

Nermin Kahveci Yağci, Kutalmış Güven* and Gökçen Dikici Yildiz

Crystal structure of aquadichlorido(2,4,6-tri-2-pyridyl-1,3,5-triazine- κ^3N,N',N'')nickel(II) monohydrate, $C_{18}H_{16}Cl_2N_6NiO_2$

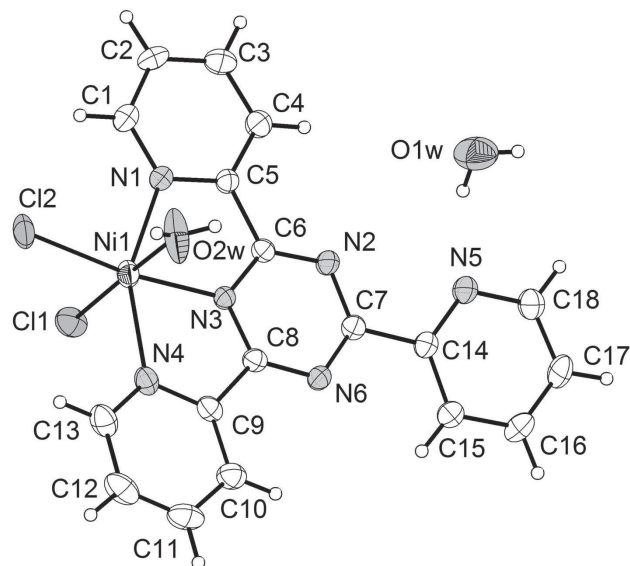


Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.15 × 0.11 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	12.9 cm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{\max}$, completeness:	57°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	46716, 4875, 0.090
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3484
$N(\text{param})_{\text{refined}}$:	278
Programs:	SHELX [1], Bruker programs [2], enCIFer [3]

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Abstract

$C_{18}H_{16}Cl_2N_6NiO_2$, monoclinic, $P2_1/n$ (no. 14), $a = 8.5737(6)$ Å, $b = 11.4177(9)$ Å, $c = 20.3031(16)$ Å, $\beta = 99.309(3)^\circ$, $V = 1961.3(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0479$, $wR_{\text{ref}}(F^2) = 0.0865$, $T = 293$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Kutalmış Güven, Kırıkkale University, Faculty of Art and Sciences, Department of Physics, Campus Yahşihan Kırıkkale, 71450 Turkey, e-mail: kutalmisguven@gmail.com

Nermin Kahveci Yağci and Gökçen Dikici Yildiz: Kırıkkale University, Faculty of Art and Sciences, Department of Physics, Campus Yahşihan Kırıkkale, 71450 Turkey

Source of materials

2,4,6-Tri-(2-pyridyl)-1,3,5-triazine (TPTZ) was purchased from Sigma Aldrich and used without purification. All the solvents, TPTZ and $NiCl_2 \cdot 6H_2O$ were obtained from Sigma Aldrich and used without any purification.

A hot EtOH solution of 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (0.312 g; 1.0 mmol) was added to $NiCl_2 \cdot 6H_2O$ (0.237 g; 1.0 mmol) in EtOH. The reaction mixture was refluxed for 40 minutes. The yellow crystals of the title complex were grown from the filtrate by slow evaporating at room temperature for six weeks.

Experimental details

Aromatic H atoms were positioned geometrically and allowed to ride on their parent atoms, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(\text{parent atom})$ with a C–H distance of 0.93 Å. Hydrogen atoms of water molecules were located from electron density map.

Comment

2,4,6-Tri-(2-pyridyl)-1,3,5-triazine (TPTZ), a well known ligand, has been used as a reagent for various metal ions (such as: Al^{III} , Cu^{II} , Ag^{II} , Co^{II} , Ni^{II} , Mn^{II}). Some physical and biological properties of these complexes have recently been reported [4–9].

The title compound $Ni[C_{18}H_{12}N_6 \cdot H_2O]Cl_2 \cdot H_2O$ is isostructural with the manganese complex [9].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Ni1	0.77445(4)	0.04329(3)	0.18674(2)	0.02493(10)
Cl1	0.84634(9)	0.17357(7)	0.10363(4)	0.03884(18)
Cl2	0.81961(10)	0.17681(6)	0.27570(4)	0.03905(19)
N1	1.0000(2)	−0.04491(19)	0.20175(11)	0.0261(5)
N2	0.8439(2)	−0.25778(19)	0.07688(10)	0.0263(5)
N3	0.7426(2)	−0.08996(18)	0.12234(11)	0.0234(5)
N4	0.5285(3)	0.05865(19)	0.14086(12)	0.0291(5)
N5	0.7854(3)	−0.4543(2)	0.00228(11)	0.0335(5)
N6	0.5749(2)	−0.19903(19)	0.04259(11)	0.0268(5)
O1w	0.9317(3)	−0.5485(3)	0.12918(13)	0.0531(7)
C9	0.4798(3)	−0.0236(2)	0.09430(13)	0.0266(6)
C7	0.6992(3)	−0.2701(2)	0.04021(13)	0.0260(6)
C5	1.0056(3)	−0.1420(2)	0.16434(13)	0.0243(6)
C10	0.3279(3)	−0.0287(3)	0.05949(15)	0.0338(7)
H10	0.298240	−0.086513	0.027639	0.041*
C13	0.4235(3)	0.1379(3)	0.15344(16)	0.0371(7)
H13	0.455362	0.195227	0.185335	0.045*
C1	1.1283(3)	−0.0172(2)	0.24420(14)	0.0329(7)
H1	1.126033	0.049787	0.270095	0.040*
C8	0.6035(3)	−0.1099(2)	0.08446(13)	0.0237(6)
C6	0.8575(3)	−0.1669(2)	0.11823(12)	0.0224(5)
O2w	0.7026(4)	−0.0668(2)	0.25776(14)	0.0534(7)
C14	0.6738(3)	−0.3708(2)	−0.00643(13)	0.0265(6)
C12	0.2685(4)	0.1383(3)	0.12082(17)	0.0428(8)
H12	0.197849	0.194726	0.131072	0.051*
C4	1.1375(3)	−0.2126(3)	0.16949(15)	0.0363(7)
H4	1.137283	−0.279653	0.143441	0.044*
C11	0.2202(3)	0.0553(3)	0.07352(16)	0.0416(8)
H11	0.116818	0.054891	0.050957	0.050*
C3	1.2696(3)	−0.1815(3)	0.21426(17)	0.0430(8)
H3	1.360457	−0.227218	0.218685	0.052*
C17	0.6323(4)	−0.5604(3)	−0.08680(14)	0.0379(7)
H17	0.620926	−0.627054	−0.113517	0.045*
C16	0.5198(4)	−0.4740(3)	−0.09563(14)	0.0379(7)
H16	0.431654	−0.480697	−0.128777	0.045*
C18	0.7624(4)	−0.5472(3)	−0.03784(15)	0.0399(7)
H18	0.838191	−0.606252	−0.032487	0.048*
C15	0.5392(3)	−0.3765(2)	−0.05445(13)	0.0317(6)
H15	0.464343	−0.316893	−0.058875	0.038*
C2	1.2658(3)	−0.0826(3)	0.25210(16)	0.0402(7)
H2	1.353721	−0.059991	0.282457	0.048*
H2A	0.702(4)	−0.132(3)	0.2549(19)	0.055(12)*
H2B	0.670(5)	−0.043(3)	0.287(2)	0.064(14)*
H1A	0.896(5)	−0.507(4)	0.097(2)	0.070(14)*
H1B	0.920(7)	−0.615(6)	0.119(3)	0.14(3)*

The compound is monomeric, with an Ni centre octahedrally coordinated by three N atoms of the TPTZ ligand, one water molecule and two chlorido ligands. Two nitrogen atoms (N1 and N4) of pyridyl rings, one nitrogen atom (N3) of the triazine ring from the TPTZ ligand and one Cl atom (Cl2) form the equatorial base, while the O atom (O2w) of a water molecule and the other Cl atom (Cl1) occupy the axial positions. The

bond distances and angles around the Ni^{II} ion significantly deviate from 180°: O2w—Ni1—Cl1 (177.61(9)°), N3—Ni1—Cl2 (170.84(7)°), N4—Ni1—N1 (152.22(8)°). As expected, the N—Ni—N chelating angles are with values of N1—Ni1—N3 (76.19(8)°) and N3—Ni1—N4 (76.10(8)°) more acute than the Cl1—Ni1—Cl2 bond angle (96.27(3)°). The Ni—Cl bond lengths are approximately equal (2.4035(8) Å and 2.3473(8) Å). The Ni—N_{py} bonds (2.158(2) and 2.170(2) Å) are longer than the Ni—N_{triaz} bond (1.996(2) Å). These results are similar to the related manganese complex [9]. The TPTZ ligands slightly deviate from planarity: the three pyridyl rings are twisted with respect to the central triazine ring by angles of 2.99(17)°, 2.54(17)° and 13.25(15)° with the N5 ring (uncoordinated pyridine ring) displaying the highest degree of twisting. The uncoordinated pyridine ring was reported as 11.8° twisting angle in the manganese analogue [9]. The TPTZ ligand, with the exception of the non-coordinating pyridyl moiety is close to planar with an rms deviation of 0.0468 Å from the best fit plane through all ligand atoms. The ligand plane also lies close to the equatorial plane of the complex defined by the Cl2, N1, N3 and N4 donor atoms with 4.60(7)° and close to the axial plane of the complex defined by the Cl1, Cl2, O2w and N3 donor atoms with 86.52(6)°.

The [Ni(C₁₈H₁₂N₆·H₂O)Cl₂·H₂O] complex molecules are assembled into a 2D network by OH···N, OH···O and OH···Cl hydrogen bonds. The crystal structure is also stabilized by intermolecular π-π stacking interactions between TPTZ ligands (centroid-centroid distance = 3.814(4) Å).

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