THIENO[3,2-*c*]PYRIDINE COMPLEX OF Ni(II) WITH UNUSUAL MAGNETIC PROPERTIES

JOZEF MIKLOVIČ[1], PETER BARAN[2], ROMAN BOČA[1]

[1] *Department of Chemistry, Faculty of Natural Science, University of SS. Cyril and Methodius in Trnava, Trnava, SK-917 01, Slovak Republic (roman.boca@ucm.sk)*
[2] *Department of Chemistry, Juniata College, Huntington, PA 16652, USA*

Abstract: Thieno[3,2-*c*]pyridine (*thpy*) has been prepared in a free form and embodied into the [Ni(*thpy*)$_2$(H$_2$O)$_2$(*ac*)$_2$] complex as a ligand. The X-ray structure shows a molecular structure of the complex with Ni–O(*ac*) = 2.059, Ni–OH$_2$ = 2.078, and Ni–N(*thpy*) = 2.124 Å. Electronically the complex behaves like a compressed tetragonal bipyramid. The molecular units are linked into a complex system of hydrogen bonds. Two units show a π–π stacking of the aromatic rings (3.8 Å). There are planes of tetragons formed of the nickel atom with the in-plane Ni...Ni separation of 7.74 Å and the inter-plane Ni...Ni contacts at a = 9.65 Å. The effective magnetic moment shows a gradual decrease on cooling from the room temperature and an abrupt drop below 20 K typical for the zero-field splitting of S = 1 systems. Above the room temperature the effective magnetic moment shows anomalies – a decrease and then an increase.

Key words: Ni(II) complex, X-ray structure analysis, magnetic data, zero-field splitting

1. Introduction

At the present, one of the dynamically developed field of heterocyclic chemistry is represented by the synthesis and characterization of new systems that can form coordination compounds with transition metals. Structural and spectral studies of complexes containing *N*-heterocyclic ligands are of a considerable interest from the standpoint of coordination and bioinorganic chemistry. Especially quinoline isosteres (furopyridines, thienopyridines) in which the benzene ring is replaced by furan or thiophene ring are components of many biologically active compounds. New pharmacophores with potential antipsychotic activity posses the thieno[3,2-*c*] and furo[3,2-*c*]pyridine ring system (NEW *et al.*, 1989). Therefore, efficient synthetic methods for these types of heterocycles are of a great interest. The synthesis of the furo[3,2-*c*]pyridines and pyrrolo[2′,3′,4,5]furo[3,2-*c*]pyridines has already been reported (KRUTOŠÍKOVÁ *et al.*, 1994; BENCKOVÁ *et al.*, 1995; KRUTOŠÍKOVÁ *et al.*, 1996; JURISTOVÁ *et al.*, 2007).

The above heterocycles can be readily coordinated to metal centres through the *N*-donor atom. The coordination chemistry of them has already been outlined (MIKLOVIČ *et al.,* 2004; BARAN *et al.*, 2005). However, systematic studies need much more effort, and in addition to the structural features also the spectral and magnetic data would be interesting. Some data along this direction has also been published (BOČA *et al.*, 2008; TITIŠ *et al.*, 2010).

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2. Experimental section

The ligand thieno[3,2-*c*]pyridine (*thpy*) has been prepared by a procedure described elsewhere (ELOY *et al*., 1970).

Nickel(II) acetate tetrahydrate (0.249 g, 1 mmol) has been dissolved in 4 cm^3 of a dry ethanol and on stirring a solution containing thieno[3,2-*c*]pyridine (0.405 g, 3 mmol) in 3 cm^3 of dry ethanol has been added. After 30 min of stirring, the volume has been reduced to a half using the vacuum rotational evaporator. On cooling a precipitate was separated, washed with 1 cm^3 of cold ethanol and dried. Anal. Calcd for $C_{18}H_{20}N_2NiO_6S_2$ (hereafter **1**): C, 44.7; H, 4.17; N, 5.80; S, 13.3. Found: C, 44.9; H, 4.10; N, 5.60; S, 13.3 %. Single crystals suitable for the X-ray analysis have been obtained by crystallization from the diethylether/tetrahydrofuran mixture (1 : 1).

IR spectra were measured on Magna-FTIR-750 spectrometer (Nicolet) in KBr pellets in the 4 000 – 400 cm^{-1} region. Carboxyl stretching frequencies can indicate a coordination mode of acetate anion. Following a tentative assignment for **1** (ν_a(COO) = 1 596, ν_s(COO) = 1 336 cm^{-1}), the difference in observed stretching modes $\Delta = 260$ cm^{-1} indicates a unidentate coordination mode for the acetate anions, what is consistent with findings from a crystallographic studies.

Electronic spectra were measured in the Nujol mull on Specord-200 (Analytical Jena). They show three principal spin-allowed d-d bands with peaks at the positions of 9 730 ($^3T_{2g} \leftarrow {}^3A_{2g}$), 15 940 ($^3T_{1g}(F) \leftarrow {}^3A_{2g}$), and 26 560 cm^{-1} ($^3T_{1g}(P) \leftarrow {}^3A_{2g}$), respectively. However, there exist arms at 13 880 and 22 500 cm^{-1}, which confirm a symmetry reduction to the tetragonal and/or rhombic pattern.

Diffraction data for **1** were collected on a three-circle-platform diffractometer equipped with a CCD detector (Bruker, SMART 1κ). The frame data were acquired with the SMART software at 300 K using Mo Kα radiation. The structure was solved by direct method (SHELX-90) and refined by least-squares method on F^2 (SHELXTL-93, incorporated SHELXTL v5.1). Hydrogen atoms were geometrically positioned and left riding on their parent atoms during structure refinement. The structural data for **1**: empirical formula, $C_{18}H_{20}N_2NiO_6S_2$; formula mass, 483.19; colour, pale turquoise; crystal system, monoclinic; space group, P2(1)/c; a = 9.6513(15) Å; b = 12.7271(19) Å; c = 8.8086(13); $\alpha = \gamma = 90$ deg; $\beta = 110.143(2)$ deg; V = 1 015.8(3) $Å^3$; T = 298(2) K; Z = 2; λ = 0.71073 Å; ρ(calcd) = 1.580 g/cm^3; μ = 1.199 mm^{-1}; *hkl* ranges, (−12, 12), (−16, 7), (−11, 10); $F(000)$ = 500; no. of data collected, 6067; $R(F)$ [$I > 2\sigma(I)$], 0.0485 (0.0332); $R_w(F^2)$ (all data), 0.0852; largest peak and hole/e $Å^{-3}$, 0.311/ −0.329; data / restraints / parameters, 2296 / 0 / 134. Deposit number in the Cambridge Crystallographic Data Centre – CCDC No 292402.

The SQUID magnetometer (Quantum Design, MPMS-XL7) was used for measurements of the magnetic data: temperature dependence of the magnetic susceptibility, and field dependence of the magnetization. The magnetic susceptibility taken at B = 0.1 T has been corrected for the underlying diamagnetism and converted to the effective magnetic moment.

3. Results and Discussion

Single crystal X-ray structural analysis confirms that the complex under study possesses a molecular structure. Two *thpy* ligands, two aqua ligands, and two acetato ligands form the $\{NiN_2O_2O'_2\}$ chromophore with an approximate rhombohedral coordination. The ORTEP drawing of the X-ray determination is shown in Fig. 1. The metal-ligand distances are Ni–O(*ac*) = 2.059, Ni–OH_2 = 2.078, and Ni–N(*thpy*) = 2.124 Å. Thus the complex approximately forms an elongated bipyramid. An average Ni-O distance in a set of $[Ni(H_2O)_6]^{2+}$ complexes adopts a value of $\bar{d}$ (Ni–O) = 2.055 Å whereas $\bar{d}$ (Ni–N) = 2.145 Å is an average value in $[Ni(NH_3)_6]^{2+}$ complexes. Therefore, the electronic properties of the $\{NiN_2O_4\}$ chromophore need be evaluated taking into account a relaxation of bond lengths relative to the complexes with homogeneous ligand sphere. The displacement parameters are $\Delta_i = (d_i - \bar{d}_i)$ and they define the (electronic) distortion parameters:

$$D_{\text{str}} = \Delta_z - (\Delta_x + \Delta_y)/2\,, \qquad E_{\text{str}} = (\Delta_x - \Delta_y)/2 \tag{1}$$

In the light of this correction to the heterogeneous donor set, i.e. $\Delta_{x,y}$(Ni-O) = +1.35 pm and Δ_z(Ni-N) = −2.10 pm, the axial and rhombic distortion parameters of the complex **1** become D_{str} = −3.45 pm, E_{str} = 0.95 pm and $E/|D|$ = 0.275. Contrary to pure geometrical aspects, the complex behaves electronically like a compressed tetragonal bipyramid. However, another choice of axes yields $\Delta_{x,y}$(Ni-O,N) = −1.70 pm and Δ_z(Ni-OH_2) = +2.30 pm, D_{str} = +4.00 pm, E_{str} = 1.25 pm and $E/|D|$ = 0.312. To this end it must be stated that the sign of the D-parameter cannot be safely fixed owing to the critically high rhombicity.

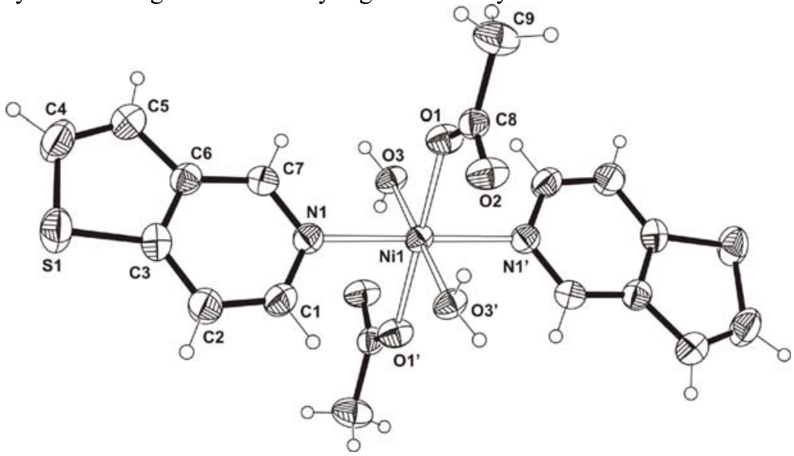

Fig. 1. ORTEP drawing of **1** with atom numbering (50 % probability ellipsoids).

A similar architecture has been found in an analogous complex, $[Ni(\mathit{fupy})_2(H_2O)_2(\mathit{ac})_2]$ hereafter **2**, with *fupy* = furo[3,2-*c*]pyridine, where Ni–O(*ac*) = 2.052, Ni–OH_2 = 2.073, and Ni–N(*fupy*) = 2.129 Å yield D_{str} = −2.35 pm. In the $[Ni(\mathit{iqu})_2(H_2O)_2(\mathit{ac})_2]$ monomeric units, **3**, containing the *iso*-quinoline ligands (*iqu*), the distances inside the chromophore are Ni–O(*ac*) = 2.061, Ni–OH_2 = 2.089, and Ni–N(*iqu*) = 2.115 Å, so that D_{str} = −5.00 pm (IVANIKOVÁ *et al.*, 2006). In both cases the pure geometric aspects refer to the elongated tetragonal bipyramid while the complexes electronically behave like a compressed tetragonal bipyramid.

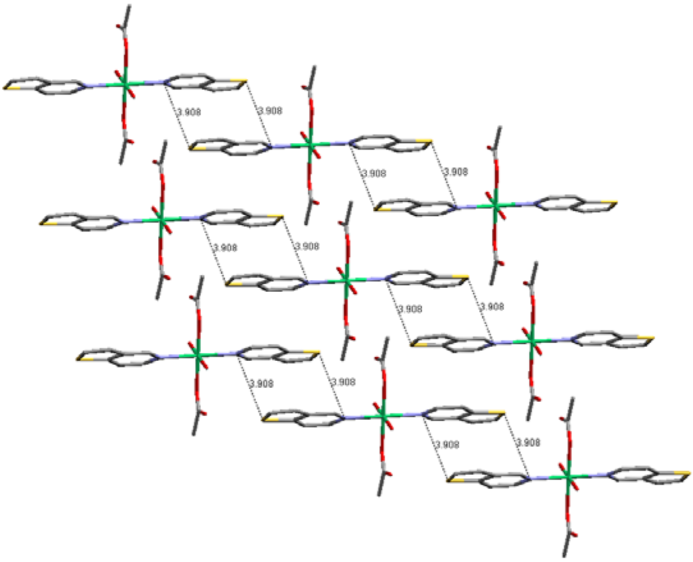

Fig. 2. MERCURY view to the π–π stacking of aromatic rings in **1**.

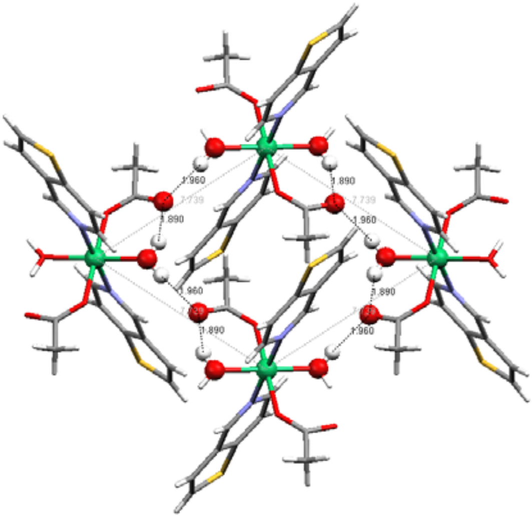

Fig. 3. The system of hydrogen bonds in **1** forming a 20-membered ring. View along the *a*-direction.

A detailed inspection to the crystal structure of **1** confirms that a complex system of the closed contacts is formed (Fig. 2, Fig. 3). Two *thpy* molecules of the adjacent centers exhibit a π–π stacking at the distance 3.84 – 3.88 Å and the N...S contacts 3.91 Å. These contacts propagate a chain. Four units inside the unit cell ale linked by hydrogen bonds which form a 20-membered ring involving 4 Ni atoms. These four Ni atoms exhibit a rhombus that is propagated along the *b*-*c* plane with the shorter Ni...Ni contact 7.74 Å. Such planes are stacked each above another with the interplane Ni...Ni contact $c = 9.65$ Å.

Temperature evolution of effective magnetic moment for **1** is rather complex (Fig. 4). On cooling from the room temperature it shows a gradual decrease until 25 K (region II) owing to some temperature-independent paramagnetism. A drop of μ_{eff} below 25 K (region I) evidences a zero-field splitting typical for $S = 1$ systems (BOČA *et al.*, 2008; TITIŠ *et al.*, 2010). Near room temperature the μ_{eff} starts to decrease (region III) and above 350 K it increases (region IV).

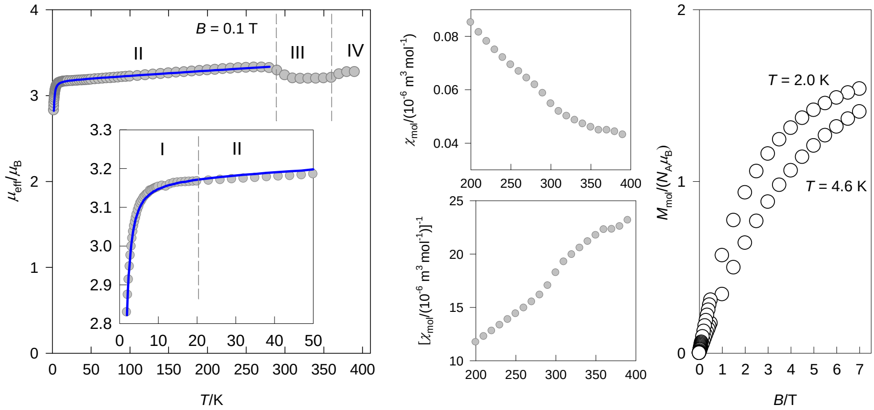

Fig. 4. The magnetic functions for **1**. Lines – fitted.

The magnetization data were taken at $T = 2.0$ K and 4.2 K not evidencing a saturation at $B = 7$ T. The magnetization per formula unit is lower than $M_{\mathrm{mol}}/N_{\mathrm{A}} = 2.0\ \mu_{\mathrm{B}}$ expected for $S = 1$ systems. This again confirms that some zero-field splitting applies. There is no evidence for the existence of a remnant magnetization when the direction of the magnetic field is reversed.

The magnetic susceptibility data was treated by the spin-Hamiltonian of the general form:

$$\begin{aligned}\hat{H}_{k,l} &= D(\hat{S}_z^2 - \vec{S}^2/3)\hbar^{-2} + E(\hat{S}_x^2 - \hat{S}_y^2)\hbar^{-2} \\ &+ \mu_{\mathrm{B}} B_m (g_x \sin\vartheta_k \cos\varphi_l \hat{S}_x + g_y \sin\vartheta_k \sin\varphi_l \hat{S}_y + g_z \cos\vartheta_k \hat{S}_z)\hbar^{-1}\end{aligned} \tag{2}$$

where the Zeeman (last) term needs averaging over a number of grid points (k, l) distributed uniformly over one hemisphere. The eigenvalues for the given "working" magnetic field enter the partition function; its derivative determines the magnetization and magnetic susceptibility (BOČA, 1999; 2012). Moreover, the magnetic susceptibility has been corrected for the constant term χ_{TIP} (temperature-independent paramagnetism plus the uncertain portion of the diamagnetic susceptibility) that reflects the linear increase of the effective magnetic moment at ambient temperature. Also a molecular-field correction (zj) has been accounted for by the formula:

$$\chi = \chi^{\text{zfs}}/[1-(zj)\chi^{\text{zfs}}]+\chi_{\text{TIP}} \tag{3}$$

As a result of the fitting procedure applied for susceptibility below 280 K the following set of magnetic parameters has been determined: $g_{\text{av}} = 2.254$, $D/hc = 2.59$ cm^{-1}, $E/hc = 0.56$ cm^{-1}, $\chi_{\text{TIP}} = 6.0 \times 10^{-9}$ m^3 mol^{-1}, and $(zj)/hc = -0.012$ cm^{-1}; the discrepancy factor on susceptibility was $R(\chi) = 0.004$. However, the same quality of the fit is obtained with $g_{\text{av}} = 2.257$, $D/hc = -2.50$ cm^{-1}, $E/hc = 0.63$ cm^{-1}, $\chi_{\text{TIP}} = 6.3 \times 10^{-9}$ m^3 mol^{-1}, and $(zj)/hc \sim 0$ (Table 1).

Table 1. Structural and magnetic parameters for related complexes [Ni(*base*)$_2$(H$_2$O)$_2$(*ac*)$_2$]. Averaged bond lengths $\bar{d}$ (Ni–O) = 2.055 Å and $\bar{d}$ (Ni–N) = 2.145 Å.

	1 (*thpy*)	**2** (*fupy*)	**3** (*iqu*)
R(Ni-*ac*)/Å	2.059	2.0735	2.0614
R(Ni-OH$_2$)/Å	2.078	2.0519	2.0886
R(Ni-N)/Å	2.124	2.1295	2.1153
D_{str}/pm	–3.45 (+4.00)	–2.2	–5.0
E_{str}/pm	0.95 (1.25)	1.0	1.4
g_x		2.147	2.094
g_y		2.149	2.104
g_z	2.257 (2.254)	2.179	2.139
D/cm^{-1}	–2.50 (2.59)	–5.0	–5.3
E/cm^{-1}	0.63 (0.56)	0.5	1.2

The detected g-value adopts a value typical for Ni(II) complexes (BOČA *et al.*, 2008; TITIŠ *et al.*, 2010). The D-parameter for rhombic zero-field splitting systems with {NiN$_2$O$_4$} chromophore is of the order of -5 cm^{-1}. Namely, in analogous complexes the following set of magnetic parameters has been detected: $D/hc = -5.0$ cm^{-1} in [Ni(*fupy*)$_2$(H$_2$O)$_2$(*ac*)$_2$], and $D/hc = -5.3$ cm^{-1} in [Ni(*iqu*)$_2$(H$_2$O)$_2$(*ac*)$_2$] (IVANIKOVÁ *et al.*, 2006). Much higher value of the TIP in the present case needs to be viewed as an effective parameter that accounts for the inter centre interactions due to the hydrogen-bond network and the π-π interaction between the aromatic rings. The molecular-field interaction of an antiferromagnetic nature is effective at the lowest temperature window. The magnetic behaviour above the room temperature (regions III and IV) stays unmodelled so far. Most probably a phase transition applies.

The present structural and magnetic data can be utilized in enrichment of the magnetostructural D-correlations and also more advanced statistical methods can be applied for them (TITIŠ *et al.*, 2010; AUGUSTÍN *et al.*, 2015).

4. Conclusions

It has been demonstrated that the complex [Ni(*thpy*)$_2$(H$_2$O)$_2$(*ac*)$_2$] possesses molecular structure with the {NiN$_2$O$_2$O'$_2$} chromophore. The bond lengths alone show geometry of the elongated tetragonal bipyramid. However, after correction to the averaged Ni-O and Ni-N distances the coordination polyhedron matches a compressed tetragonal bipyramid with a large rhombicity. Magnetic susceptibility data confirms the $S = 1$ state and the magnetic response at low temperature is influenced by the zero-field splitting. The data fitting yields D/hc = -2.5 cm^{-1}; however also $D/hc = +2.6$ cm^{-1} is a good solution so that the sign of the D-parameter cannot be fixed reliably owing to a critically high rhombicity. There is a magnetic anomaly near and above the room temperature.

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