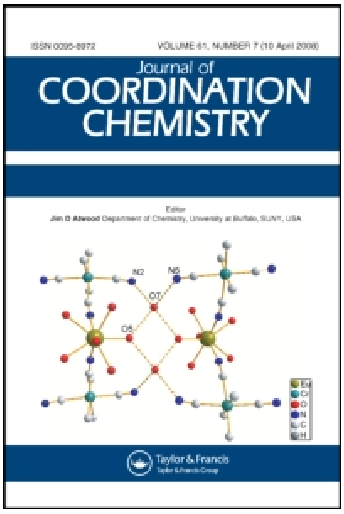

ISSN 0095-8972 VOLUME 61, NUMBER 7 (10 April 2008)
Journal of
COORDINATION
CHEMISTRY

Taylor & Francis

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Nickel and copper complexes of cyclopropyltetrazole: crystal structures of $[Ni(C_3tz)_6](BF_4)_2$ and $[Cu(C_3tz)_6](BF_4)_2$

A. A. Soliman[a]; M. M. Khattab[a]; W. Linert[b]
[a] Department of Chemistry, Faculty of Science, UAEU, Al-Ain, UAE [b] Institute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

To cite this Article Soliman, A. A. , Khattab, M. M. and Linert, W.(2005) 'Nickel and copper complexes of cyclopropyltetrazole: crystal structures of $[Ni(C_3tz)_6](BF_4)_2$ and $[Cu(C_3tz)_6](BF_4)_2$', Journal of Coordination Chemistry, 58: 5, 421 — 427

To link to this Article: DOI: 10.1080/0095897042000327914
URL: http://dx.doi.org/10.1080/0095897042000327914

Journal of Coordination Chemistry
Vol. 58, No. 5, 20 March 2005, 421–427

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Nickel and copper complexes of cyclopropyltetrazole: crystal structures of $[Ni(C_3tz)_6](BF_4)_2$ and $[Cu(C_3tz)_6](BF_4)_2$

A. A. SOLIMAN*†, M. M. KHATTAB† and W. LINERT‡

†Department of Chemistry, Faculty of Science, UAEU,
PO Box 17551, Al-Ain, UAE
‡Institute of Inorganic Chemistry, Vienna University of Technology,
Getreidemarkt 9, A-1060 Vienna, Austria

(Received in final form 2 August 2004)

Cyclopropyltetrazole (C_3tz) and its nickel(II) and copper(II) complexes $[M(C_3tz)_6](BF_4)_2]$ were isolated and characterized by elemental analyses, electronic spectroscopy, molar conductances, magnetic susceptibilities and single-crystal X-ray analyses.

Keywords: Cyclopropyltetrazole; Nickel(II); Copper(II); X-ray structures

1. Introduction

One of the challenging issues in molecular chemistry is the use of molecular compounds in electronic devices and systems [1]. Such devices must incorporate compounds exhibiting the phenomenon of *bistability*, which may be defined as the property of a molecular assembly existing in two stable (or metastable) electronic states in a given range of external environmental parameters (temperature, pressure, etc.). Probably the most spectacular example of molecular bistability concerns spin transitions, in particular for iron(II) complexes [2].

Tetrazole complexes $[Fe(Rtz)_6](BF_4)_2$ (Rtz = 1-alkyltetrazole) are spin crossover complexes exhibiting entropy-driven spin transitions from the low-spin (LS) $^1A_1$ ground state at low temperatures to the high-spin (HS) $^5T_2$ state at high temperature [3]. Detailed spin crossover behavior varies with the substituent R and is strongly influenced by cooperative effects of elastic origin due to large differences in metal–ligand bond lengths or the concomitant difference in volume between the two states [4]. Simple 1-alkyl-substituted ligands can easily be obtained by the method of

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*Corresponding author. E-mail: ahmed.soliman@uaeu.ac.ae

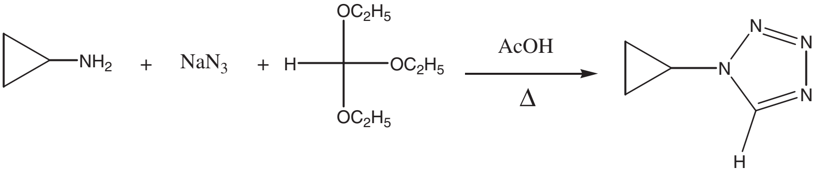
Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/0095897042000327914

Satoh [5] with yields of about 40–70%. Other methods [6–11] are also useful. Monodentate tetrazoles arrange themselves octahedrally around the central metal ion [12–14]. The coordinating atom of the tetrazole ring is generally the nitrogen atom at position 4.

The material below concerns the preparation and characterization of some new tetrazole complexes. A problem with iron(II) complexes is the difficulty in preparation of single crystals suitable for X-ray diffraction analysis. To throw some light on the orientation of the six tetrazole ligands around the central metal ion, nickel, copper and zinc complexes are prepared in the crystalline state and can be used as models for the iron analogue. In this article we report the preparation of cyclopropyltetrazole and its nickel(II) and copper(II) complexes. The crystal structures of $[Ni(C_3tz)_6](BF_4)_2$ and $[Cu(C_3tz)_6](BF_4)_2$ are reported.

2. Experimental

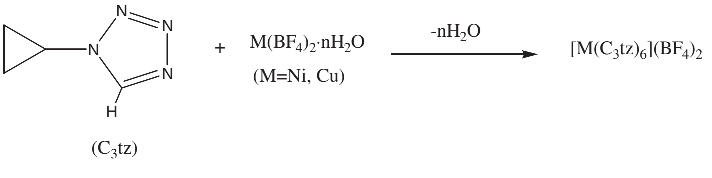
2.1. *Synthesis of cyclopropyltetrazole (C_3tz)*



Cyclopropyltetrazole (C_3tz) was prepared after the method of Franke *et al.* [11]; 5.71 g (0.1 mol) of cyclopropylamine, 23.71 g (0.16 mol) of triethylorthoformate and 9.752 (0.16 mol) of sodium azide were dissolved in 80 cm^3 of acetic acid and heated at 90°C for 5 h. The solvent was removed at 70°C under reduced pressure. The product was dissolved in 70 cm^3 of 2 M aqueous HCl and extracted three times with 70 cm^3 of isopropanol. The organic phase was washed with 100 cm^3 of water, 50 cm^3 of saturated aqueous $NaHCO_3$ and saturated NaCl solution. After drying the organic phase over Na_2SO_4 and evaporation of ethyl acetate, the yellow, oily, raw product was distilled at 123°C and 1 mbar, yielding a colorless liquid (3.3 g, 29 m mol, 29% yield).

2.2. *Preparation of complexes*

The complexes were prepared according to the following scheme.



2.2.1. $[Cu(C_3tz)_6](BF_4)_2$. C_3tz (0.30 g, 2.7 m mol) dissolved in 30 cm^3 of ethanol and 0.14 g (0.45 m mol) of $Cu(BF_4)_2 \cdot 4H_2O$ dissolved in 15 cm^3 of ethanol were mixed together. The mixture was left in a refrigerator for several weeks when tetragonal, blue crystals of $Cu(C_3tz)_6(BF_4)_2$ separated out. The complex was filtered off and dried.

2.2.2. $[Ni(C_3tz)_6](BF_4)_2$. C_3tz (0.30 g, 2.7 m mol) dissolved in 30 cm^3 of ethanol and 0.10 g (0.45 m mol) of $Ni(BF_4)_2 \cdot 4H_2O$ dissolved in 15 cm^3 of ethanol were mixed together. The mixture was left in a fridge for several weeks when violet, prismatic crystals of $Ni(C_3tz)_6(BF_4)_2$ separated out. The complex was filtered off and dried.

2.3. *X-ray structure determination*

Intensity data were collected for $[Cu(C_3tz)_6](BF_4)_2$ and $[Ni(C_3tz)_6](BF_4)_2$ on a Nonius Kappa-CCD area detector diffractometer [16] equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All calculations were performed using the maXus crystallographic software package (Bruker Nonius, Delft, and MacScience, Japan). The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2. The nonhydrogen atoms were refined anisotropically. The H-atoms were placed in calculated positions and refined isotropically with a riding model. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [17]. Summaries of crystal data and refinement details for $[Cu(C_3tz)_6](BF_4)_2$ and $[Ni(C_3tz)_6](BF_4)_2$ are listed in tables 1 and 2.

3. Results and discussion

3.1. *Spectroscopic and magnetic characterization*

The compositions, partial elemental analyses, electronic spectra data (DMSO solutions) and room temperature magnetic data for $[Cu(C_3tz)_6](BF_4)_2$ and $[Ni(C_3tz)_6](BF_4)_2$ are

Table 1. Crystal data and refinement details for $[Ni(C_3tz)_6](BF_4)_2$.

Empirical formula	$C_{24}H_{36}B_2F_8N_{24}Ni$
Formula weight	893.10
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, $R\bar{3}$
Unit cell dimensions	$a = 10.7651(4)$ Å $b = 10.7651(4)$ Å $c = 29.784(2)$ Å
Volume	2989.2(3) Å^3
Z, Calculated density	3, 1.488 Mg m^3
Absorption coefficient	0.578 mm^{-1}
$F(000)$	1374
Scan type	ω and ϕ scans
θ range for data collection	3.50 to 26.01°
Index ranges	$-13 \le h \le 13$, $-10 \le k \le 10$, $-36 \le l \le 34$
Reflections collected/unique	2291/1309 [R(int) = 0.0460]
Completeness to $\theta = 26.01°$	99.4%
Data/restraints/parameters	1309/0/97
Goodness-of-fit on F^2	1.037
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0451$, $wR2 = 0.0838$
R indices (all data)	$R1 = 0.0727$, $wR2 = 0.0960$
Extinction coefficient	0.0001(2)
Largest diff. peak and hole	0.271 and −0.310 e A^{-3}

Table 2. Crystal data and refinement details for $[Cu(C_3tz)_6](BF_4)_2$.

Empirical formula	$C_{24}H_{36}B_2F_8N_{24}Cu$
Formula weight	897.93
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, $R\bar{3}$
Unit cell dimensions	$a = 10.7792(5)$ Å
	$b = 10.7792(5)$ Å
	$c = 30.006(2)$ Å
Volume	3019.3(3) $Å^3$
Z, Calculated density	3, 1.481 $Mg\,m^3$
Absorption coefficient	0.633 mm^{-1}
$F(000)$	1377
Scan type	ω and ϕ scans
θ range for data collection	3.48 to 27.49°
Index ranges	$-14 \le h \le 14$, $-11 \le k \le 11$, $-38 \le l \le 23$
Reflections collected/unique	2108/1532 [R(int) = 0.0470]
Completeness to $\theta = 27.49°$	99.4%
Data/restraints/parameters	1532/0/96
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0445$, $wR2 = 0.1083$
R indices (all data)	$R1 = 0.0560$, $wR2 = 0.1171$
Largest diff. peak and hole	0.305 and −0.361 e A^{-3}

Table 3. Elemental analyses, electronic absorption and magnetic moment data for the ligand and its complexes.

		% Found (Calc.)			Absorption bands/nm		
Compound	Color	C	H	N	λ_{max}	Assignment	μ_B/BM
C_3tz	Colorless				312	n–π	
$[Cu(C_3tz)_6](BF_4)_2$	Blue	32.0 (32.1)	4.2 (4.0)	37.3 (37.4)	390(sh) 530	CT d–d	2.2
$[Ni(C_3tz)_6](BF_4)_2$	Violet	32.4 (32.2)	4.1 (4.0)	36.5 (37.6)	395(sh) 520	CT d–d	2.7

shown in table 3. Electronic spectra exhibit a charge transfer transition at approximately 400 nm, with poorly resolved shoulders. The d–d absorption bands at 530 and 520 nm for $[Cu(C_3tz)_6](BF_4)_2$ and $[Ni(C_3tz)_6](BF_4)_2$, respectively, indicate octahedral geometry [18], which is supported by crystal structure analyses. Molar conductivities in DMSO fall into the range expected for 1 : 2 electrolytes [19]. $[Cu(C_3tz)_6](BF_4)_2$ and $[Ni(C_3tz)_6](BF_4)_2$ have normal moments consistent with uncoupled, monomeric, complex Cu(II) and Ni(II) ions.

3.2. *Crystal structures*

Six tetrazole ligands act as monodentates with copper and nickel ions through N4. The $[Cu(C_3tz)_6](BF_4)_2$ and $[Ni(C_3tz)_6](BF_4)_2$ structures show that both copper and nickel ions are six coordinated and are both best described as having octahedral geometry. The molecular structures of $[Cu(C_3tz)_6](BF_4)_2$ and $[Ni(C_3tz)_6](BF_4)_2]$ in the solid state are shown in figures 1 and 2. Bond lengths and angles are listed in table 4. Nickel exhibits almost undistorted octahedral coordination, whereas copper exhibits slightly distorted octahedral geometry due to Jahn–Teller effects as seen

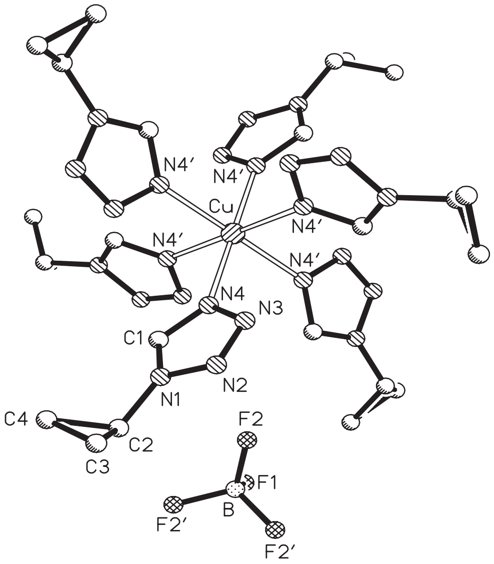


Figure 1. Molecular structure of $[Cu(C_3tz)_6](BF_4)_2$ showing the atom numbering scheme.

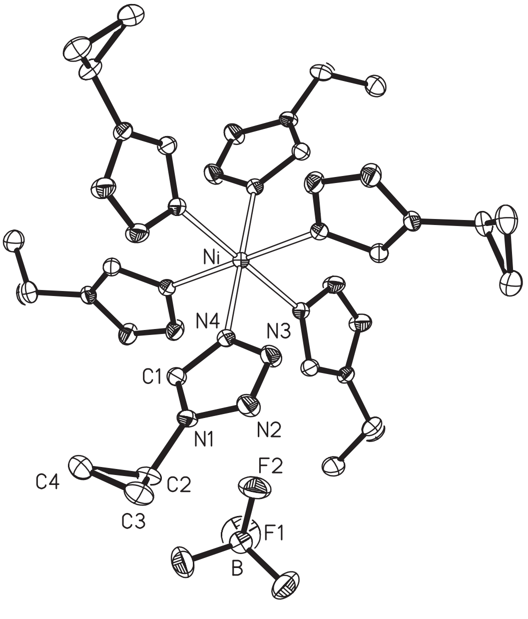


Figure 2. Molecular structure of $[Ni(C_3tz)_6](BF_4)_2$ showing the atom numbering scheme.

from the N–Cu–N angles. Both complexes have the same crystal packing with two tetrafluoroborate ions per octahedral cation. The BF_4 groups are disordered in two orientations with B, F1 and F2 describing the major orientation and B, F1′ and F2′ the minor orientation. Isotropic temperature factors were used in the refinement of the F atoms.

Table 4. Selected bond lengths and angles (Å, °) for $[M(C_3tz)_6](BF_4)_2$.

	M = Ni	M = Cu
M–N(4)	2.100(2)	2.134(2)
N(4)–Ni–N(4)$^{\#1}$	180	180
N(4)–Ni–N(4)$^{\#2}$	90.01(8)	90.14(7)
N(4)–Ni–N(4)$^{\#3}$	89.99(8)	89.86(7)
B–F(1)	1.339(8)	1.339(7)
B–F(2)	1.372(3)	1.371(3)
F(1)–B–F(2)	110.5(3)	110.2(2)
F(2)$^{\#4}$–B–F(2)$^{\#5}$	108.4(3)	108.7(3)

Symmetry transformations used to generate equivalent atoms: $^{\#1}-x, -y, -z$; $^{\#2}y, -x+y, -z$; $^{\#3}-y, x-y, z$; $^{\#4}-y+1, x-y, z$; $^{\#5}-x+y+1, -x+1, z$.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 220634 for $[Cu(C_3tz)_6](BF_4)_2$ and CCDC 244640 for $[Ni(C_3tz)_6](BF_4)_2$. Copies can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Thanks for financial support are due to the Research Affairs Center at the UAE University under contract 15-03-2-11/03 and to Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich (Project 15874-N03). We also acknowledge the help of Prof. K. Mereiter, TU Wien, for refining the crystal data and for providing the drawings.

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