.0116(4) | 0.0136(4) | 0.0025(4) | 0.0028(3) | −0.0008(3) |
Geometric parameters (Å, °)

|                  | x           | y           | z           | x           | y           | z           | x           | y           | z           |
|------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Ni1—N1           | 1.9613 (12) | Ni1—C3i     | 1.3327 (11) | Ni1—C3i     | 1.3994 (12) |
| Ni1—O3           | 2.0040 (11) | Ni1—C2i     | 1.3995 (12) | Ni1—C2i     | 1.3995 (12) |
| Ni1—O4           | 2.0934 (7)  | Ni1—C1     | 0.9500      | Ni1—C1     | 0.9500      |
| Ni1—O4i          | 2.0934 (7)  | Ni1—O1i    | 1.3927 (14) | Ni1—O1i    | 1.3927 (14) |
| Ni1—O1           | 2.1130 (7)  | Ni1—O1     | 0.9500      | Ni1—O1     | 0.9500      |
| S1—O4            | 1.5316 (7)  | C1—C2      | 1.5296 (13) | C1—C2      | 1.5296 (13) |
| S1—C5            | 1.7860 (11) | C2—C1      | 0.9800      | C2—C1      | 0.9800      |
| S1—C6            | 1.7872 (12) | C2—C5      | 0.9800      | C2—C5      | 0.9800      |
| O1—C4            | 1.2686 (12) | C2—C6      | 0.9800      | C2—C6      | 0.9800      |
| O2—C4            | 1.2476 (12) | C3—C2      | 0.9800      | C3—C2      | 0.9800      |
| O3—H3            | 0.790 (17)  | C3—C4      | 0.9800      | C3—C4      | 0.9800      |
| N1—C3            | 1.3326 (11) | C3—N1      | 0.9800      | C3—N1      | 0.9800      |

Symmetry code: (i) −x, y, −z+1/2.

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### Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A     | D—H···A |
|-------------|------|-------|-----------|---------|
| O3—H3···O2   | 0.790 (17) | 1.867 (17) | 2.6555 (10) | 176.3 (18) |
| C5—H5B···O2  | 0.98 | 2.58  | 3.3650 (14) | 137     |
| C6—H6A···O2  | 0.98 | 2.62  | 3.3504 (13) | 132     |
| C6—H6B···O4  | 0.98 | 2.38  | 3.3302 (14) | 162     |

Symmetry codes: (ii) −x+1/2, y+1/2, −z+1/2; (iii) x−1/2, −y+1/2, z+1/2; (iv) −x+1/2, −y+1/2, −z+1.