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Diaquabis(4,5-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidin-5-one-N^3)bis(thiocyanato-*N*)nickel(II)

Mohammad Abul-Haj, Miguel Quirós* and Juan M. Salas

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain
Correspondence e-mail: mquiros@ugr.es

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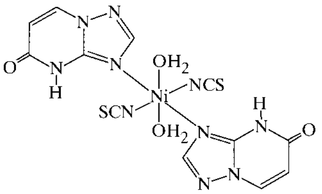
The title compound, $[Ni(NCS)_2(C_5H_4N_4O)_2(H_2O)_2]$, crystallizes in the triclinic space group $P\overline{1}$. The molecular unit contains two neutral molecules of 4,5-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidin-5-one (5HtpO) coordinated through the N atom in position 3, two thiocyanate ligands coordinated through their N atoms and two water molecules completing an octahedral environment around the Ni^{II} ion, which lies on a centre of inversion. The structure is stabilized by hydrogen bonding. Distances in the coordination sphere are Ni—N3(5HtpO) 2.132 (2), Ni—O(water) 2.085 (2) and Ni—N(thiocyanato) 2.040 (2) Å.

Comment

1,2,4-Triazolo[1,5-*a*]pyrimidine derivatives are interesting compounds for studying their interaction with metal ions since their molecules present several possible binding sites. This explains their versatile coordination chemistry, which has recently been reviewed by our group (Salas *et al.*, 1999). This versatile behaviour is enhanced by the presence of different auxiliary ligands, thiocyanate being one such ligand that leads to heterometallic compounds (Biagini-Cingi *et al.*, 1985) and can act as a very efficient transmitter of magnetic interaction (Navarro *et al.*, 1997). Following this line, we have studied the interaction of Ni^{II} with the ligand 4,5-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidin-5-one (5HtpO) in the presence of thiocyanate, which produces a simple mononuclear compound with formula $[Ni(5HtpO)_2(NCS)_2(H_2O)_2]$, (I), the structure of which is described here. In this case, as expected from its monomeric nature, magnetic interaction among the metal centres is not observed and the compound shows a temperature-independent magnetic moment of 3.28 BM.

The crystal structure is properly described in the centrosymmetric space group $P\overline{1}$ with the asymmetric unit comprising half of the complex and the metal atom lying in a crystallographic inversion centre. The environment of this atom is octahedral with two 5HtpO ligands coordinated in a monodentate manner through the N atom in position 3, which is the most frequent binding site for this type of ligand (Salas *et al.*, 1999). Thiocyanate ions are linked to the metal though their N atoms, and two water molecules complete the coordination sphere in an 'all-*trans*' disposition. A view of the molecular structure of the compound is shown in Fig. 1, which also indicates the labelling scheme.



(I)

The Ni—N3 bond is somewhat longer than in nickel(II) complexes of the analogous ligand 5,7-dimethyl-1,2,4-triazolo[1,5-*a*]pyrimidine (2.07–2.09 Å; Lenstra *et al.*, 1989), which may be attributed to a higher basicity of this latter ligand when compared with 5HtpO due to the absence of the exocyclic O atom. Coordination does not appreciably affect the geometry of the ligand, the difference in bond distances and angles compared with free 5HtpO (Abul Haj *et al.*, 2000) being below 0.02 Å and 1°, respectively. The ligand is in its neutral form, so the H atom at position 4 remains in place, which is confirmed by the formation of a hydrogen bond with the carbonyl group of a neighbouring molecule [N4···O5($-x$, $-y$, $-z$) 2.834 (3) Å]. The H atoms of the water ligands are likewise involved in hydrogen bonding [O1*W*···O5($1+x$, $1+y$, $1+z$) 2.728 (2) Å and O1*W*···S($-x$, $1-y$, $1-z$) 3.231 (2) Å]. The contacts N4···O5($-x$, $-y$, $-z$) and O1*W*···S($-x$, $1-y$, $1-z$) join pairs of molecules related by an inversion centre, whereas the contact O1*W*···O5($1+x$, $1+y$, $1+z$) creates chains in the [111] direction. The combination of the three types of hydrogen bonds gives rise to two-dimensional arrays which lie in the ($0\overline{1}1$) plane.

The angle Ni—N1*T*—C1*T* deviates appreciably from linearity. Such a situation is not unusual for isothiocyanatonickel complexes (Moore & Squattrito, 1999; Kersting *et al.*, 1999) and the analogous compounds of other first transition metals (Biagini-Cingi *et al.*, 1986); values can be found even below

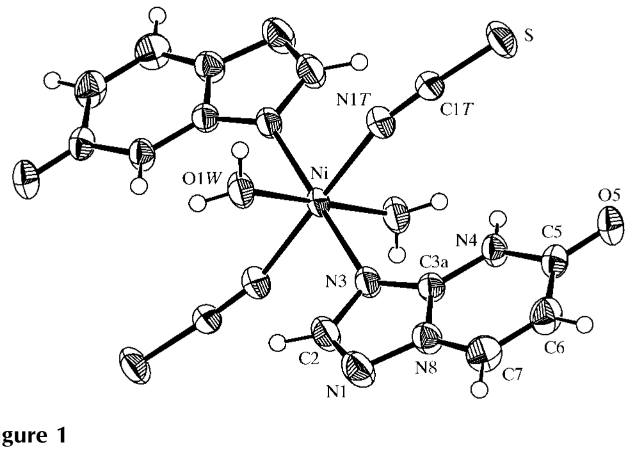


Figure 1
View of the title compound, with the non-H atoms represented by 50% probability ellipsoids.

140° (Battaglia *et al.*, 1980). Conversely, examples with almost linear geometry have also been described (Fontaine *et al.*, 1987), which shows the great flexibility of the metal–thiocyanato bond. The value of the *M*—N—C angle probably depends on the interaction with neighbouring species more than on the electronic structure of the complex itself.

Experimental

The 5HtpO ligand was prepared according to a published method (Abul Haj *et al.*, 2000) from 3-amino-1,2,4-triazole and ethyl 3,3-diethoxypropionate. The nickel complex was prepared by mixing three solutions, 10 ml each, the first one containing 0.11 g of nickel nitrate hexahydrate in water, the second 0.075 g KSCN in water, and the third 0.136 g of the 5HtpO ligand in acetonitrile–water (2:1). The resulting solution was filtered off and left to evaporate at room temperature. Green crystals of the compound were obtained after 5 d, whereupon they were collected by filtration and air dried.

Crystal data

$[Ni(NCS)_2(C_5H_4N_4O)_2(H_2O)_2]$
$M_r = 483.15$
Triclinic, $P\overline{1}$
$a = 7.8040$ (3) Å
$b = 7.9946$ (3) Å
$c = 8.9870$ (3) Å
$\alpha = 106.331$ (3)°
$\beta = 108.534$ (3)°
$\gamma = 105.041$ (3)°
$V = 471.17$ (3) Å^3

$Z = 1$
$D_x = 1.703$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 54 reflections
$\theta = 12.5$–18.7°
$\mu = 1.296$ mm^{-1}
$T = 293$ (2) K
Irregular, green
0.50 × 0.35 × 0.18 mm

Data collection

Stoe Stadi-4 four-circle diffractometer
$2\theta/\omega$
Absorption correction: ψ scan (*X-RED*; Stoe & Cie, 1996)
$T_{\min} = 0.562$, $T_{\max} = 0.686$
2746 measured reflections
2746 independent reflections

2390 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 30°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 10$
$l = 0 \rightarrow 12$
3 standard reflections frequency: 60 min intensity decay: 6.5%

Table 1
Selected geometric parameters (Å, °).

Ni—N1*T*	2.040 (2)	S—C1*T*	1.633 (2)
Ni—O1*W*	2.085 (2)	C1*T*—N1*T*	1.161 (3)
Ni—N3	2.132 (2)		
N1*T*—Ni—O1*W*	90.01 (8)	C2—N3—Ni	120.9 (2)
N1*T*—Ni—N3	90.80 (8)	N1*T*—C1*T*—S	176.3 (2)
O1*W*—Ni—N3	85.85 (8)	C1*T*—N1*T*—Ni	163.2 (2)
C3*A*—N3—Ni	134.6 (2)		

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.106$
$S = 1.255$
2742 reflections
139 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.25P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}

H atoms attached to C and N atoms were introduced in ideal positions and allowed to ride on their parent atoms. Those of the water ligand were located in the difference maps and were refined while restraining the O—H distance to 0.84 Å. The displacement parameters of the H atoms were constrained to $1.2U_{\rm eq}$ of their parent atoms.

Data collection: *STADI*4 (Stoe & Cie, 1996); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1106). Services for accessing these data are described at the back of the journal.

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