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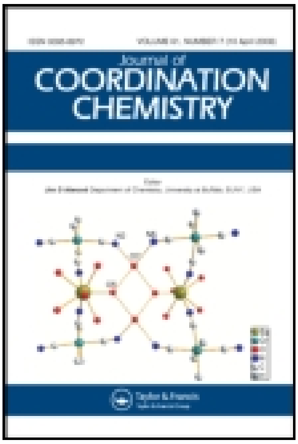

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Synthesis and reactivity with M(II) (M=Co and Cu) chloride of 1-[(2-carboxyethyl)benzene]-3-[benzothiazole]triazene

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Synthesis and reactivity with M(II) (M = Co and Cu) chloride of 1-[(2-carboxyethyl)benzene]-3-[benzothiazole]triazene

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Reaction of ethyl anthranilate, sodium nitrite, and 2-aminobenzothiazole produces a new triazenide compound, 1-[(2-carboxyethyl)benzene]-3-[benzothiazole]triazene (HL), which has been characterized by X-ray crystallography and NMR spectrum. In the presence of Et_3N, reaction of HL and $CuCl_2 \cdot 2H_2O$ or $CoCl_2 \cdot 6H_2O$ in THF/methanol affords a tetranuclear copper(II) complex $[Cu_4L_4(\mu\text{-OMe})_4] \cdot 4THF$ (**1**) and a cobalt(III) complex $[CoL'_3]$ (**2**) (L′ is 1-[benzothiazole] triazene ion), accompanied by C–N bond cleavage of HL. They are characterized by X-ray crystallography and magnetic susceptibility measurement. Magnetic studies indicate significant antiferromagnetic coupling between the copper(II) centers for **1**. The value obtained for the coupling constant J is $-585\,\text{cm}^{-1}$.

Keywords: Reactivity of triazenide compound; Crystal structures; Magnetic property; C–N bond cleavage

1. Introduction

Metal complexes containing triazenido $[RN=N\text{–}NR']^-$ ligands have potential reactivity in relation to their several modes of coordination [1, 2]. This anion is a "small bite" three-atom donor that can act as a monodentate group (a) [3, 4], a chelating ligand (b) (generating highly strained, four-membered rings) [5–8], or a bridging ligand between two metal centers (c) [9–13] (scheme 1). Complexes with 1,3-(aryl) triazines have been done well [14–19]. However, the development of other triazenide complexes is limited [20]. Our interests have extended to the design, synthesis, and reactivity with transition metals of a series of new triazenide ligands (scheme 1d), which can delocalize electron density through their bonding network and strongly donate π electron density to the metal and control the organization of polynuclear metal complexes [21].

A new triazenide compound, 1-[(2-carboxyethyl)benzene]-3-[benzothiazole]triazene (HL), has been synthesized by the reaction of ethyl anthranilate, sodium nitrite, and 2-aminobenzothiazole in a modification of the literature procedure [22]. In the presence of Et_3N, reaction of HL and $CuCl_2 \cdot 2H_2O$ or $CoCl_2 \cdot 6H_2O$ in THF/methanol affords

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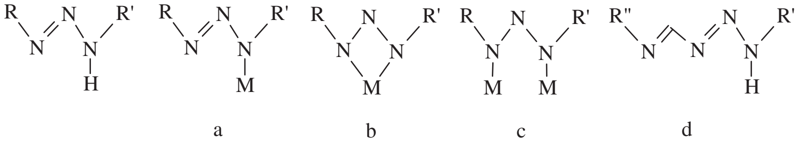


Scheme 1. Generic triazenes, triazenido binding modes, and new triazenes.

a tetranuclear copper(II) complex $[Cu_4L_4(\mu\text{-}OMe)_4]\cdot 4THF$ (**1**) and a cobalt(III) complex $[CoL'_3]$ (**2**), respectively. In this article, we present the design, synthesis, and characterization of HL and its complexes **1** and **2**.

2. Experimental

2.1. *Physical measurements*

^{1}H NMR spectrum was measured on a Bruker AM 500 spectrometer in $CDCl_3$ solutions. Magnetic susceptibility data for crystal samples were collected from 2 to 300 K with a Quantum Design SQUID Magnetometer MPMS XL-7. Effective magnetic moments were calculated by the equation $\mu_{eff} = g[\sum ZS(S+1)]^{1/2}$, where χ_M is the molar magnetic susceptibility.

2.2. *Synthesis*

2.2.1. Synthesis of 1-[(2-carboxyethyl)benzene]-3-[benzothiazole]triazene (HL). A solution of ethyl anthranilate (10 mmol) in water (5 mL) was mixed with 1 mol L^{-1} HCl (30 mL, 30 mmol) at 0°C. An aqueous solution (15%) of sodium nitrite (15 mmol) was added dropwise with stirring. Once the amine was dissolved, a 15% solution of 2-aminobenzothiazole in ethanol (10 mmol) was added at 0°C and the mixture was stirred for 6 h. The reaction mixture was neutralized with a 15% aqueous of $NaCH_3CO_2$ to give a yellow precipitate. The reaction mixture was filtered and the solid was purified by crystallization at −4°C from 9 : 1 ethyl acetate/hexanes to obtain yellow crystals, which were collected and dried *in vacuo* (59%). Calcd for $C_{16}H_{14}N_4O_2S$ (%): C, 58.82; H, 4.29; N, 17.16. Found (%): C, 59.17; H, 4.24; N, 17.35. ^{1}H NMR ($CDCl_3$, ppm): δ 13.06 (s, 1H, N–H), 8.08 (d, $J = 4.8$ Hz, 1H, Ar), 8.01 (d, $J = 4.8$ Hz, 1H, Ar), 7.93 (d, $J = 4.8$ Hz, 1H, Ar), 7.79 (d, $J = 3.6$ Hz, 1H, Ar), 7.61 (t, $J = 3.6$ Hz, 1H, Ar), 7.45 (t, $J = 2.4$ Hz, 1H, Ar), 7.19 (t, $J = 2.4$ Hz, 1H, Ar), 4.43 (tetra, $J = 2.3$ Hz, 2H, –CH_2), 1.44 (t, $J = 2.4$ Hz, 3H, –CH_3).

2.2.2. Synthesis of $[Cu_2(\mu\text{-}OMe)_2L_2]$ (1). To a solution containing HL (0.33 g, 1.0 mmol) and triethylamine (0.10 g, 1.0 mmol) in THF/methanol (30 mL, 1 : 1), $CuCl_2\cdot 2H_2O$ (0.17 g, 1.0 mmol) was added and the mixture was stirred for 1 h. The solution was allowed to slowly evaporate to afford deep green crystals, which were

Table 1. Crystallographic data for HL, **1** and **2**.

Parameter	HL	**1**	**2**
Empirical formula	$C_{16}H_{14}N_4O_2S$	$C_{42}H_{50}Cu_2N_8O_8S_2$	$C_{21}H_{12}CoN_{12}S_3$
Formula weight	326.40	986.10	587.54
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/n*	*P2(1)/c*	*P2(1)/n*
Unit cell dimensions (Å, °)			
a	7.5932(18)	15.0697(18)	8.8611(7)
b	8.2906(17)	18.613(2)	11.3844(8)
c	14.212(3)	15.664(2)	22.907(2)
α	94.77(3)	90	90
β	104.11(3)	101.986(2)	101.052(3)
γ	112.53(3)	90	90
Z	2	4	4
Calculated density ($Mg\,m^{-3}$)	1.392	1.524	1.721
$F(000)$	346	2048	1188
θ range for data collection (°)	3.01–27.44	1.71–27.08	3.21–27.00
Reflections collected/unique	7744/3564	21,824/9304	14,540/4924
Data/restraints/parameters	3564/0/208	9304/0/554	4924/0/334
Goodness-of-fit on F^2	0.798	0.999	1.133
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0544$; $wR_2 = 0.1629$	$R_1 = 0.0518$; $wR_2 = 0.1329$	$R_1 = 0.0485$; $wR_2 = 0.1070$
R indices (all data)	$R_1 = 0.0658$; $wR_2 = 0.1884$	$R_1 = 0.0823$; $wR_2 = 0.1546$	$R_1 = 0.1109$; $wR_2 = 0.1582$

collected and dried *in vacuo* (0.26 g, 72.1%). Calcd for $C_{42}H_{48}Cu_2N_8O_8S_2$ (%): C, 51.21; H, 4.88; N, 11.38. Found (%): C, 52.12; H, 4.85; N, 11.47.

2.2.3. Synthesis of [Co(L_A)$_3$] (2).

To a solution containing HL (0.32 g, 1.0 mmol) and triethylamine (0.10 g, 1.0 mmol) in methanol (25 mL), $CoCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol) was added and the mixture was stirred for 30 min. Slow evaporation afforded red crystals, which were collected and dried *in vacuo* (0.131 g, 66.8%). Calcd for $C_{21}H_{12}CoN_{12}S_3$ (%): C, 42.89; H, 2.04; N, 28.59. Found (%): C, 42.27; H, 2.07; N, 28.62.

2.3. *X-ray crystallography*

Data were collected with a Bruker SMART CCD area detector using graphite-monochromated Mo-Kα radiation (0.71073 Å) at room temperature for HL, 110 K for **1** and 150 K for **2**. All empirical absorption corrections were applied by using SADABS [23]. The structures were solved using direct methods and the corresponding non-hydrogen atoms were refined anisotropically. All hydrogens of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL computer program [24]. Table 1 gives details of the crystal parameters, data collection, and refinement for HL, **1**, and **2**. Selected bond distances and angles for HL, **1** and **2** are listed in tables 2–4.

Table 2. Selected bond distances (Å) and angles (°) for HL.

N(1)–N(2)	1.3284(18)	N(1)–C(8)	1.399(2)
N(3)–N(2)	1.267(2)	N(3)–C(7)	1.386(2)
N(4)–C(7)	1.294(2)	N(4)–C(1)	1.397(2)
N(1)–N(2)–N(3)	110.76(15)	N(3)–C(7)–N(4)	119.12(15)

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

Table 3. Selected bond distances (Å) and angles (°) for **1**.

Cu(1)–O(5)	1.908(3)	Cu(1)–O(6)	1.930(3)
Cu(1)–N(1)	1.982(3)	Cu(1)–N(6)	2.007(3)
Cu(1)–Cu(2)#1	2.9897(7)	Cu(1)–Cu(2)	2.9914(7)
Cu(2)–O(5)#1	1.915(2)	Cu(2)–O(6)#1	1.940(3)
Cu(2)–N(5)	1.980(3)	Cu(2)–N(2)	2.010(3)
Cu(2)–Cu(1)#1	2.9897(7)	O(5)–Cu(2)#1	1.915(2)
O(6)–Cu(2)#1	1.940(3)	N(5)–C(16)	1.318(5)
N(6)–C(16)	1.348(5)	N(6)–N(7)	1.356(4)
N(1)–C(17)	1.325(5)	N(2)–C(17)	1.346(5)
N(5)–C(16)	1.318(5)	N(6)–C(16)	1.348(5)
O(5)–Cu(1)–O(6)	77.18(11)	O(5)–Cu(1)–Cu(2)#1	38.63(7)
O(6)–Cu(1)–Cu(2)#1	39.55(8)	N(1)–Cu(1)–Cu(2)#1	134.42(9)
N(6)–Cu(1)–Cu(2)#1	130.84(10)	O(5)–Cu(1)–Cu(2)	84.45(8)
O(6)–Cu(1)–Cu(2)	104.38(8)	N(1)–Cu(1)–Cu(2)	87.55(9)
N(6)–Cu(1)–Cu(2)	74.10(9)	Cu(2)#1–Cu(1)–Cu(2)	88.924(17)
O(5)#1–Cu(2)–O(6)#1	76.77(11)	O(5)#1–Cu(2)–Cu(1)#1	38.46(8)
O(6)#1–Cu(2)–Cu(1)#1	39.30(8)	N(5)–Cu(2)–Cu(1)#1	133.28(9)
N(2)–Cu(2)–Cu(1)#1	132.12(9)	O(5)#1–Cu(2)–Cu(1)	86.16(8)
O(6)#1–Cu(2)–Cu(1)	106.02(8)	Cu(1)#1–Cu(2)–Cu(1)	91.076(17)
Cu(1)–O(5)–Cu(2)#1	102.91(12)	Cu(1)–O(6)–Cu(2)#1	101.15(12)

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

Table 4. Selected bond distances (Å) and angles (°) for **2**.

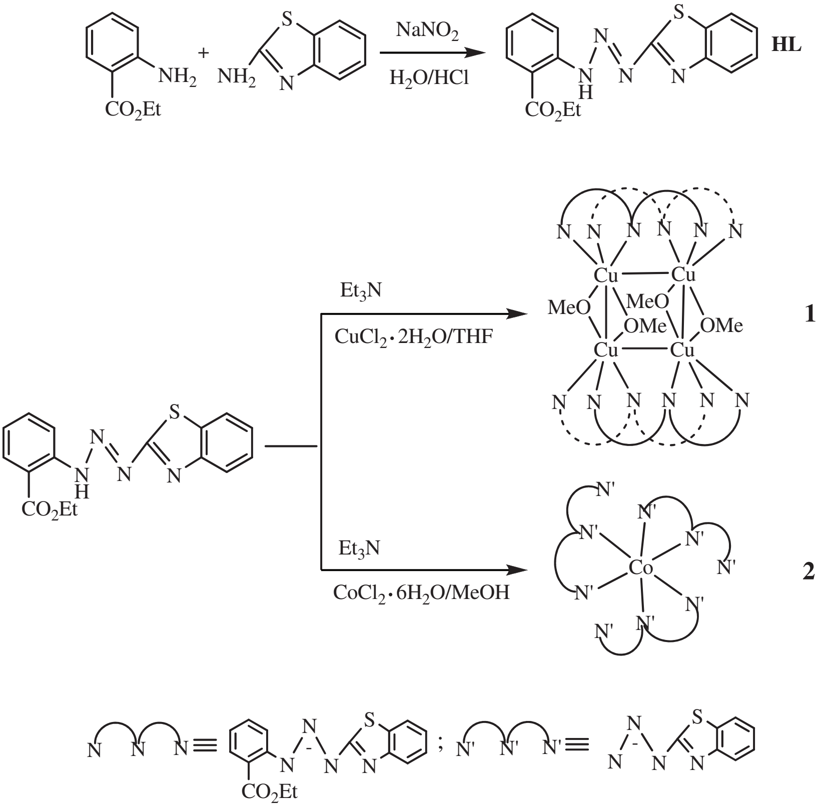
Co(1)–N(11)	1.921(4)	Co(1)–N(9)	1.930(4)
Co(1)–N(1)	1.931(4)	Co(1)–N(3)	1.941(4)
Co(1)–N(7)	1.944(4)	Co(1)–N(5)	1.953(4)
N(2)–N(3)	1.323(6)	N(3)–N(4)	1.234(6)
N(6)–N(7)	1.314(6)	N(7)–N(8)	1.234(5)
N(10)–N(11)	1.324(6)	N(11)–N(12)	1.220(6)
N(11)–Co(1)–N(9)	81.33(18)	N(1)–Co(1)–N(3)	81.32(19)
N(7)–Co(1)–N(5)	80.94(18)	N(4)–N(3)–N(2)	117.7(4)
N(8)–N(7)–N(6)	117.9(4)	N(12)–N(11)–N(10)	119.7(4)

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

3. Results and discussion

3.1. *General properties*

The reaction of ethyl anthranilate, sodium nitrite, and 2-aminobenzothiazole gave a triazenide (HL) (see supporting information, figure S1, ^{1}H NMR spectrum of HL) in 59% yield. The ^{1}H NMR spectrum of HL shows a singlet of triazene group hydrogen at 13.06 ppm, in agreement with the structural analysis for triazene. ^{1}H resonances are found from 8.1 to 7.1 ppm for the aromatic protons, 4.43 and 1.44 ppm for ethyl. HL contains a potential N_4O_2 donor set, making it L^- when deprotonated.



Scheme 2. Schematic representation of the synthesis of HL, **1**, and **2**.

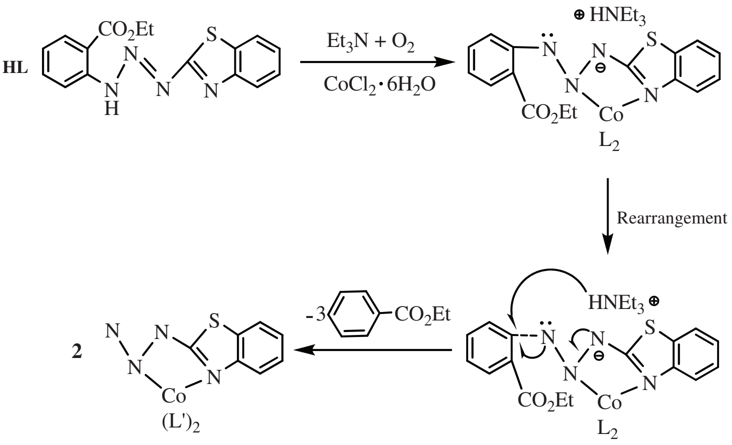
Scheme 2 shows the procedure of the synthesis of HL, **1**, and **2**. In the presence of Et_3N, the reaction of HL and $CuCl_2 \cdot 2H_2O$ provides a tetranuclear copper(II) complex $[Cu_4L_4(\mu\text{-OMe})_4]$, bridged by methoxy.

Compound **2** is obtained as red crystals by the reaction of HL and $CoCl_2 \cdot 6H_2O$ in ethanol in the presence of Et_3N. The procedure for the formation of **2** can be illustrated by scheme 3. In the presence of Et_3N, the reaction of HL and $CoCl_2 \cdot 6H_2O$ gives a Co(III) complex, CoL_3. Furthermore, the rearrangement of CoL_3 provides an intermediate. Finally, C–N bond cleavage of HL affords a new Co(III) complex, $Co(L')_3$ (L'^- is 1-[benzothiazole] triazene ion), accompanied by the loss of benzoic acid methyl ester.

3.2. *X-ray structural analysis*

3.2.1. Crystal structure of HL.

As shown in figure 1, HL contains a rigid N(2)=N(4) double bond and a potential NNNCN donor set. The N(1)–N(2) and N(2)–N(3) bond distances are 1.315(2) and 1.267(2) Å, respectively. N(3)–C(7) and N(4)–C(7) bond lengths are 1.386(2) and 1.294(2) Å, respectively. N(1)–N(2)–N(3) and N(3)–C(7)–N(4) bond angles are 110.76(15) and 119.12(15)°, respectively.



Scheme 3. The possible mechanism of the formation of L'^-.

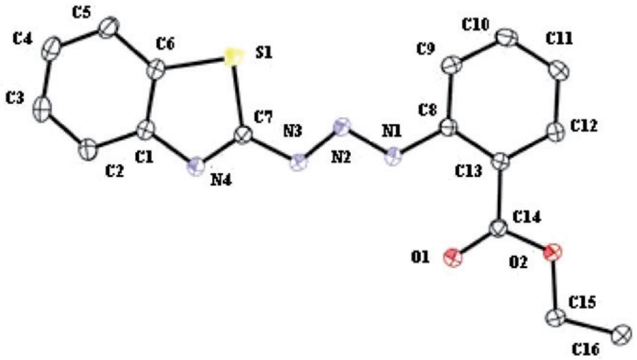


Figure 1. ORTEP of HL.

3.2.2. Crystal structure of 1. Complex **1** consists of a square-planar Cu4, in which the four coppers are bridged by four bridged anionic ligands (L^-) and four bridged methoxy groups. An ORTEP drawing with the atomic labeling scheme, excluding solvent molecules, is shown in figure 2.

In **1**, each copper presents a similar approximately tetrahedral coordination. **1** can be divided into two dinuclear copper(II) units (Cu1–Cu2 and Cu1#–Cu2#), which are supported by four nitrogens from two anionic ligands (L^-). The bond distances between Cu and N fall in the range 1.980(3) to 2.010(3) Å, similar to those found in copper(II) triazenide which range from 1.973 to 2.088 Å [25, 26]. The Cu–Cu bond length (2.9916(7) Å) is longer than that found in $Cu_2(dpt)_4$ (2.441 Å) (dpt = 1,3-diphenyltriazenide) [26]. The tetranuclear copper(II) complex is completed by connection of two dinuclear copper units *via* four bridged methoxy groups. Adventitious methanol solvent serves as a source of the μ-OMe ligand. The Cu–O bond lengths are within the range of 1.908(3) to 1.940(3) Å, and Cu–O–Cu angles fall in the range 101.15(12)–102.89(12)°.

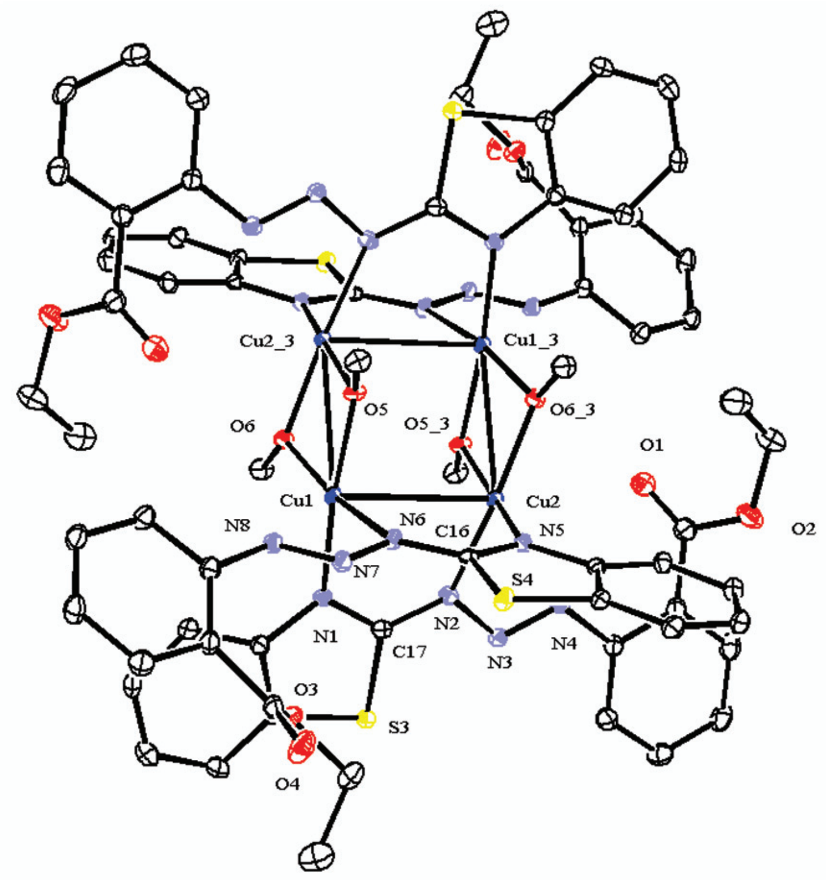


Figure 2. ORTEP of **1**. THFs are omitted for clarity.

Compared with the structure of HL, the triazenide ligand in **1** shows a little variation of the bonding on coordination. The N(2)–C(7) and N(3)–C(7) bond distances are 1.390(2) and 1.292(2) Å, respectively. It would be expected that the N–C bond distances would be dissimilar as a consequence of the different bond order between these atoms. The corresponding bond distances (N(1)–C(17) and N(2)–C(17)) are 1.346(5) and 1.325(5) Å, respectively.

3.2.3. Crystal structure of 2. As shown in figure 3, crystal structure of **2** consists of one cobalt and three 1-[benzothiazole] triazene ions (L'^-). Cobalt is six-coordinate by six nitrogens of L'^-. The Co–N bond distances fall in the range 1.921(4) to 1.953(4) Å. The N(2)–N(3) bond length (1.323(6) Å) is longer than that of HL (1.264(3) Å), due to electronic dislocation in 1-[benzothiazole] triazene ion.

3.3. *Magnetic property of 1*

Magnetism of **1** was investigated from 2 to 300 K and shown in figure 4 in the form of χ_M *versus* T or $\chi_M T$ *versus* T at 500 Oe. The value of $\chi_M T$ for **1** is 0.73 $cm^3\,K\,mol^{-1}$

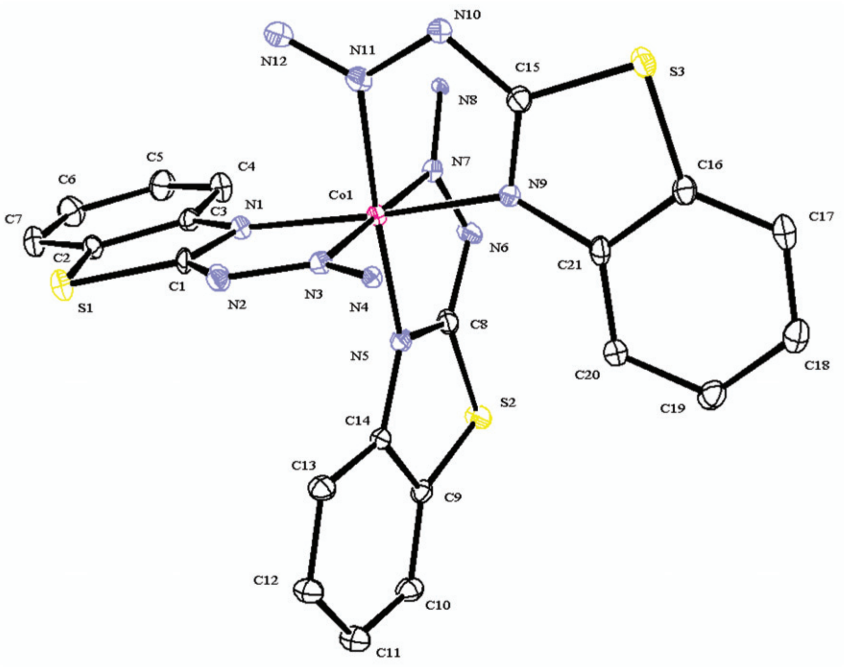


Figure 3. ORTEP of **2**.

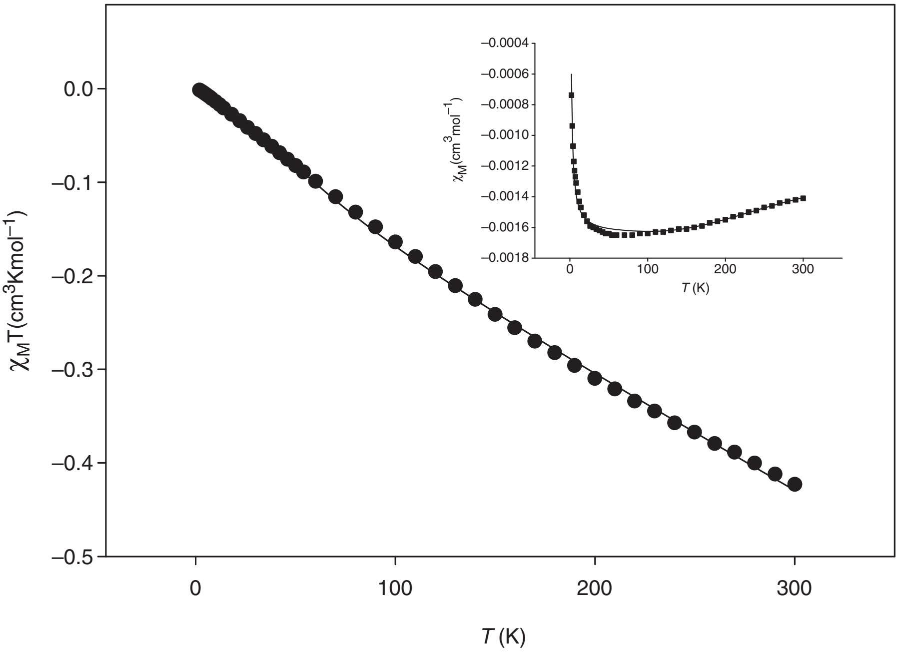


Figure 4. Plot of the $\chi_M T$ *vs.* T and χ_M *vs.* T (inset) for **1** at 3000 Oe. Solid line corresponds to the best fit.

(2.4 μ_B per Cu_4) at 300 K, much smaller than the expected value for four Cu(II) (S = 1/2) ions (3.46 μ_B) and decreases with decreasing temperature to a minimum value of 0.0064 $cm^3\,K\,mol^{-1}$ (0.23 μ_B) at 2 K. In the range 50–2 K, the increase in the molar magnetic susceptibilities with decreasing temperature is often seen in antiferromagnetically coupled systems [27].

Three different exchange pathways can occur in **1**: Cu–N–C–N–Cu, Cu–O–C–O–Cu, and Cu–O–Cu. To explain the magnetic behavior of **1**, its structure can consequently be reduced to a central $Cu_4N_4O_2$ core. The Cu–N–C–N–Cu and Cu–O–C–O–Cu pathways in **1** are assumed to have only a second-order effect upon the magnetic exchange between the copper centers. The tetranuclear copper(II) can be formally divided into two dinuclear Cu_2N_2O subunits. The interdimer coupling *via* nitrogens is assumed to be weaker than the intradimer exchange interactions *via* the oxygens (μ_2-O). Hence, the data can be fitted on the basis of the Heisenberg model $\mathbf{H} = -2JS_1 \cdot S_2$. The molar magnetic susceptibility for Cu(II)–Cu(II) units is expressed as equation 1 [28], where ρ is the fraction of monomeric impurity and χ_M is the magnetic susceptibility.

$$\chi_M = \frac{2N\beta^2 g^2}{kT}\left[3 + \exp\left(-\frac{J}{kT}\right)\right]^{-1}(1-\rho) + \frac{N\beta^2 g^2}{2kT}\rho + 2N\alpha \qquad (1)$$

Least-squares fitting of the experimental data led to $J = -620\,cm^{-1}$, $N\alpha = 1.58 \times 10^{-3}\,cm^3\,mol^{-1}$ and $\rho = 4.6 \times 10^{-3}$. As a consequence, there are very strong antiferromagnetic exchange interactions between copper(II) ions. The major factor controlling the exchange interactions in hydroxy-, alkoxy-, and phenoxy-bridged copper(II) is the Cu–O–Cu bridge angle [29, 30]. A possible reason for the strong exchange coupling in **1** is that the (μ-O) bridges with shorter Cu–O (average 1.9025 Å) distance and a larger Cu–O–Cu angle (122.15°) than those with the phenoxide ion, providing a better pathway for antiferromagnetic exchange coupling [31–34].

4. Conclusion

The present study shows that 1,3-RR′-triazenes (HL) can build a series of copper complexes in which the structures and properties can be controlled by the design of bridged ligands. Currently we are exploring this line, as well as the assembly for other metals.

Supplementary material

CCDC 778810, 778813, and 775008 contain the supplementary crystallographic data for this article. The data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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