

Synthesis and structures of nickel(II) complexes with xanthurenate ions



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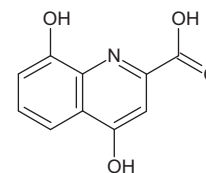
ABSTRACT

The reaction of nickel(II) chloride with xanthurenic acid afforded two crystalline products, $[\text{Ni}(\text{HXan})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**1**) and $[\text{Ni}_3(\text{Xan})_2(\text{H}_2\text{O})_{10}][\text{Ni}(\text{Xan})_2] \cdot 4\{(\text{CH}_3)_2\text{CO}\} \cdot 2\text{H}_2\text{O}$ (**2**), with HXan^- and Xan^{2-} standing for the deprotonated forms of the acid. Both compounds were unambiguously characterized by means of X-ray structure analysis. Their solid state structures give evidence of a presence of different xanthurenate ions and their tautomeric forms in the solution. Compound **1** is a mononuclear nickel (II) complex with metal ion in a nearly octahedral environment of six ligands: four aqua ligands and two *trans* positioned HXan^- ions, each coordinated in a monodentate manner *via* a carboxylate oxygen. Compound **2** consists of trinuclear complex cations $[\text{Ni}_3(\text{Xan})_2(\text{H}_2\text{O})_{10}]^{2+}$ and mononuclear complex anions $[\text{Ni}(\text{Xan})_2]^{2-}$. The Xan^{2-} ions of the complex ions in **2** are not the same, they differ in the position of the ionized hydroxyl moiety. With both compounds possessing several hydrogen bond donors and acceptors, intricate patterns of intramolecular connectivity may be observed in their solid state structures.

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1. Introduction

The biological role of xanthurenic acid (IUPAC name: 8-hydroxy-4-oxo-1H-quinoline-2-carboxylic acid) was first recognized in 1943 [1]. It is a tryptophan metabolite whose presence was observed in the urine of humans, monkeys and rats in the case of vitamin B₆ deficiency [2,3]. Although little is known of the role of xanthurenic acid in the cell, several studies reported the acid to be toxic [4]. Among other, it forms a complex with insulin and damages pancreatic β cells [5,6]. Xanthurenic acid, from hereafter abbreviated as H_2Xan , possesses three functional groups (Scheme 1) which can give off their protons and thereupon act together with quinoline nitrogen as donors in the formation of complexes with the transition metal ions. Provided the carboxyl functional group is ionized and the quinoline nitrogen remains intact, the relative positions of the carboxylate and 8-hydroxyl are optimal for a tridentate chelating coordination. In $[\text{VO}_2(\text{Xan})]^-$, the first xanthurenato complex, whose structure was determined by single-crystal X-ray structure analysis, the coordination manner of the Xan^{2-} ion was tridentate chelating *via* a carboxylate oxygen, a quinoline nitrogen and a deprotonated 8-hydroxyl moiety [7]. The xanthurenate ions of the same type, *i.e.*, with the same functional groups having undergone ionization and having employed the same binding manner, were observed also in two copper(II)



Scheme 1. Xanthurenic acid, H_2Xan .

complexes, $[\text{Cu}(\text{Xan})(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{Xan})(\text{H}_2\text{O})(\text{NA})]$ (NA = nicotinamide). The copper(II) complexes were prepared in our group as a result of the ongoing studies of the role of xanthurenic acid in the coordination chemistry of various transition metal ions [8–10]. The acid and both copper(II) complexes were tested for their antioxidant activity. One of the tested compounds, $[\text{Cu}(\text{Xan})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, met the expectations: it displayed a more pronounced 2,2-diphenyl-1-picrylhydrazyl scavenging activity than the acid itself. Our research efforts have been focused recently on nickel(II). Nickel forms part of the active sites in several metalloenzymes that play important roles in the global nitrogen, carbon and oxygen cycles, as exemplified by nickel superoxide dismutase, carbon monoxide dehydrogenase etc. [11]. It appears that nickel has been selected for this role for its ability to cycle through redox states from 1+ to 3+ and its extreme plasticity in coordination [12]. Prior to this work, nickel(II) complexes with the anions of two related acids, 2-quinolinecarboxylic acid (Hqc) and 8-hydroxy-2-quinolinecarboxylic acid (Hhqc), were prepared [13–16]. Whereas the

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2-quinolinecarboxylate adopted a bidentate chelating coordination *via* nitrogen and carboxylate oxygen, the anion of 8-hydroxy-2-quinolinecarboxylic acid employed in coordination also 8-hydroxyl moiety and coordinated in a tridentate chelating manner. One of our goals was to assess the influence of another functional group present in xanthurenic acid, *i.e.*, the hydroxyl function at position 4, over the coordination manner and/or the composition of the resulting complex. Herein, we report on the preparation and the structural characterization of two novel compounds, $[\text{Ni}(\text{HXan})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**1**) and $[\text{Ni}_3(\text{Xan})_2(\text{H}_2\text{O})_{10}][\text{Ni}(\text{Xan})_2] \cdot 4\{(\text{CH}_3)_2\text{CO}\} \cdot 2\text{H}_2\text{O}$ (**2**).

2. Experimental

2.1. General

Chemicals were obtained from Aldrich Chemical Co. They were used without further purification. Distilled water was used for the preparation of solutions. For the adjustment of pH, a 0.10 M solution of sodium hydroxide was used. pH was measured using a Mettler Toledo MP 120 pH meter with a Mettler Toledo Inlab Expert Pro combination electrode. Elemental analyses were performed by the Chemistry Department service at the University of Ljubljana. The infrared spectra were measured on solid samples using a Perkin Elmer Spectrum 100 series FT-IR spectrometer, equipped with ATR.

2.2. Preparation procedures

Xanthurenic acid (103 mg, 0.50 mmol) was dissolved in water (4 mL). pH of the resulting solution was adjusted to 7 with a sodium hydroxide solution. Nickel(II) chloride hexahydrate (60 mg, 0.25 mmol) was dissolved in water (4.0 mL). The solution of nickel(II) chloride was added dropwise to the xanthurenate solution with constant stirring at room temperature. After 2 h, a yellow-green precipitate was filtered off, washed with acetone and thoroughly dried. The solid was identified by infrared spectroscopy as compound **1** with impurities. *The recrystallization of 1*: poorly soluble solid (0.1 mg/mL) was dissolved in the mixture of acetonitrile and water (25:75, v/v) under reflux. The resulting solution was left in an open beaker at 8 °C. After one week, the yellow-green plate-like crystals of **1** were obtained in a 35% yield. The crystals of **1** are stable in the air and are poorly soluble in water, methanol or ethanol. Found: C, 37.70; H, 5.12; N, 4.70%. $\text{C}_{20}\text{H}_{32}\text{N}_2\text{NiO}_{18}$ requires C, 37.12; H, 4.98; N, 4.33%. IR (ATR, cm^{-1}): 3612w, 3354m, 1627w, 1596m, 1571m, 1552w, 1473s, 1448s, 1415vs, 1377vvs, 1328s, 1289vs, 1228m, 1178vs, 1156s, 1114m, 1064s, 1021vs, 861vs, 796vs, 773vs, 738vvs, 708s. *The preparation of 2*: poorly soluble compound **1** (0.02 mg/mL) was dissolved in the mixture of acetone and water (25:75, v/v). After slow evaporation of solvents at ambient conditions, a small amount of the pale yellow block-like crystals of **2** was obtained. The crystals of **2** decompose when taken out from the mother liquor. They are poorly soluble in water, methanol or ethanol. Found: C, 40.09; H, 4.42; N, 4.55%. $\text{C}_{46}\text{H}_{56}\text{N}_4\text{Ni}_4\text{O}_{30}$ (molecular formula of a residue with one half of the acetone molecules of crystallization) requires C, 40.04; H, 4.09; N, 4.06%. IR (ATR, cm^{-1}): 3342vs, 1630s, 1592vs, 1573vs, 1467vs, 1377vvs, 1334vs, 1285vs, 1226m, 1180vs, 1158m, 1115m, 1071m, 1020vs, 969w, 931w, 900w, 865s, 820m, 797m, 777m, 736vvs, 691vvs.

2.3. X-ray structure determinations

Each crystal was mounted on the tip of a glass fiber with a small amount of silicon grease and transferred to a goniometer head.

Data were collected on a Nonius Kappa CCD (compound **1**) or an Agilent SuperNova (**2**) diffractometer, using graphite monochromated Mo K α radiation at 150 K. Data reduction and integration were performed with the software package DENZO-SMN (data for **1**) [17] or CRYSLIS PRO (**2**) [18]. Corrections for the absorption (multi-scan) were made in both cases. The coordinates of the majority of non-hydrogen atoms were found *via* direct methods using the structure solution program SHELXS [19]. The positions of the remaining non-hydrogen atoms were located by use of a combination of least-squares refinement and difference Fourier maps in the SHELXL-97 program [19]. The crystals of **2** contained interstitial solvent molecules of water and acetone: a water and two acetone molecules per asymmetric unit. One of the two acetone molecules appeared as a set of disordered peaks in the electron density map. The contribution of the disordered solvent to the scattering factors was accounted for by the SQUEEZE program [20]. The positions of OH, NH⁺ and water hydrogen atoms in **1** were unambiguously located from the residual electron density maps. The same pertains to the hydrogen atoms of OH groups and coordinated water molecules in compound **2**. The hydrogen atom positions of the solvent water molecule in **2** could not be located. In both structures, all other hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. Figures depicting the structures were prepared by ORTEP3 [21], Mercury [22] and CrystalMaker [23]. Crystal data for **1**, $\text{C}_{20}\text{H}_{32}\text{N}_2\text{NiO}_{18}$ (647.19 g mol⁻¹): monoclinic *C* 2/*c*, $a = 27.4906(6)$ Å, $b = 6.6601(2)$ Å, $c = 16.3440(4)$ Å, $\beta = 122.0365(15)^\circ$, $V = 2536.71(11)$ Å³, $Z = 4$, $\rho_{\text{calc.}} = 1.695$ g cm⁻³, $\mu = 0.858$ mm⁻¹; 5449 reflections collected (2911 independent, $R_{\text{int}} = 0.0199$). The final residues were $R = 0.0402$, and $wR_2 = 0.1119$ [2460 reflections, $I > 2\sigma(I)$], and $R = 0.0499$, and $wR_2 = 0.1171$ [all data]. Crystal data for **2**, $\text{C}_{52}\text{H}_{68}\text{N}_4\text{Ni}_4\text{O}_{32}$ (1495.94 g mol⁻¹): monoclinic *I* 2/*a*, $a = 20.3636(4)$ Å, $b = 13.4334(3)$ Å, $c = 21.9418(5)$ Å, $\beta = 102.034(2)^\circ$, $V = 5870.3(2)$ Å³, $Z = 4$, $\rho_{\text{calc.}} = 1.693$ g cm⁻³, $\mu = 1.365$ mm⁻¹; 19416 reflections collected (7821 independent, $R_{\text{int}} = 0.0271$). The final residues were $R = 0.0384$, and $wR_2 = 0.1026$ [6526 reflections, $I > 2\sigma(I)$], and $R = 0.0478$, and $wR_2 = 0.1081$ [all data].

3. Results and discussion

3.1. Solid state structures

The crystal structure of $[\text{Ni}(\text{HXan})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**1**) consists of nickel(II) complex molecules and water molecules of crystallization. The ORTEP drawing of the $[\text{Ni}(\text{HXan})_2(\text{H}_2\text{O})_4]$ complex is shown in Fig. 1, whereas the relevant bond lengths and angles are given in Table 1. The complex has crystallographically imposed symmetry, with a central metal ion lying on a proper twofold rotation axis. An almost octahedral coordination environment of nickel ion consists of four aqua ligands and two xanthurenate ions, HXan⁻. A pair of nearly coplanar HXan⁻ ligands are positioned *trans* to each other. There are several charged functional groups in the xanthurenate ion: an ionized carboxyl group, a protonated nitrogen and a deprotonated hydroxyl at position 4.¹ The other hydroxyl functional group of the parent xanthurenic acid, *i.e.*, the one at position 8, has remained intact. As a result, the ion bears a negative charge of -1. The bonding pattern within the HXan⁻ ion agrees with the location of ionized functional groups: the C–O bond for the hydroxyl moiety is 1.348(3) Å, whereas the corresponding bond for the deprotonated group is significantly shorter, *i.e.*, 1.287

¹ The labeling scheme used for the atoms of the xanthurenate ions in compounds **1** and **2** does not follow the numbering used for the IUPAC name. For example, in compound **1** the label O(2) pertains to the OH oxygen at position 8 and the label O(7) to the OH oxygen at position 4. Similar labeling scheme was used for **2**.

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