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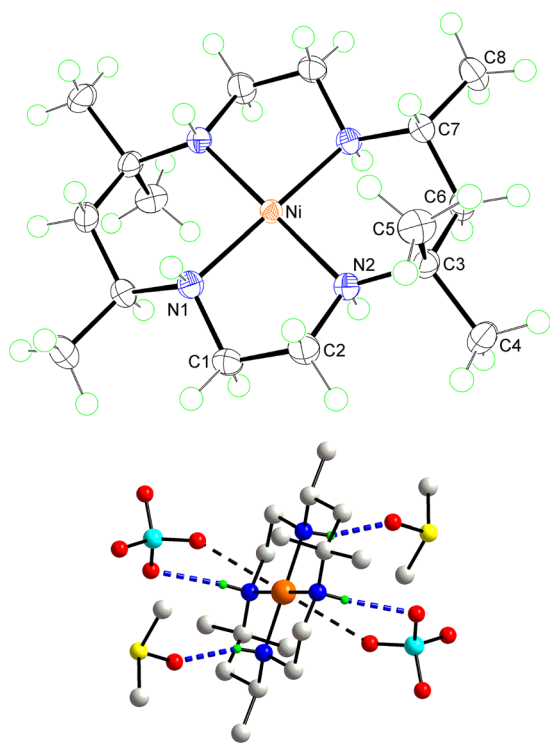Z. Kristallogr. - N. Cryst. Struct. 2021; 236(6): 1243–1245

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Crystal structure of [*meso*-5,7,7,12,14,14,-hexamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) diperchlorate – dimethylsulphoxide (1/2), C20H48Cl2N4NiO10S2

Abstract

$C_{20}H_{48}Cl_2N_4NiO_{10}S_2$, monoclinic, $P2_1/n$ (no. 14), $a = 8.657(2)$ Å, $b = 15.233(4)$ Å, $c = 11.956(3)$ Å, $\beta = 102.737(2)°$, $V = 1537.9(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0237$, $wR_{ref}(F^2) = 0.0655$, $T = 93(2)$ K.

CCDC no.: 2100053

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.25 \times 0.25 \times 0.15$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.00 mm^{-1}
Diffractometer, scan mode:	Rigaku Saturn724, ω
θ_{max}, completeness:	27.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15,153, 3495, 0.012
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3265
$N(param)_{refined}$:	189
Programs:	Reqab [1], CrystalClear [2], Shelx [3, 4], WinGX/Ortep [5], Diamond [6]

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Source of material

Hexamethyl tetrazacyclotetradecane (tet-a) was synthesized as per the literature procedure and exhibited the expected spectroscopic characteristics [7]. The tet-a macrocycle reacted with $CH_2=CH-CN$ to form the N-pendent bis-cyanoethyl derivative, hereafter tet-ax. The nickel(II) perchlorate salt of tet-ax, i.e. [Ni(tet-ax)](ClO$_4$)$_2$, was synthesised from the reaction of tet-ax with Ni(CH$_3$COO)$_2$·4H$_2$O followed by the addition of NaClO$_4$·6H$_2$O. Then, [Ni(tet-ax)](ClO$_4$)$_2$ was dissolved in a solvent mixture of

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$).

Atom	x	y	z	$U_{iso}*/U_{eq}$
Ni	1.000000	0.500000	1.000000	0.01129 (7)
N1	1.10221 (11)	0.45536 (6)	0.88109 (8)	0.0143 (2)
H1N	1.0319 (15)	0.4640 (10)	0.8173 (9)	0.017*
N2	0.94353 (11)	0.37734 (6)	1.02323 (8)	0.01392 (19)
H2N	1.0201 (14)	0.3633 (10)	1.0825 (10)	0.017*
C1	1.12174 (15)	0.35874 (8)	0.89629 (11)	0.0190 (2)
H1A	1.214730	0.345358	0.958593	0.023*
H1B	1.137653	0.331201	0.824676	0.023*
C2	0.97389 (16)	0.32465 (8)	0.92587 (11)	0.0209 (3)
H2A	0.883717	0.330031	0.858998	0.025*
H2B	0.986898	0.261956	0.947715	0.025*
C3	0.79124 (13)	0.35039 (8)	1.05604 (10)	0.0155 (2)
C4	0.80129 (16)	0.25389 (8)	1.09419 (12)	0.0227 (3)
H4A	0.807789	0.216225	1.028930	0.027*
H4B	0.706705	0.238554	1.122385	0.027*
H4C	0.895788	0.245309	1.155587	0.027*
C5	0.65008 (14)	0.36276 (8)	0.95484 (11)	0.0207 (2)
H5A	0.551552	0.360797	0.982359	0.025*
H5B	0.649487	0.315718	0.898830	0.025*
H5C	0.658786	0.419671	0.918521	0.025*
C6	0.77500 (14)	0.40616 (8)	1.15869 (10)	0.0174 (2)
H6A	0.685662	0.382830	1.189061	0.021*
H6B	0.872382	0.398906	1.219412	0.021*
C7	0.74781 (14)	0.50358 (7)	1.13607 (11)	0.0157 (2)
H7	0.664405	0.511041	1.064143	0.019*
C8	0.68932 (15)	0.54592 (9)	1.23515 (11)	0.0217 (3)
H8A	0.598276	0.512952	1.249260	0.026*
H8B	0.657655	0.606710	1.215290	0.026*
H8C	0.774550	0.545212	1.304387	0.026*
Cl1	0.33610 (3)	0.35563 (2)	0.23185 (2)	0.01959 (8)
O1	0.43273 (14)	0.29308 (8)	0.18891 (11)	0.0391 (3)
O2	0.41679 (14)	0.38404 (7)	0.34374 (9)	0.0352 (3)
O3	0.18808 (12)	0.31445 (7)	0.23700 (10)	0.0320 (2)
O4	0.30474 (14)	0.43046 (7)	0.15612 (9)	0.0350 (3)
S1	0.79332 (4)	0.46004 (2)	0.55269 (3)	0.02282 (9)
O5	0.93506 (12)	0.47545 (8)	0.64862 (9)	0.0332 (2)
C9	0.8438 (2)	0.36922 (11)	0.47325 (13)	0.0334 (3)
H9A	0.879134	0.319976	0.525364	0.040*
H9B	0.929250	0.386400	0.435889	0.040*
H9C	0.750831	0.351458	0.414901	0.040*
C10	0.65008 (16)	0.40529 (10)	0.61465 (12)	0.0267 (3)
H10A	0.622941	0.442427	0.674449	0.032*
H10B	0.694032	0.349570	0.648398	0.032*
H10C	0.554645	0.393834	0.555118	0.032*

DMSO and H_2O (1:1 v/v) followed by the addition of triethylamine and $HClO_4$ with the aim to prepare [Ni(tet-am)](ClO_4)$_2$ (tet-am is the *N*-bound bis-carbamoylethyl derivative of isomeric ligand tet-a) by converting the cyanoethyl branches to carbamoylethyl branches, but a few yellow crystals of the unexpected product, [Ni(tet-a)](ClO_4)$_2$·

$2(CH_3)_2S=O$, without any branches, was identified by X-ray crystallography.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. The N-bound atoms were located from a Fourier difference map and refined with N–H = $0.88 ± 0.01$ Å, and with $U_{iso}(H) = 1.2U_{eq}(N)$.

Comment

Some new *N*-pendent derivative macrocycles bearing bis-cyanoethyl branches were recently synthesised by combining certain macrocyclic ligands with an alkylating agent, acrylonitrile [8, 9]. In continuation of this work, an attempt was made to prepare a new *N*-pendent derivative containing *N*-bound bis-carbamoylethyl branches employing a different procedure [10]. It was observed during these investigations that a small quantity of yellow crystals were obtained (see Source of material) which were shown by X-ray crystallography to be [Ni($C_{16}H_{36}N_4$)](ClO_4)$_2$·$2(CH_3)_2S=O$, hereafter (I).

The crystallographic asymmetric unit of (I) comprises half a complex cation, as this is disposed about a centre of inversion, a perchlorate anion and a molecule of DMSO of crystallisation. The molecular structure of the complex cation is shown in the upper part of the Figure (70% probability displacement ellipsoids). The nickel(II) centre is coordinated by four amine-nitrogen atoms with the two independent Ni–N1, N2 bond lengths of 1.9548(10) and 1.9665(11) Å differing insignificantly. The resulting N_4 donor set defines a square-planar geometry. The isomeric form of the tet-a ligand in (I) is *meso* and this has been characterised previously as the perchlorate salt [11] as have other configurational isomeric forms of tet-a [12]. The closest related structure to (I) is the isostructural copper(II) salt [13].

In the crystal, the perchlorate-O4 atom forms a weak contact with the nickel(II) atom [Ni···O4^i = 3.0651(14) Å for symmetry operation (i): $1 - x$, $1 - y$, $1 - z$] leading to a tetragonally distorted 4 + 2 coordination geometry. Further links between the complex cation and the perchlorate anion are mediated by amine-N–H···O(perchlorate) [N2–H2n···O3^{ii}: H2n···O3^{ii} = 2.213(12) Å, N2···O3^{ii} = 3.0897(17) Å with angle at H2n = 171.9(13)° for (ii): $1 + x$, y, $1 + z$] hydrogen bonds. The DMSO molecules are also associated with the complex cation,

via amine-N–H···O(DSMO) hydrogen bonds [N1–H1n···O5: H1n···O5 = 2.014(11) Å, N1···O5 = 2.8529(16) Å with angle at H1n = 160.5(12)°]. The aforementioned contacts lead to the formation of a five-molecule aggregate, as represented in the lower part of the figure (the Ni···O and N–H···O interactions are shown as black and blue dashed lines, respectively, and non-participating H atoms are omitted). The aggregates are assembled into the crystal via a combination of DMSO-methyl-, methylene-, methyl-C–H···O(perchlorate) and methyl-C–H···O(DMSO) interactions.

Finally, the Hirshfeld surfaces and of the full and delineated two-dimensional fingerprint plots were calculated with the program Crystal Explorer 17 [14] in accord with literature methods [15]. For the complex cation, the surface contacts are clearly dominated by H···H [62.8%] and O···H/H···O [35.1%] contacts, with minor contributions from S···H/H···S [1.5%] and Ni···O/O···Ni [0.5%] contacts. For the DMSO molecule, H···H contacts also predominate, contributing 51.1% followed by O···H/H···O [36.1%] and S···H/H···S [9.5%] contacts. Minor contributions to the Hirshfeld surface of DMSO are contributed by O···O [1.7%] and S···O/O···S [1.6%] contacts. By contrast, the surface contacts for the perchlorate anion are dominated by O···H/H···O contacts, at 95.2%. This is followed by small contributions from O···O [2.4%], S···O/O···S [1.3%] and Ni···O/O···Ni [1.0%] contacts.

References

1. REQAB. Rigaku Corporation: Tokyo, Japan, 1998.

2. CrystalClear. Rigaku Corporation: Tokyo, Japan, 2010.

3. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, *A64*, 112–122.

4. Sheldrick G. M. Crystal structure refinement with CrystalClear. *Acta Crystallogr.* 2015, *C71*, 3–8.

5. Farrugia L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, *45*, 849–854.

6. Brandenburg K. DIAMOND; Crystal Impact GbR: Bonn, Germany, 2006.

7. Hay R. W., Lawrance G. A., Curtis N. F. A convenient synthesis of the tetra-aza-macrocyclic ligands trans-[14]-diene, tet-a, and tet-b. *J. Chem. Soc. Perkin Trans.* 1975, *1*, 591–593.

8. Dey L., Rabi S., Hazari S. K. S., Roy T. G., Buchholz A., Plass W. Copper(II) and nickel(II) complexes of an N-pendent bis-(cyanoethyl) derivative of an isomeric hexamethyl tetraazamarocyclic ligand: synthesis, characterization, electrolytic behavior and antimicrobial studies. *Inorg. Chim. Acta*. 2021, *517*, 120172.

9. Dey L., Rabi S., Palit D., Hazari S. K. S., Begum Z. A., Rahman I. M. M., Roy T. G. Syntheses, characterization, and antimicrobial studies of Ni(II), Cu(II), and Co(III) complexes with an N-pendant azamacrocyclic chelator. *J. Mol. Struct.* 2021, *1240*, 130579.

10. Kang S.-G., Kim N.-H., Lee R.-E., Jeong J.-H. Synthesis and characterization of various di-N-functionalized tetraaza macrocyclic copper(II) complexes. *Bull. Korean Chem. Soc.* 2007, *28*, 1781–1786.

11. Drew M. G. B., Mok K. F. Structure of a nickel(III) perchlorate complex of a 14-membered tetraaza macrocycle. *Acta Crystallogr.* 1987, *C43*, 666–668.

12. Curtis N. F., Swann D. A., Waters T. N. Structural studies on co-ordinated macrocyclic ligands. Part III. Preparations and crystal structure analyses of salts of the nickel(II) complex C-rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, [Ni(tetb)]²⁺, in the α-, β-, and γ-configurations. *J. Chem. Soc. Dalton Trans.* 1973, 1963–1974; https://doi.org/10.1039/dt9730001963.

13. Bharadwaj P. K., Potenza J. A., Schugar H. J. Doping of copper(II) into the macrocyclic amine tet-a: structural and spectroscopic studies. *Inorg. Chem.* 1988, *27*, 3172–3175.

14. Turner M. J., McKinnon J. J., Wolff S. K., Grimwood D. J., Spackman P. R., Jayatilaka D., Spackman M. A. *Crystal Explorer v17*; The University of Western Australia: Australia, 2017.

15. Tan S. L., Jotani M. M., Tiekink E. R. T. Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. *Acta Crystallogr.* 2019, *E75*, 308–318.