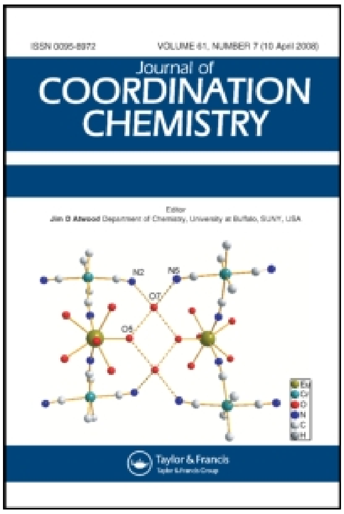

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Synthesis, Characterization and Crystal Structure of a Binuclear Copper(II) Diethylenetriamine Complex Bridged Through a Centrosymmetric 1,3-μ-Thiocyanato Group

Changjian Feng[a]; Deping Cheng[a]; Duanjun Xu[a]; Yueqing Zhen[b]; Jianli Lin[b]; Yuanzhi Xu[a]
[a] Department of Chemistry, Zhejiang University, Hangzhou, China [b] Department of Chemistry, Ninbo University, Ninbo, China

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A BINUCLEAR COPPER(II) DIETHYLENETRIAMINE COMPLEX BRIDGED THROUGH A CENTROSYMMETRIC 1,3-μ-THIOCYANATO GROUP

CHANGJIAN FENG[a,*], DEPING CHENG[a], DUANJUN XU[a],
YUEQING ZHEN[b], JIANLI LIN[b] and YUANZHI XU[a]

[a]*Department of Chemistry, Zhejiang University, Hangzhou 310027, China;*
[b]*Department of Chemistry, Ninbo University, Ninbo 315211, China*

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The binuclear copper(II) complex $[Cu_2(dien)_2(NCS)_2](ClO_4)_2$, where dien = diethylenetriamine, has been synthesized and characterized by analysis, infrared (IR) and electron paramagnetic resonance (EPR) spectra. A centrosymmetric axial–equatorial 1,3-μ-NCS bridged binuclear copper(II) complex has been identified by X-ray diffraction, in which each copper(II) is five-coordinated with an elongated square pyramidal geometry with four nitrogen atoms on its basal plane and one sulfur atom at the apical position. Frozen solution EPR spectra at 77 K indicate that the interaction between the two copper centers is weak and the bridge is retained in solution.

Keywords: Binuclear copper(II) complex; diethylenetriamine; crystal structure

INTRODUCTION

The diethylenetriamine (dien) ligand is known to form two fused five-membered rings with metal ions.[1] Five-coordinated Cu-dien complexes have been reviewed extensively as to their molecular structures and the possible

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[*] Corresponding author.

sources of electronic origin that may contribute to structural distortion.[2] Recently, some copper(II) complexes of dien with different counter-ions and axial ligands have been reported.[3,4] To evaluate magnetic exchange interactions between transition metal ions bridged through multi-atomic ligands, Srinivas studied the electron paramagnetic resonance (EPR) spectrum of binuclear copper(II) complexes of dien bridged through varying length dicarboxylato spacers.[5]

Herein we report the crystal structure of a centrosymmetric 1,3-μ-NCS bridged binuclear copper(II) complex with dien, $[Cu_2(dien)_2(NCS)_2](ClO_4)_2$, in which the five-coordinated geometry is an elongated square pyramid. EPR studies show that the interaction between the two copper centers is negligible and the thiocyanato bridge is retained in solution.

EXPERIMENTAL

Preparation

A methanol solution (10.0 cm^3) containing dien (0.112 g, 1.10 mmol) was added dropwise to a stirred solution of 0.281 g (1.20 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in 20.0 cm^3 of methanol. After refluxing the mixture for two hours, 0.092 g (1.2 mmol) of NH_4SCN was added to the solution. The mother liquid was evaporated at room temperature for a week. The obtained blue polycrystalline precipitate was filtered off and dried under vacuum to give $[Cu_2(dien)_2(NCS)_2](ClO_4)_2$ in 78% yield. Single crystals suitable for X-ray analysis were isolated by slow evaporation of a methanol solution in a refrigerator. Nitrogen, carbon and hydrogen were analyzed with a Carlo Erba 1160 instrument. *Anal.* calcd. for $C_{10}H_{26}N_8O_8Cl_2S_2Cu_2$ (%): C, 18.43; H, 3.99; N, 17.20; S, 9.83. Found: C, 18.60; H, 4.04; N, 17.19; S, 9.79.

Crystal Structure Determination

A blue prism with dimensions 0.30 × 0.20 × 0.25 mm was mounted on a glass fiber and used for structure determination. The intensities were collected at 293 K on a Bruker AXS P4 diffractometer using the $\theta/2\theta$ scan mode. Some 4235 reflections (3493 unique, 3163 observed $[I > 2\sigma(I)]$) were collected in the range of $1.80° < \theta < 30.14°$ with $R_{int} = 0.0159$. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.[6]

The crystal structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods. The four oxygen atoms of perchlorate

O(11), O(12), O(13) and O(14) were disordered. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in a difference Fourier map. The contributions of these hydrogen atoms were included in structure–factor calculations. The weighing scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants adjusted by the program. The final R_w was 0.111, with conventional $R = 0.039$ and goodness of fit 1.039. All computations were carried out on a PC-586 using the SHELXTL program package.[7]

Physical Measurements

IR spectra were measured on KBr discs using a Nicolet 5DX FT-IR spectrophotometer. EPR measurements were conducted on frozen DMF solutions using a JES-FEXING JEOL ESR spectrometer at X-band frequencies at 77 K and 100 kHz field modulation. Studies at liquid nitrogen temperature (77 K) were performed with a quartz insert Dewar.

RESULTS AND DISCUSSION

Crystal Structure

Crystal data for $[Cu_2(dien)_2(NCS)_2](ClO_4)_2$: $C_{10}H_{26}N_8O_8Cl_2S_2Cu_2$, $M = 648.48$, triclinic, space group $P\bar{1}$, $a = 7.473(1)$, $b = 7.486(1)$, $c = 11.797(1)$ Å, $\alpha = 90.53(1)°$, $\beta = 105.35(1)°$, $\gamma = 109.06(1)°$, $U = 598.20(12)$ Å^3, $Z = 1$, $D_c = 1.804\ \mathrm{g\,cm^{-3}}$, $F(000) = 330$, μ (Mo-Kα) $= 2.233\ \mathrm{mm^{-1}}$.

Atomic coordinates and equivalent isotropic displacement parameters for non-H atoms are listed in Table I. Selected bond distances and bond angles are listed in Table II. The crystal structure of $[Cu_2(dien)_2(NCS)_2](ClO_4)_2$ consists of $[Cu_2(dien)_2(NCS)_2]^{2+}$ cation and disordered ClO_4^- anions as shown in Figure 1. In the $[Cu_2(dien)_2(NCS)_2]^{2+}$ cation, Cu(1) involves a five-coordinate square pyramidal geometry, with the sixth potentially bonding position occupied by a disordered oxygen atom O(11)$^{\#}$ at 2.886(4) Å apart from the copper(II) ion, a distance which is considered to be too great for even weak coordination (with symmetry element $\# = 3-x, 3-y, 1-z$). The basal plane consists of three nitrogen atoms N(1), N(2), N(3) from dien and one nitrogen atom N(4)$^{\#\#}$ from bridged NCS$^-$ (with symmetry element $\#\# = -x, -y, -z$). Cu(1) is lifted 0.17 Å above the mean plane fitted to the four in-plane nitrogen atoms in the direction towards the apical sulfur atom S(1). The distance Cu(1)–S(1)

TABLE I Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	U_{eq}
Cu1	1.46319(4)	1.22810(4)	0.17053(2)	0.03433(11)
S1	1.23928(11)	0.84591(9)	0.12223(7)	0.0476(2)
N1	1.6905(4)	1.1944(4)	0.2949(2)	0.0459(5)
N2	1.3528(3)	1.2419(3)	0.3073(2)	0.0360(4)
N3	1.2584(4)	1.3383(4)	0.0849(2)	0.0468(5)
N4	1.4153(4)	0.7670(3)	−0.0432(2)	0.0464(5)
C1	1.6327(6)	1.1554(5)	0.4050(3)	0.0552(7)
C2	1.5135(5)	1.2798(4)	0.4177(2)	0.0478(6)
C3	1.2481(4)	1.3798(4)	0.2858(3)	0.0471(6)
C4	1.1260(4)	1.3384(4)	0.1581(3)	0.0492(6)
C5	1.3453(4)	0.8036(3)	0.0255(2)	0.0374(4)
Cl1	1.15065(10)	1.25662(9)	0.69666(7)	0.0505(2)
O11	1.2933(8)	1.3756(7)	0.7959(4)	0.153(2)
O12	1.2436(10)	1.2320(7)	0.6151(6)	0.175(3)
O13	1.0271(6)	1.3641(6)	0.6569(5)	0.124(2)
O14	1.0475(7)	1.0800(4)	0.7244(5)	0.126(2)

TABLE II Selected bond distance (Å) and bond angles (°)

Cu(1)–N(4)#1	1.949(2)	Cu(1)–N(1)	2.009(3)
Cu(1)–N(3)	2.011(2)	Cu(1)–N(2)	2.017(2)
Cu(1)–S(1)	2.7633(13)	S(1)–C(5)	1.636(3)
C(5)–N(4)	1.152(3)		
N(4)[#1]–Cu(1)–N(1)	94.24(11)	N(4)[#1]–Cu(1)–N(3)	96.32(11)
N(1)–Cu(1)–N(3)	160.67(12)	N(4)[#1]–Cu(1)–N(2)	175.77(9)
N(1)–Cu(1)–N(2)	84.32(10)	N(3)–Cu(1)–N(2)	83.99(10)
N(4)[#1]–Cu(1)–S(1)	95.12(8)	N(1)–Cu(1)–S(1)	95.59(9)
N(3)–Cu(1)–S(1)	99.54(8)	N(2)–Cu(1)–S(1)	88.98(7)
C(5)–S(1)–Cu(1)	94.70(9)	C(4)–N(3)–Cu(1)	109.4(2)
C(2)–N(2)–Cu(1)	108.5(2)	C(3)–N(2)–Cu(1)	108.0(2)
C(5)–N(4)–Cu(1)[#1]	164.9(2)	C(1)–N(1)–Cu(1)	108.7(2)
N(4)–C(5)–S(1)	177.5(2)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+3, -y+2, -z$.

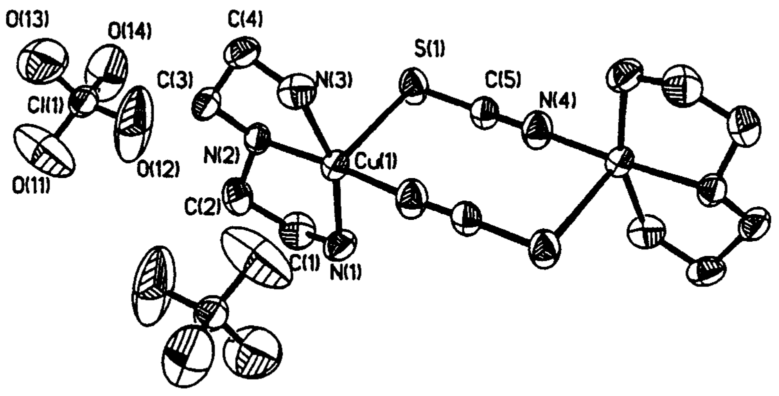

FIGURE 1 Crystal structure of the complex $[Cu_2(dien)_2(NCS)_2](ClO_4)_2$.

2.7633(13) Å is rather longer than those of Cu–N in the range 1.949–2.017 Å and the coordination polyhedron can be described as an elongated square pyramid. When thiocyanate coordinates *via* sulfur, a Cu–S–C angle of *ca.* 90° (94.70(2)°) is observed, whereas when N is the donor, the Cu–N–C geometry (164.9(2)°) is close to linear. Thus the NCS^- anion is in a distorted centrosymmetric axial–equatorial 1,3-μ-bridge mode in which one end is disposed axially towards the first metal ion and the other equatorially towards the second metal ion. The distortion from ideal axial–equatorial 1,3-μ-bridging is due to the rigidity of the dien ligand. The Cu···Cu distance is 5.507(3) Å, which is in the range of known metal···metal distances in centrosymmetric di-1,3-μ-thiocyanate bridges (5.3–5.8 Å).[8]

The crystal packing is characterized by intermolecular hydrogen bonds. A three-dimensional network of hydrogen-bonded cations is formed by means of the following interactions: $N(1)\cdots O(14)^{i}$ (N···O = 3.312(3) Å, N–H···O = 153.7(3)°), $N(1)\cdots O(13)^{ii}$ (N···O = 3.236(4) Å, N–H···O = 150.0(3)°) and $N(2)\cdots O(14)^{iii}$ (N···O = 3.092(4) Å, N–H···O = 148.5(3)°), with symmetry element $i = -x+3, -y+2, -z+1$; $ii = -x+3, -y+3, -z+1$ and $iii = -x+2, -y+2, -z+1$.

Infrared Spectrum

The 3360 and 3295 cm^{-1} bands could be assigned to primary and secondary amine groups, respectively, in the infrared spectrum of free dien ligand. In the spectrum of the complex they are shifted to lower wavelength numbers by 65 and 78 cm^{-1}, respectively. These shifts are strong evidence that the ligand is coordinated in a tridentate mode.[1]

It is a well-established infrared spectroscopic criterion that $\nu_{aym}(NCS) < 2000\,cm^{-1}$ characterizes single-atom >NCS bridging, while ν_{aym} $(NCS) \geq 2100\,cm^{-1}$ indicates the usual three-atom -NCS-bridge.[9] The IR spectrum of the complex shows an $\nu_{aym}(NCS)$ absorption (2090 cm^{-1}) in the range typical of 1,3-μ-NCS-bridging. The strong and broad absorptions at 1080, 1110 and 1140 cm^{-1} are assigned to the ν_3 mode of ClO_4^-.[10] Slight splitting of the ν_4 mode of ClO_4^- at 625 cm^{-1} suggests weak coordination of the ClO_4^- groups, which is consistent with the crystal structure.[11]

Electron Paramagnetic Resonance Spectrum

At 77 K, frozen solution of the complex in DMF showed a spectrum characteristic of axial g and A tensors with $g_{\parallel}$, $A_{\parallel}$ and $g_{\perp} = 2.178$, 188.9 G and 2.071, respectively. Three of the four parallel hyperfine features due to copper are well resolved, while the fourth is overlapped by $g_\perp$ features which has superhyperfine structure arising from the interaction of the copper(II) electron with a nitrogen atom. Hyperfine splitting in the $\Delta m = 1$ signal of the complex can be explained on the basis of independent Cu(II) ions. These observations suggest that the 1,3-μ-thiocyanato bridge is not a good transmitter of magnetic interactions, which is analogous to the behavior reported by Nelson *et al.*[8] The observation $g_\parallel > g_\perp$ suggests an elongated square pyramidal structure with the unpaired electron in $d_{x^2-y^2}$ orbital.[4,12] The $g_\parallel/A_\parallel$ value can be used to estimate the distortion of the square planar complex toward the tetrahedron;[13] $g_\parallel/A_\parallel$ of the complex is $118\,\text{cm}^{-1}$ and reflects a square plane in DMF solution.

The forbidden $\Delta m = 2$ half band transition was observed at 10^{-2} times the intensity of the $\Delta m = 1$ transition, clear evidence of interaction between the paramagnetic centers leading to a ground singlet and triplet state. It confirms that the bridge is retained in DMF solution.[12]

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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