研究简报

二氯四(苯丙酮 -1, 2, 4- 三唑)合钴六水配合物晶体结构

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Structure of Tetra(1-propiophenone-1, 2, 4-triazole-N^4) Dichloro Cobalt(Ⅱ) Solvate Hexahydrate Complex: $[CoCl_2(C_2H_2N_3CH_2CH_2COPh)_4]\cdot 6H_2O$

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The crystal and molecular structure of $[CoCl_2(N^4\text{-trz}CH_2CH_2COPh)_4]\cdot 6H_2O$ (trz = 1, 2, 4-triazole) has been determined by X-ray diffraction. It crystallizes in the monoclinic system, space group $P2_1/c$, with unit-cell parameters $a = 0.8039(2)$ nm, $b = 1.0822(2)$ nm, $c = 2.9013(6)$ nm, $\beta = 94.79(3)°$, and $Z = 4$. Each cobalt atom is coordinated by four N atoms of triazole from four 1-propiophenone-1, 2, 4-triazole ligands and two chloride anion in *cis* arrangement with almost perfect octahedral coordination geometry. In addition to the coordinating cobalt complex, there are six uncoordinated water molecules, which complete the crystal structure. In the solid state, the title compound forms three dimensional network structure through hydrogen bonds. The intermolecular hydrogen bonds connect the $[CoCl_2(C_2H_2N_3CH_2CH_2COPh)_4]$ and H_2O moieties. CCDC: 200711.

Keywords: 1-propiophenone-1, 2, 4-triazole ligand single crystal structure dichorocobalt(Ⅱ) complex hydrogen bonds network

0 Introduction

Recently, the compounds containing 1H-1, 2, 4-triazole group have attracted much interest because of their exhibiting some fungicidal activity and plant growth regulating activity[1], and showing 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 azoles 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 hystereses 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 metal-triazole complexes have been

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carried out for many transition metal[8~10]. To our knowledge, there are a little crystal structure of Co (Ⅱ) with 1, 2, 4-triazole ligands forming coordinating complexes which have been reported so far because of Co (Ⅱ) instability. In this paper we report the preparation and crystal structure of the title compound.

1 Experimental

1.1 Synthesis

All chemicals used were of analytical reagent grade and used directly without further purification. α-bromic-propiophenone [$PhCOCH_2CH_2Br$] was prepared according to literature method[11]. α-(1, 2, 4-triazole-1-yl) -propiophenone [($C_2H_2N_3CH_2CH_2COPh$) was prepared according to literature method[12].

The $CoCl_2$ complex (0.65g, 5.0mmol) was dissolved in hot water (50mL), stirred, and the warm solution of α-(1, 2, 4-triazole-1-yl)-propiophenone (1.0g, 5.0mmol) in EtOH (50mL) was added. The mixture was refluxed for 20min. The red solution was filtered and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, a red crystalline solid appeared several weeks later and was separated by filtration. The C, H and N contents were determined by elemental analysis (Found(%): C, 50.28; H, 5.17; N, 15.96. $C_{44}H_{56}Cl_2CoN_{12}O_{10}$ Calc. (%): C, 50.63; H, 5.36; N, 16.11).

1.2 Crystallographic Data Collection and Structure Determination

A summary of the key crystallographic information is given in Table 1. The selected crystal of [$CoCl_2(C_2H_2N_3CH_2CH_2COPh)_4$] · $6H_2O$ was mounted on SMART CCD diffractometer. Reflection data were measured at 293K, using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073$nm), ω-2θ scan mode. Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction was carried out using SADABS[13] program. 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. The hydrogen atoms were located by difference synthesis and refined isotropically. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave $R = 0.0586$, $wR = 0.1246$ for 3591 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. (Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography[15].)

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Table 1 Summary of Crystallographic Results for the Title Compound

empirical formula	$C_{22}H_{28}ClCo_{0.5}N_6O_5$
formula weight	521.42
temperature/K	293(2)
wavelength/nm	0.071073
crystal system	monoclinic
space group	$P2_1/c$
a/nm	0.8039(2)
b/nm	1.0822(2)
c/nm	2.9013(6)
β/(°)	94.79(3)
volume/nm^3	2.5152(9)
Z	4
calculated density/(Mg · m^{-3})	1.377
absorption coefficient/mm^{-1}	0.514
F(000)	1090
crystal size/mm^3	0.38 × 0.08 × 0.06
theta range for data collection/(°)	1.41 to 28.41
limiting indices	$-10 \leqslant h \leqslant 10$ $-14 \leqslant k \leqslant 12$ $-35 \leqslant l \leqslant 38$
reflections collected/unique	17526/6129 [R(int) = 0.0880]
completeness to $\theta = 28.41$	96.9%
absorption correction	empirical
max. and min. transmission	0.9701and 0.8302
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	6129/0/322
goodness-of-fit on F^2	0.950
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0586$, $wR_2 = 0.1246$
R indices (all data)	$R_1 = 0.1118$, $wR_2 = 0.1425$
Extinction coefficient	0.011(1)
largest diff. peak and hole/(e · nm^{-3})	463 and −761

2 Results and Discussion

The X-ray structure of the title compound [$CoCl_2$ (N^4-trzCH_2CH_2COPh)$_4$] · $6H_2O$ consists of the [$CoCl_2$ (N^4-trzCH_2CH_2COPh)$_4$] molecules and six uncoordinated molecules of water. Fig. 1 shows structure of the title compound with atomic numbering scheme, and Fig. 2 a perspective view of the crystal packing in the

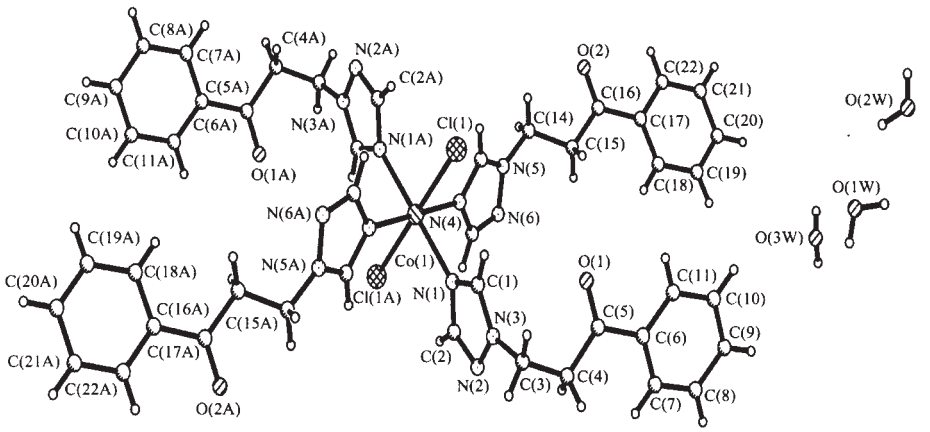

Fig. 1　Molecular structure for $[CoCl_2(N^4\text{-trzCH}_2CH_2COPh)_4]$ with the atomic numbering scheme

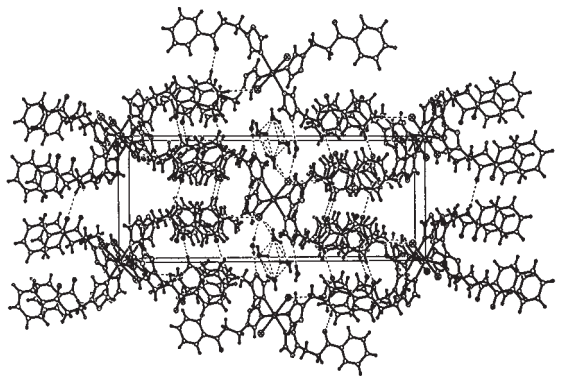

Fig. 2　A view of the crystal packing down the *a* axis for $[CoCl_2(C_2H_2N_3CH_2CH_2COPh)_4]$

unit cell. Selected bond lengths and angles are presented in Table 2, and potentially weak intermolecular interactions in Table 3.

The central Co atom is located on an inversion center, and surrounded by four α-(1, 2, 4-triazole-1-yl)-propiophenone ligands and two Cl^- anions. The $CoCl_2N_4$ core involving the central atom is an almost perfect octahedron. The basal plane is formed by four nitrogen donor atoms of triazole from four 1-propiophenone-1, 2, 4-triazole ligands, which is an almost perfect plane with the central Co 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 88.97(9)° ~91.03(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 Co atom are normal. The Co-N bond distances [0.2129(2) nm and 0.2148(2) nm] are in good agreement with the corresponding octahedron Co-N distances reported, in references[16~24].

The triazole ring [N(1), N(2), N(3), C(1) and C(2)] with the conjunction carbon atom C(3) and cobalt atom are fairly planar, the deviation from the least squares plane through the ring atoms is smaller than 0.0008(3)nm. The phenyl ring [C(6), C(7), C(8), C(9), C(10) and C(11)] with the conjunction carbon atom C(5) are also quite planar, the largest deviation from the least squares plane is 0.0012(3) nm. The dihedral angle between these two planes is 69.3(3)°.

The most interesting structural feature of the

Table 2　Selected Bond Lengths(nm) and Angles(°) for the Title Compound

Co(1)-N(4)	0.2129(2)	Co(1)-N(1)	0.2148(2)	Co(1)-Cl(1)	0.25221(9)
O(1)-C(5)	0.1215(4)	O(2)-C(16)	0.1208(4)	N(2)-C(2)	0.1317(4)
N(1)-C(2)	0.1340(4)	N(4)-C(12)	0.1324(3)	N(2)-N(3)	0.1358(3)
N(5)-C(12)	0.1307(4)	N(3)-C(3)	0.1461(4)	N(6)-C(13)	0.1302(4)
N(5)-N(6)	0.1354(3)				
N(1)-Co(1)-Cl(1)	90.58(7)	N(4)-Co(1)-N(1)	91.11(9)	C(2)-N(2)-N(3)	102.5(2)
N(4)-Co(1)-Cl(1)	90.26(7)	N(2)-N(3)-C(3)	120.1(2)	C(1)-N(1)-C(2)	103.0(2)

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

Table 3 Hydrogen Bond

D – H···A	D-H/nm	H···A/nm	D···A/nm	D – H···A/(°)
O(1W) – H(11W)···O(3W)[a]	0.08499	0.24525	0.28336	108.06
O(2W) – H(12W)···Cl(1)[b]	0.08460	0.25161	0.32049	139.24
O(3W) – H(13W)···Cl(1)[c]	0.10100	0.23325	0.32258	146.86
O(1W) – H(21W)···O(2W)	0.08501	0.23839	0.28275	113.09
O(1W) – H(21W)···O(2W)[d]	0.08501	0.23694	0.27813	110.32
O(2W) – H(22W)···O(1W)	0.08548	0.21213	0.28275	139.66
O(3W) – H(23W)···N(2)[e]	0.08196	0.21119	0.28769	155.28
C(1) – H(1A)···N(6)[a]	0.09300	0.25044	0.33454	150.51
C(2) – H(2B)···Cl(1)[b]	0.09300	0.27668	0.33180	118.92
C(4) – H(4A)···O(2)[f]	0.09700	0.25488	0.34566	155.84
C(8) – H(8A)···O(1)[g]	0.09300	0.25472	0.34222	156.92

Symmetry code: a: $-1+x,\ y,\ z$; b: $-x,\ 2-y,\ -z$; c: $1+x,\ -1+y,\ z$; d: $1-x,\ 1-y,\ -z$; e: $1+x,\ y,\ z$; f: $-1+x,\ -1+y,\ z$; g: $-x,\ -1/2+y,\ 1/2-z$.

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. The O(3w) – H(11w)···O(1w) distance is 0.2833(6)nm, which is compared with that of pure water (0.283nm)[25]. The Cl(1), O(1) and O(2) with C atoms in 1-propiophenone-1H-1, 2, 4-triazole 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 $[CoCl_2(C_2H_2N_3CH_2CH_2COPh)_4]$ and H_2O molecules altogether and form three dimensional hydrogen bond network which stabilizes the structure.

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