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A second crystal form of $[Ni(2,2'\text{-bipyridine})(H_2O)_3(NO_3)](NO_3)$ featuring a different molecular orientation

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ABSTRACT

The molecular structure of a second form of $[Ni(2,2'\text{-bipyridine})(H_2O)_3(NO_3)](NO_3)$ is reported. The previous report is for a blue monoclinic polymorph. The second form is orthorhombic and crystallises as green blocks with unit cell parameters $a = 9.1201(12)$ Å, $b = 14.444(2)$ Å, $c = 21.805(4)$ Å, $V = 2872.4(8)$ Å^3, $Z = 8$. The complex was characterised by elemental analysis, infrared spectroscopy, UV–Vis spectroscopy, and thermogravimetry. The bipyridine acts as a bidentate ligand to Ni^{2+} and the octahedral coordination is completed by three water molecules and one monodentate nitrate ion. A second nitrate forms hydrogen bonds to the bound water molecules. The difference between the two forms in terms of the molecular geometry is described in relation to other similar compounds. The key difference between the two forms is the orientation of the two nitrate anions, and hence the hydrogen bonding present.

1. Introduction

2,2′-Bipyridine is one of the most widely employed ligands in the synthesis of metal complexes [1]. At present there are over 5500 structures reported that feature 2,2′-bipyridine bound to a transition metal [2]. The vast majority of these (>99.6%) feature 2,2′-bipyridine acting as a bidentate ligand. There are many further examples that contain derivatives of 2,2′-bipyridine [1] and other similar ligands [3]. Complexes containing 2,2′-bipyridine have been widely used in studies of electron transfer [4] and chemiluminescence [5], and as model systems for optical isomerism [6].

In contrast to purely organic systems, it is somewhat unusual to observe polymorphism in inorganic compounds, particularly where two or more polymorphs are stable at the same temperature. Often the difference in crystal packing is accompanied by a change in colour, as is the case for some compounds containing 2,2′-bipyridine. For example, $Pt(2,2'\text{-bipyridine})Cl_2$ exists as two different crystal forms under ambient conditions depending on the solvent employed: a red form [7] that crystallises in space group *Cmcm* and a yellow form [8] that adopts space group *Pbca*.

2,2′-Bipyridine has been utilised as an auxiliary (non-framework) ligand in the synthesis of coordination polymers. For example it has been used with metal ions and the framework formers 1,3,5-benzenetricarboxylate [9], squarate [10], and succinate [11]. We sought to employ 1,4-benzenedicarboxylic acid in the presence of a cation and 2,2′-bipyridine to synthesise similar frameworks. Our aim was to control the initial pH and ratio of reactants to influence the product obtained from hydrothermal synthesis. Here we report the structure of a second crystal form of the compound $[Ni(2,2'\text{-bipyridine})(H_2O)_3NO_3](NO_3)$ and demonstrate that the structure determined at low temperature persists above room temperature. The relationship with earlier structure of the same composition is described in detail.

2. Materials and methods

2.1. Microwave synthesis

Crystals of the title compound were grown from a solution of 0.5826 g nickel(II) nitrate hexahydrate ($Ni(NO_3)\cdot 6H_2O$, Carlo Erba 99%) with 0.1562 g 2,2′-bipyridine ($C_{10}H_8N_2$, Fluka >99%) and 0.1670 g terephthalic acid ($C_6H_4(COOH)_2$, BDH 97%) in 10.00 cm^3 deionized water (Ni:nitrate:2,2′-bipyridine:terephthalic:water molar ratio = 2:2:1:1:556). Reagents were loaded into a 23 cm^3 Teflon lined pressure vessel. The reaction was performed for 3 h, under an autogenous pressure generated at 630 W (96 °C) using a domestic microwave oven (Whirlpool XT – 25ES/S, 900 W, 2.45 GHz). The initial pH of the solution was 3, measured using universal pH strips (Merck, 1.09535.0001). It may be noted that the pH of the solution did not change after the reaction.

The crystals obtained were present as aggregates of mid-green plates, separated from supernatant by filtration, then washed with deionized water and dried in air. The sample appeared visibly

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homogeneous under magnification. X-ray diffraction analysis of several crystals at room temperature confirmed this. Satisfactory chemical analysis data were obtained for **2**.

2.2. X-ray diffraction analysis

Routine X-ray diffraction data collection and structure solution procedures were adopted. A single crystal of dimensions $0.21 \times 0.11 \times 0.06\ \mathrm{mm}^3$ was cut from a larger aggregate, coated in perfluoropolyether oil and mounted at the end of a glass fibre. Data were collected in series of ω-scans using a Stoe IPDS2 diffractometer operating with Mo radiation. The crystal temperature was maintained using an Oxford Instruments nitrogen gas cryostream. The structure was solved by direct methods [12]. Full matrix least squares refinement against F^2 implemented within SHELXL [12] was employed for structure refinement.

Hydrogen atoms attached to 2,2′-bipyridine were positioned and refined using a riding model. Those of water were located in difference Fourier maps and their positions refined subject to the restraint that all O–H bond lengths were the same with a standard deviation 0.03 Å. Sensible restraints were also applied to the geometry of the water molecules.

For the first data collection the crystal was held at 120 K and a full set of data collected. Subsequently, the crystal was glued to the fibre and further sets of data frames collected, sufficient to determine the unit cell. The unit cell was determined at a further nine temperatures. A set of twenty data frames were collected at 353 K and the data from these were used to refine the structure at this temperature.

Routine X-ray diffraction data collection and structure solution procedures were adopted for form **1** using a crystal of dimensions $0.48 \times 0.12 \times 0.11\ \mathrm{mm}^3$.

2.3. Spectroscopic characterisation

IR spectra were collected from ground crystals of **2** as a KBr disc, using a Bruker Tensor 27 FT-IR spectrometer (4000–400 cm^{-1}, resolution 0.5 cm^{-1}).

UV–Vis reflectance spectra were collected from lightly ground crystals loaded in a $BaSO_4$ matrix using a Cary 5E UV-vis-NIR Spectrophotometer.

2.4. Thermogravimetry

Samples were placed into platinum pans, loaded into a Mettler-Toledo TGA/DSC1 Thermogravimetric Analyzer and heated under a flow of nitrogen from room temperature to 1000 °C at a ramp rate of 30 °C min^{-1}.

3. Results and discussion

3.1. Crystal structure analysis

A report of the structure of [Ni(2,2′-bipyridine)$(H_2O)_3NO_3$](NO_3) at room temperature has appeared previously [13]. This compound (hereafter **1**) crystallises in the centrosymmetric monoclinic space group *P*2$_1$/*c* and is isostructural with the manganese analogue [14]. Here we describe a second crystal form (**2**) for this compound obtained under microwave-assisted hydrothermal conditions that displays the same connectivity as **1**, but differs in the orientation of the groups present. A description of the structure of **1** and its relation to **2** appears later.

The structure of **2** was initially determined at 120 K. At this temperature [Ni(2,2′-bipyridine)$(H_2O)_3NO_3$](NO_3) was found to crystallise in the centrosymmetric space group *Pbca* (number 61) with $Z' = 1$. Each Ni^{2+} is approximately octahedral in coordination geometry, bound to a bidentate molecule of 2,2′-bipyridine, three molecules of water, and a monodentate nitrate. The lengths of the coordination bonds about nickel are in good agreement with others of similar complexes. The CCDC [2] has 133 structures containing nickel, bipyridine, and ligated water. For these, the mean Ni–O (water) and Ni–N bond lengths are 2.08(4) and 2.07(4) Å, respectively, while the mean N–Ni–N angle is 79.0(15)°. For form **2** at 120 K, the bond lengths are 2.054(4), 2.078(4) and 2.083(5) Å (Ni–O), and 2.050(5) and 2.081(5) Å (Ni–N), while the N–Ni–N angle is 79.4(2)°. For 63 structures with monodentate nitrate and at least two pyridyl donors, the mean Ni–O (nitrate) bond length is 2.10(7)Å and for **2** this bond length is 2.082(4). A further uncoordinated nitrate anion forms hydrogen bonds to the bound water. The distance between hydrogen atoms of water and unbound nitrate are: 1.91(3) Å (O1–H1B···O10) and 1.94(3) Å (O2–H2B···O9). An ORTEP representation of **2** is shown in Fig. 1. Basic crystal data are given in Table 1.

The bound nitrate forms a single hydrogen bond to water in an adjacent complex. Every hydrogen atom of the three water molecules is involved in hydrogen bonding to nitrate. A full list of these is given in Table 2. There is a tendency to short, linear, hydrogen bonds with few bifurcated interactions (Fig. 2b). The combination of hydrogen bonds between the complexes and unbound nitrate generates infinite puckered sheets of thickness 5.552 Å that extend in the *xy* plane. These sheets are two molecules thick and the [Ni(2,2′-bipyridine)$(H_2O)_3NO_3$]$^+$ ions are arranged such that the aromatic rings of the bipyridine are approximately perpendicular to the layers and project above and below them. The sheets are stacked along *c* in ABAB fashion at a separation of *c*/2 (10.903(4) Å). This arrangement facilitates two types of intermolecular interactions. The hydrogen bonding within the layer is illustrated in Fig. 2. Interdigitation of the aromatic rings on adjacent layers leads to relatively close approach of the π-systems of neighbouring bipyridine ligands. The distance between these is of the order of 3.43 Å; for example C7^i ($i = x - ½$, y, $1 - z$) lies 3.376(6) Å above the ring formed from N1 and C1–C5. This close approach is suggestive of a π–π interaction. In addition the proximity of H3 to an adjacent bipyridine (H3···C9^{ii} = 2.80 Å, $ii = -x$,

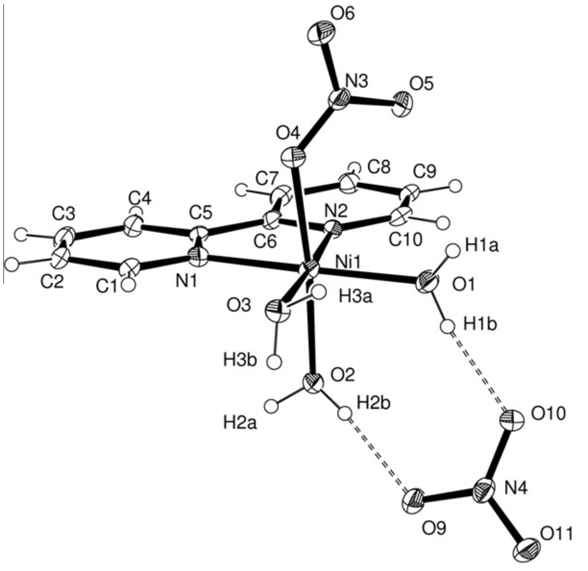

Fig. 1. ORTEP plot of the asymmetric unit of **2**. Atoms are shown as 30% thermal ellipsoids. Hydrogen bonds are illustrated by dashed lines. Selected bond lengths: Ni1–N1 2.081(5) Å, Ni1–N2 2.050(5) Å, Ni1–O1 2.054(4) Å, Ni1–O2 2.078(4) Å, Ni1–O3 2.083(5) Å, Ni1–O4 2.082(4) Å.