Structure of Tetra[β-(1,2,4-triazole-1-yl)propiophenone] Dichloro Nickel(II) Solvate Hexahydrate Complex: $[NiCl_2(C_2H_2N_3CH_2CH_2COPh)_4]\cdot 6H_2O$

JIAN, Fang-Fang(建方方) XIAO, Hai-Lian(肖海连) YU, Bing(于冰) JIAO, Kui*(焦奎)

New Materials & Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao, Shandong 266042, China

The mononuclear complex, $[NiCl_2(trzCH_2CH_2COPh)_4]\cdot 6H_2O$ (trz = 1,2,4-triazole), was synthesized and its structure was determined by single crystal X-ray determination. It crystallizes in the monoclinic system, space group $P2_1/c$, with lattice parameters: a = 0.80391(2) nm, b = 1.08215(2) nm, c = 2.90133(2) nm, β = 94.792 (1)° and Z = 2. Each nickel atom is coordinated by four N atoms of triazole from four β-(1,2,4-triazole-1-yl)propiophenone ligands and two chloride anions in *trans* arrangement with octahedral coordination geometry. In addition to the coordinating nickel complex, there are six uncoordinated water molecules. The Ni—Cl distance is 0.24865(8) nm and the Ni—N distances are in the range of 0.2072(2) to 0.2099(2) nm, respectively. In the solid state, the title compound forms three dimensional network structure through hydrogen bonds. The intermolecular hydrogen bonds connect the $[NiCl_2(C_2H_2N_3CH_2CH_2COPh)_4]$ and H_2O moieties. The deep green crystals were also examined by elemental analysis, FT-IR and UV spectra, which are in agreement with the structural data.

Keywords β-(1,2,4-triazole-1-yl)propiophenone ligand, single crystal structure, octahedral coordination geometry, dichloronickel(II) complex

Introduction

Recently, the compounds containing 1*H*-1,2,4-triazole group have attracted much interest because they exhibit some fungicidal activity, plant growth regulating activity,[1] antibacterial activity against Puccinia recondite and roots growth regulation for cucumber.[2] Also, such compounds are increasingly being studied because of the coordination chemistry of triazoles acting as ligands in transition metal compounds. As a matter of fact, the triazole derivatives have been extensively used as terminal and bridging ligands, and they lead to compounds exhibiting interesting magnetic properties.[3] Some iron(II)-1,2,4-triazole compounds present extremely abrupt thermal hysteresis and well-pronounced thermochromic effects.[4,5] Some of these compounds could be utilized as active elements of display devices.[6,7] While structural and physical studies of many transition metal triazole complexes have been carried out,[8-10] few nickel-triazole complexes have been reported. In this paper, we report the preparation and crystal structure of tetra [β-(1, 2, 4, triazole-1-yl) propiophenone] dichloro Ni(II) hexahydrate solvate to expand our knowledge in this area.

Experimental

Materials and preparation

All chemicals used were of analytical reagent grade and used as received. The β-bromic-propiophenone [$PhCOCH_2CH_2Br$] and β-(1,2,4-triazole-1-yl)propiophenone ($C_2H_2N_3CH_2CH_2COPh$) were prepared according to the reported method.[11,12]

$NiCl_2$(0.64 g, 5.0 mmol) was dissolved in hot water (50 mL), stirred, and the warm solution of β-(1,2,4-triazole-1-yl) propiophenone (1.0 g, 5.0 mmol) in EtOH (50 mL) was added. The mixture was refluxed for 20 min. The green solution was filtered and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, a deep green crystal appeared several weeks later and was separated by filtration. The C, H and N contents were determined by elemental analysis (Anal. calcd for $C_{44}H_{56}Cl_2N_{12}NiO_{10}$: C 50.64%, H 5.37%, N 16.11%; found C 50.19%, H 5.14%, N 15.96%). The chemical diagram of the complex is shown in Fig. 1.

Physical measurements

Elemental analysis for carbon, hydrogen and nitrogen was performed on a Perkin-Elmer 240C analysis instrument. Solid state electronic spectra were measured on a

* E-mail: ffj2001@public.qd.sd.cn

Received December 18, 2002; revised March 17, 2003; accepted May 2, 2003.

Project supported by the Natural Science Foundation of Shandong Province (No. Y2002B06) and the Outstanding Adult-Young Scientific Research Encouraging Foundation of Shandong Province (No. O1BS18).

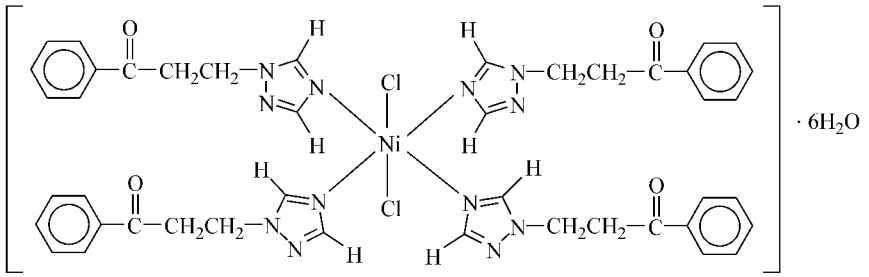

Fig. 1 Structural chemical diagram of the title complex.

Shimadzu UV-200 recording spectrophotometer, furnished with a reflectance attachment using $BaSO_4$ as the reference sample. IR spectra were recorded in the range of 4000—300 cm^{-1} on a Perkin-Elmer 467 spectrometer using KBr pellets.

Crystallographic study

The crystal of $[NiCl_2(C_2H_2N_3CH_2CH_2COPh)_4]\cdot 6H_2O$ with approximate dimensions of 0.34 mm × 0.18 mm × 0.10 mm was mounted on a glass fiber. The data were collected on SMART CCD diffractometer. Reflection data were measured at 293 K, using graphite monochromated Mo Kα (λ = 0.071073 nm). The technique used was ω-2θ scan with θ limits $1.41° < \theta < 28.30°$. Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction using SADABS[13] (T_{min} = 0.837 and T_{max} = 0.9462) program. 17458 reflections were measured, of which 6134 were unique (R_{int} = 0.1052).

The structure was solved by direct methods using SHELXS-97.[14] All the non-hydrogen atoms were refined on F^2 anistropically by full-matrix least squares method. Hydrogen atoms were located from the difference Fourier map and added to the structure calculations, but their positions were not refined. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave R = 0.0595, R_w = 0.1108 for 3326 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. The maximum and minimum difference peaks and holes are 357 and − 763 e/nm^3, respectively. S = 0.930 and $(\Delta/\sigma)_{max}$ = 0.0095(7). Atomic scattering factors and anomalous dispersion corrections were taken from *International Table for X-Ray Crystallography*.[15] The final position parameters of non-hydrogen atoms are given in Table 1.

Results and discussion

IR *and electronic spectra*

In the infrared spectrum, the broad absorption at 3438 cm^{-1} is assigned to the C—H in triazole ring stretching vibration. It exhibits characteristic bands at 1573, 1401, 1341 and 767 cm^{-1} for the triazole ring.

The strong band at 1694 cm^{-1} is assigned to the stretching vibration of $\nu_{C=O}$ of PhCO. It exhibits characteristic strong bands at 1460, 1348 (C = N), and 730 cm^{-1} (ν_{C-H} triazole ring) for the coordination triazole ligands. The bands at 1460 and 1348 and 730 cm^{-1} are shifted from their positions for the free triazole ligand (1500, 1380 and 690 cm^{-1}),[16] indicating nitrogen coordination.

The solid reflectance electronic spectrum of the title compound shows two broad band around 250, 285 nm and one peak band at 510 nm. The band around 250 nm is ascribed to intra-ligand, probably $\pi \rightarrow \pi^*$, transition of the triazolyl group. The peak at 285 nm may be responsible for ligand to metal charge transfer (LMCT). The d—d band at 510 nm might be taken as evidence for octahedral nickel (II) complexes, while the parent four-coordinate nickel (II) complexes show the d—d band at 400 nm.[17]

Crystal and molecular structure of the title compound

The crystal structure of the title compound $[NiCl_2(trzCH_2CH_2COPh)_4]\cdot 6H_2O$ consists of the $[NiCl_2(trzCH_2CH_2COPh)_4]$ molecules and six uncoordinated H_2O molecules. Fig. 2 shows a perspective view of the title compound with atomic numbering scheme, and Fig. 3 shows a perspective view of the crystal packing in the unit cell. Selected bond lengths and angles are presented in Table 2, and potentially weak intermolecular interaction in Table 3.

The central Ni atom is located on an inversion center, and surrounded by four β-(1,2,4,triazole-1-yl)propiophenone ligands and two Cl^- anions. The $NiCl_2N_4$ core involving the central atom is an almost perfect octahedron. The basal plane is formed by four nitrogen donor atoms of triazole from four β-(1,2,4,triazole-1-yl)propiophenone ligands, which is an almost perfect plane with the central Ni atom. The axial sites are occupied by two Cl^- anions located in *anti*-conformations. The bond angles are very close to either 90° or 180°. The *trans* angles are all 180° for symmetry requirements and the *cis* ones are in the range 89.14(9)°—90.86(9)°. It is evident that only bond distances around the metal are responsible for some small deformations in the polyhedron. The bond lengths in the coordination polyhedron of the Ni atom are normal. The

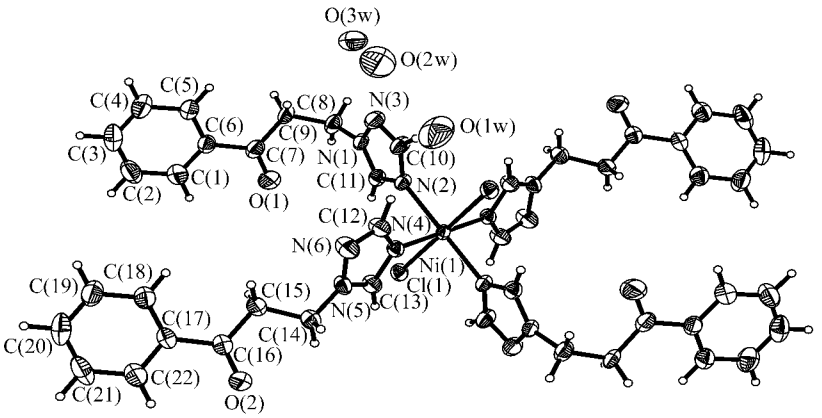

Fig. 2 Molecular structure for $[NiCl_2(C_2H_2N_3CH_2CH_2COPh)_4]\cdot 6H_2O$ with the atomic numbering scheme.

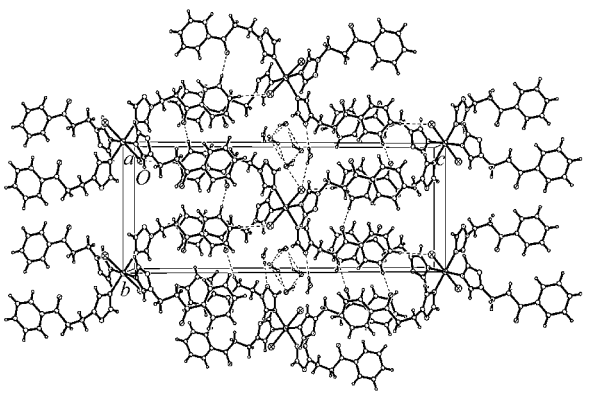

Fig. 3 A view of the crystal packing down the *a*-axis for $[NiCl_2(C_2H_2N_3\ CH_2CH_2COPh)_4]\cdot 6H_2O$.

Ni—N bond distances [0.2095(2) and 0.2106(2) nm] are in good agreement with the corresponding octahedron Ni—N distances reported, such as $Ni(cbim)_4(NO_3)_2$[18] [cbim = 4′-cyanobenzyl-1-imidazole; Ni—N 0.2072(2) and 0.2099(2) nm], $Ni(NCS)_2(MeOH)_2(Mebta)_2$[19] [Mebta = 1-methylbenzotriazole; Ni—N 0.2031(2) and 0.2122(2) nm] and $[Ni(Im)_6](Sal)_2$[20] [Im = imidazole, Sal = Salicylate; average Ni—N 0.2128 nm]. The coordinating Ni—Cl distances [0.24865(8) nm] are a little longer than the average corresponding distances reported before for related metal complexes with NiN_4Cl_2 octahedron environments, such as $[NiCl_2(H_2L_3)]ClO_4\cdot 2H_2O$[21] [$L_3$ = 2,5,9,12,16,19-hexaaza-7-spiro[6,13] eicosane; Ni—Cl 0.2401(6) and 0.2430(6) nm] and *trans*-dichloronickel(II) cyclam complex[22] [Ni—Cl 0.2451(1) nm].

The triazole ring **1** [N(1), N(2), N(3), C(10) and C(11)] with the conjunction carbon atom C(9) and nickel atom are fairly planar, the deviation from the least squares plane through the ring atoms is smaller than 0.0048(3) nm. Plane equation: $4.547x + 2.437y + 21.566z = 0.0477$. The phenyl ring **3** [C(1), C(2), C(3), C(4), C(5) and C(6)] with the conjunction carbon atom C(7) is also quite planar, plane equation: $7.317x + 3.329y - 10.23z = -4.494$, the largest deviation from the least squares plane is 0.0013(3) nm. The dihedral angle between the triazole ring **1** moiety and the phenyl ring **3** is 69.4(2)°. The triazole ring **2** [N(4), N(5), N(6), C(12) and C(13)] with the conjunction carbon atom C(14) and nickel atom are also fairly planar, plane equation: $-4.571x - 3.687y + 23.027z = 0$, the deviation from the least squares plane through the ring atoms is smaller than 0.0017(2) nm. The phenyl ring **4** [C(17), C(18), C(19), C(20), C(21) and C(22)] with the conjunction carbonyl-methylene group [C(15), C(16) and O(2)] is also quite planar, the largest deviation from the least squares plane is 0.0027(3) nm. Plane equation: $7.429x - 3.095y - 9.571z = 1.671$. The dihedral angle between the plane of triazole ring **2** moiety and the plane of methyl phenyl ketone is 51.8(1)°

The most interesting structural feature of the complex is the intramolecular and intermolecular hydrogen bonds and potentially weak (C—H···Y hydrogen bonds, Y = O, N and Cl) intermolecular interactions. The six lattice water molecules are hydrogen bonded to each other, and O(3w) forms the strongest hydrogen bond with O(2w). The O(3w)—H(32w)···O(2w) distance is 0.2804(6) nm, which is a little shorter than that of pure water (0.283 nm).[23] The O(1w) water molecules form hydrogen bond network with Cl(1) anion and N(3) atom. The Cl(1), O(1) and O(2) with C atoms in β-(1,2,4-triazole-1-yl)-propiophenone ligands form potentially weak (C—H···Y hydrogen bonds, Y = O and Cl) intermolecular interactions as shown in Table 3. All above hydrogen bonds in this structure connect $[NiCl_2(C_2H_2N_3CH_2CH_2COPh)_4]$ and H_2O molecules altogether and form three dimensional hydrogen bond network which stabilizes the structure.

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($nm^2 \times 10^5$) for the title compound

Atom	*x*	*y*	*z*	U_{eq}[a]
Ni(1)	0	0	0	24(1)
Cl(1)	-1611(1)	1382(1)	483(1)	35(1)
O(1)	-2695(4)	-1654(2)	1787(1)	64(1)
O(2)	6165(4)	3435(2)	1939(1)	61(1)
O(1w)	215(4)	3996(3)	755(1)	64(1)
O(2w)	3456(5)	4603(4)	501(2)	93(1)
O(3w)	5711(6)	3279(4)	3(2)	99(1)
N(1)	-2144(3)	-2789(2)	790(1)	31(1)
N(2)	-743(3)	-1547(2)	373(1)	28(1)
N(3)	-973(4)	-3507(2)	616(1)	41(1)
N(4)	2120(3)	229(2)	463(1)	29(1)
N(5)	3974(3)	1043(2)	963(1)	33(1)
N(6)	4548(3)	-113(3)	883(1)	46(1)
C(1)	-1493(4)	-2965(3)	2369(1)	36(1)
C(2)	-1446(5)	-2046(3)	2698(1)	52(1)
C(3)	-733(5)	-2241(4)	3142(1)	60(1)
C(4)	-37(5)	-3369(4)	3259(1)	58(1)
C(5)	-76(5)	-4295(4)	2939(1)	57(1)
C(6)	-807(5)	-4098(3)	2490(1)	46(1)
C(7)	-2250(4)	-2694(3)	1895(1)	38(1)
C(8)	-2490(4)	-3732(3)	1550(1)	39(1)
C(9)	-3332(4)	-3327(3)	1085(1)	40(1)
C(10)	-1983(4)	-1633(3)	646(1)	32(1)
C(11)	-164(4)	-2725(3)	370(1)	38(1)
C(12)	552(4)	1223(3)	710(1)	35(1)
C(13)	3388(4)	-549(3)	583(1)	40(1)
C(14)	4920(4)	1902(3)	1271(1)	39(1)
C(15)	5152(4)	1427(3)	1764(1)	36(1)
C(16)	5934(4)	2401(3)	2085(1)	36(1)
C(17)	6423(4)	2083(3)	2582(1)	35(1)
C(18)	7176(5)	2993(4)	2860(1)	52(1)
C(19)	7685(5)	2733(4)	3320(1)	65(1)
C(20)	7428(5)	1574(5)	3497(1)	62(1)
C(21)	6677(5)	681(4)	3223(1)	56(1)
C(22)	6169(4)	929(3)	2764(1)	45(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2 Select bond lengths (nm) and angles (°) for the title compound

Ni(1)—N(4)	0.2095(2)	Ni(1)—N(2)	0.2106(2)
Ni(1)—Cl(1)	0.24865(8)	O(2)—C(16)	0.1215(4)
N(1)—C(10)	0.1329(4)	N(1)—N(3)	0.1350(4)
O(1)—C(7)	0.1214(4)		
N(4)#1-Ni(1)-N(2)	89.14(9)	N(4)-Ni(1)-N(2)	90.86(9)
N(4)-Ni(1)-Cl(1)	90.06(7)	N(4)#1-Ni(1)-Cl(1)	89.94(7)
N(2)#1-Ni(1)-Cl(1)	89.72(7)	N(2)-Ni(1)-Cl(1)	90.28(7)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$.

Table 3 Intermolecular interaction distances (nm × 10) of the title compound

D	H	A	Symm.	D—H	H···A	D···A	D—H···A
O(1w)	H(11w)	Cl(1)		0.86(4)	2.44(3)	3.254(3)	160(3)
O(2w)	H(21w)	O(1w)		0.84(3)	2.01(4)	2.844(5)	168(5)
O(1w)	H(12w)	N(3)	$x, 1+y, z$	0.77(4)	2.17(3)	2.883(4)	154(4)
O(2w)	H(22w)	O(3w)	$1-x, 1-y, -z$	0.86(5)	2.28(6)	2.829(6)	122(5)
O(3w)	H(32w)	O(2w)		0.91(8)	1.97(8)	2.804(6)	150(8)
C(5)	H(5A)	O(1)	$-x, -1/2+y, 1/2-z$	0.9303	2.5607	3.437(5)	157.2
C(8)	H(8A)	O(2)	$-1+x, -1+y, z$	0.9702	2.5633	3.471(4)	155.82
C(10)	H(10A)	N(6)	$-1+x, y, z$	0.9304	2.5177	3.358(4)	150.39

D: donor; A: acceptor; symm.: symmetry applied in acceptor.

References

1 Xu, L. Z.; Zhang, S. S.; Li, H. J.; Jiao, K. *Chem. Res. Chin. Univ.* **2002**, *18*(3), 284.

2 Zhao, J.; Zhou, Z. Z.; Peng, Y. B.; Zhao, G. F. *Chin. Chem. Lett.* **1998**, *8*, 35.

3 Vos, G.; de Graaf, R. A. G.; Haasnoot, J. G.; van derKraan, A. M.; de Vaal, P.; Reedijk, J. *Inorg. Chem.* **1984**, *23*, 2905.

4 Sugiyarto, K. H.; Goodwin, H. A. *Aust. J. Chem.* **1994**, *47*, 263.

5 Thomann, M.; Kahn, O.; Guilhem, J.; Varret, F. *Inorg. Chem.* **1994**, *33*, 6029.

6 Kahn, O.; Kröber, J.; Jay, C. *Adv. Mater.* **1991**, *15*, 181.

7 Kröber, J.; Codjovi, E.; Kahn, O.; Grolière, F.; Jay, C. *J. Am. Chem. Soc.* **1993**, *115*, 9810.

8 Pei, Y.; Lang, A.; Bergerat, P.; Kahn, O.; Fettouhi, M.; Ouahab, L. *Inorg. Chem.* **1996**, *35*, 193.

9 Laverenova, L. G.; Yudina, N. G.; Ikorskii, V. N.; Varnek, V. A.; Oglezneva, I. M.; Larionov, S. V. *Polyhedron* **1995**, *14*, 1333.

10 Garcia, Y.; van Koningsbruggen, P. J.; Bravic, G.; Guionneau, P.; Chasseau, D.; Cascarano, G. L.; Moscovici, J.; Lambert, K.; Michalowicz, A.; Kahn, O. *Inorg. Chem.* **1997**, *36*, 6357.

11 Hill, G. H.; Kropa, L. E. *J. Am. Chem. Soc.* **1933**, *55*, 2509.

12 Han, G. D.; Zhao, S. W.; Li, S. W. *Handbook of Org. Preparation Chem.* **1980**, 304.

13 Sheldrick, G. M. SADABS, *Program for Empirical Absorption Correction of Area Detector Data*, University of Gottingen, Germany, **1996**.

14 Sheldrick, G. M. *SHELXTL V5.1* Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA, **1997**.

15 Wilson, A. J. *International Table for X-Ray Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, **1992**, Tables 6.1.1.4 (pp. 500—502) and 4.2.6.8 (pp. 219—222) respectively.

16 Socrates, G. *Infrared Characteristic Group Frequencies*, John Wiley & Sons, Chichester, New York, Brisbane, Toronto, **1989**.

17 Tian, Y. P.; Duan, C. Y.; Lu, Z. L.; You, X. Z.; Fun, H. K.; Sivakumar, K. *Polyhedron* **1996**, *15*, 4033.

18 Sun, W. Y.; Fei, B. L.; Okamura, T. A.; Zhang, Y. A.; Ye, T.; Tang, W. X.; Ueyama, N. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2733.

19 Diamantopoulou, E.; Zafiropoulos, T. F.; Perlepes, S. P.; Raptopoulou, C. P.; Terzis, A. *Polyhedron* **1994**, *13*, 1593.

20 Jian, F. F.; Wang, Z. X.; Bai, Z. P.; You, X. Z.; Fun, H. K.; Chinnakali, K. *J. Chem. Crystallogr.* **1999**, *29*, 359.

21 McAuley, A.; Subramanian, S. *Inorg. Chem.* **1991**, *30*, 371.

22 Ito, T.; Sugimoto, M.; Toriumi, K.; Ito, H. *Chem. Lett.* **1981**, 1477.

23 Xiong, R. G.; Liu, C. M.; Zuo, J. L.; Li, H. Z.; You, X. Z.; Fun, H. K.; Sivakumar, K. *Polyhedron* **1997**, *16*, 2315.

(E0212187 ZHAO, X. J.; DONG, H. Z.)