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Synthesis and Reactivity of 1-[(2-methoxy)benzene]-3-[benzothiazole]Triazene With Copper(II) or Cobalt(II) Chloride

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Synthesis and Reactivity of 1-[(2-methoxy)benzene]-3-[benzothiazole]Triazene With Copper(II) or Cobalt(II) Chloride

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A new triazene, 1-[(2-methoxy)benzene]-3-[benzothiazole] triazene (HL), has been synthesized and charaterized. In the presence of Et₃N, the reaction of HL and CuCl₂·2H₂O or CoCl₂·6H₂O gives the triazenide complexes [Cu₄L'₄(μ -OMe)₄] 1 (L' 1-[benzothiazole]triazene ion) and [Co₂L₄] 2, respectively. The X-ray crystal structures of both complexes have been obtained. Magnetic studies indicate significant antiferromagnetic coupling between the copper(II) centers or cobalt(II) centers for complexes 1 and 2, with coupling constants (J) of -587 cm⁻¹ for 1 and -147 cm⁻¹ for 2. Complex 2 shows one reversible one-electron redox wave at -0.835 V, and one irreversible oxidation at -0.193 V, which are in accord with the redox potentials of [Co^{III}-Co^{II}]/[Co^{II}-Co^{II}] and [Co^{III}-Co^{III}]/[Co^{II}-Co^{II}] couples, respectively.

Keywords electrochemical property, C-N bond cleavage, crystal structures, magnetic properties, reactivity of triazene

INTRODUCTION

A fundamental aim of coordination chemistry is the assembly of compounds that exhibit novel properties. An approach toward this important goal is the preparation of unique ligands that impart novel chemistry when incorporated into the metal coordination sphere. By designing the appropriate ligands, we can chelate metal centers in special frame and control the electron withdrawal from the metal ion core, thereby modifying the intramolecular exchange interactions. The use of different bridging and polydentate ligands has afforded an impressive array of nuclear coordination complexes with new architectures. Among them, the triazenide ligands have attracted our attention, as these compounds can serve as a monodentate (a),^[1,2] a bidentate chelating (b),^[3–5] or a bridging ligand (c) (Scheme 1).^[1,2,6–8] With this mind, we extended our interests to the synthesis and their reactivity with transition metals of new triazenide ligands (such as Scheme 1).

As part of this research, a new triazenide ligand, namely 1-[(2-methoxy)benzene]-3-[benzothiazole]triazene (HL), has been synthesized from the reaction of o-anisidine, sodium nitrite, and 2-aminobenzothiazole. In the presence of Et₃N, the reaction of H₂L and CuCl₂·2H₂O or CuCl₂·2H₂O or CoCl₂·6H₂O affords the complex [Cu₄L'₄(μ -OMe)₄] **1** or [Co₂L₄] **2**, respectively. In this paper, we present the synthesis and characterization of H₂L, its complexes **1** and **2**, as well as the possible procedure of the formation of 1-[benzothiazole]triazene (L') from HL thereof.

EXPERIMENTAL

Physical Measurements

¹H NMR spectrum was measured on a Bruker AM 500 spectrometer in CDCl₃ (Switzerland). Magnetic susceptibility data for crystal samples were collected in the temperature range of 2–300 K with a Quantum Design SQUID Magnetometer MPMS XL-7 (USA). Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = g[\sum ZS(S+1)]^{1/2}$, where χ_{M} is the molar magnetic susceptibility. The electrolytic cell used was a conventional three-compartment cell, in which a Pt working electrode, a Pt auxiliary electrode, and a saturated calomel electrode (SCE) was employed. The CV measurement was performed at room temperature using 0.10 mol·L⁻¹ tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte.

Synthesis of 1-[(2-methoxy)benzene]-3-[benzothiazole] Triazene (HL)

O-anisidine (1.23 g, 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 (1.50 g, 10 mmol) was added at 0°C and stirred for 8 h. The reaction mixture was neutralized

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SCH. 1. Generic triazenido binding modes and new triazenes.

with a 15% aqueous of CH₃CO₂Na 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. The crystals were collected and dried *in vacuo* (1.89 g, 67%). Anal. Calcd. for C₁₄H₁₂N₄OS: C, 59.16; H, 4.23; N, 19.72. Found: C, 58.67; H, 4.19; N, 19.90. ¹H NMR (CDCl₃, ppm): δ 13.04 (s, 1H, N-H), 8.09 (d, J = 2.7 Hz, 1H, Ar), 7.82 (d, J = 2.5 Hz, 1H, Ar), 7.96 (d, J = 2.8 Hz, 1H, Ar), 7.47 (t, J = 5 Hz, 1H, Ar), 7.39 (t, J = 5 Hz, 1 Hz, Ar), 7.21 (t, J = 5 Hz, 1 Hz, Py), 3.99 (s, 3H, -OCH₃).

Synthesis of Complex $[Cu_4(\mu-OMe)_4L'_4]$ 1

To a solution of HL (0.29 g, 1.0 mmol) and triethylamine (0.10 g, 1.0 mmol) in ethanol (25 ml), CuCl₂·2H₂O (0.17 g, 1.0 mmol) was added and stirred for 30 min. Slow evaporation afforded deep green crystals, which were collected and dried *in vacuo* (0.15 g, 54.1%). Anal. Calcd. for C₁₆H₁₄Cu₂N₈O₂S₂: C, 35.45; H, 2.59; N, 20.68. Found: C, 35.89; H, 2.85; N, 20.12.

Synthesis of Complex [Co₂L₄] 2

The procedure was performed in the same way as that for the synthesis of complex **1** except that $CuCl_2 \cdot 2H_2O$ was replaced by $CoCl_2 \cdot 6H_2O$, complex **2** was obtained in 54.1% yield (0.15 g). Calcd for $C_{56}H_{44}Co_2N_{16}O_4S_4$: C, 53.71; H, 3.52; N, 17.90. Found: C, 52.87; H, 3.46; N, 18.41.

X-Ray Crystallography

Data were collected with a Bruker SMART CCD area detector using graphite monochromated Mo-K radiation (0.71073 Å). All empirical absorption corrections were applied by using the SADABS program.^[9] The structures were solved using direct methods and the corresponding non-hydrogen atoms were refined anisotropically. All the hydrogen atoms 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.^[10] Table 1 lists details of the crystal parameters, data collection, and refinement for complexes **1** and **2**. The selected bond distances and angles for complexes **1** and **2** are listed in Tables 2 and 3.

 TABLE 1

 Crystallographic data for complexes 1 and 2

Parameter	1	2	
Empirical formula	C ₃₂ H ₂₈ Cu ₄ N ₁₆ O ₄ S ₄	C ₅₆ H ₄₄ Co ₂ N ₁₆ O ₄ S ₄	
Formula weight	1083.18	1251.17	
λ(Å)	0.71073	0.71073	
Temperature (K)	295	150	
Crystal system	triclinic	monoclinic	
Space group	P-1	C2/c	
U	nit cell dimension (Å,	°)	
a	8.976(6)	31.977(3)	
b	11.950(8)	22.7264(19)	
c	12.065(8)	20.8859(17)	
α	91.318(8)	90.00	
β	100.804(8)	120.032(2)	
γ	102.832(8)	90.00	
Z	1	8	
$Dc(Mgm^{-3})$	1.455	1.265	
F(000)	544	5136	
θ range for data collection	2.37–25.50°	3.07–26.00°	
Reflections collected/unique	8066/4515	28798/12507	
Data/restraints/	4515/0/271	12507/0/744	
Goodness-of-fit on F ²	1.045	0.971	
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0403$	$R_1 = 0.0868$	
	$wR_2 = 0.1166$	$wR_2 = 0.2280$	
R índices (all data)	$R_1 = 0.0565$ $wR_2 = 0.1237$	$R_1 = 0.1479$ $wR_2 = 0.2770$	

RESULTS AND DISCUSSION

Synthesis

The reaction of o-anisidine, sodium nitrite, and 2aminobenzothiazole provided a triazene (HL). Complexes **1** and **2** were obtained by the reaction of HL and CuCl₂·2H₂O or CoCl₂·6H₂O, respectively. Interestingly, the reaction of HL and CuCl₂·2H₂O in the presence of Et₃N provided complex **1** [Cu₄L'₄(μ -OMe)₄] with a new L'⁻ ligand (1-[benzothiazole]triazene ion) (Scheme 2). The procedure of the formation of L'⁻ can be illustrated by Scheme 3, the treatment of HL with Et₃N gives a triethylammonium triazenide salt ([Et₃NH]L) A.^[11]Furthermore, the rearrangement of A provides an intermediate B. Finally, C-N bond cleavage of HL affords a new L'⁻ ligand, accompanied loss of phenyl methyl ether.

Structures of Complexes 1 and 2

As shown in Figure 1, the metallic core comprises four copper centers, all in distorted planar geometries, arranged in a

Selected bond distances (A) and angles (°) for complex 1					
Cu(1)-N(5)	1.969 (3)	Cu (1)-N(2)	2.025 (3)		
Cu(2)-N(6)	2.009 (3)	Cu(2)-N(1)	1.979 (3)		
Cu(2)-O(1)#	1.927 (3)	Cu(2)-O(2)#	1.907 (3)		
Cu(2)-Cu(1)	3.0163 (17)	Cu (2)-Cu(1)#	2.9697 (15)		
O(1)-Cu(1)-O(2)	77.09 (12)	Cu(1)-O(1)-Cu(2)#	100.89 (12)		
Cu(1)-(O(2)-Cu(2)#	102.33 (13)				
Cu(1)-Cu(2)-Cu(2)#-Cu(1)#1	0	O(1)-Cu(1)-Cu(2)#-O(2)	5.91		

 TABLE 2

 Selected bond distances (Å) and angles (°) for complex 1

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

square-planar array with the torsion angle Cu(1)-Cu(2)-Cu(2)#-Cu(1)#1 of 0°. The structure of **1** consists of two symmetryrelated di- μ_2 -methoxo-bridged copper(II) dimeric units (Cu(1)-Cu(2)# and Cu(1)-Cu(2)#). The Cu-O bond lengths are within the range of 1.906(3) to 1.927(3) Å, and Cu-O-Cu angles fall in 100.87(12) to 102.33(13)°.

Similar to the "roof-shaped" $Cu_2(\mu_2-OMe)_2$ geometry found in $[Cu_4L^{dur}(\mu_2-OMe)_4]^{4+}$ ($L^{dur} = 1,4,7$ -triazacyclonon) complex,^[12] the Cu_2O_2 bridging units in complex **1** also adopt bent, or "roof-shaped" conformations. This distortion is evident from the torsion angle O(1)-Cu(1)-Cu(2)#-O(2) of 5.97°. In the case of **1**, the Cu···Cu separation (2.9697 Å) is similar to that found in $[Cu_4L^{dur}(\mu_2-OMe)_4]^{4+}$ (2.962(1) Å). "Roof-shaped" Cu_2O_2 cores have been observed in $[Cu_2(C_6H_{11}NH_2)_4(\mu_2-OH)_2](ClO_4)_2^{[13]}$ and $[Cu_2(CH_3NH_2)_4(\mu_2-OH)_2](SO_4)\cdot H_2O,^{[14]}$ and Cu···Cu distances of 2.934(8) and 2.782(5) Å, respectively.

The two Cu_2O_2 units are capped by four L'^- ligands. The bond distances of between Cu and N fall in the range 1.969(3) to 2.025(3) Å, which are similar to those found in copper(II) triazenide complexes 1.973 to 2.088 Å.^[15,16] The Cu…Cu distance,

3.0163(17) Å is longer than that found in Cu₂(Ac)₃(triazenide) (2.5316(6) Å).^[15]

As shown in Figure 2, the structure of complex **2** shows the L^- ligand doesn't bind in a bis(bidentate) manner bridging the two cobalt centers, but coordinate to the cobalt center by two terminal N atoms of each L^- ligand. The average N-N-N angle of 108.4(5)° and the average N-N bond length of 1.3219 Å agree with those reported for the Co(dpt)₃ complex.^[17]

Two cobalt atoms are bridged by four L⁻ ligands to form two 12-membered $Co_2N_8C_2$ rings, which lie vertically. Each cobalt sphere may be described as a distorted octahedral geometry with axial and equatorial ligands, the axial atoms being N(1) and N(9) for Co(1) and N(5) and N(13) for Co(2). The Co-Nax distances are homogeneous with an average value of 2.133 Å, but the Co-Neq distances are in the 2.148–2.226 Å range for both cobalt spheres.

Magnetic Properties of Complexes 1 and 2

The magnetic behavior of **1** is shown in Figure 3 in the form of χ_M versus T or $\chi_M T$ versus T. Copper(II), which has the d⁹ configuration, is expected to exhibit paramagnetic behavior.

Selected bold distances (Y) and angles () for complex 2					
Co(1)-N(9)	2.124 (5)	Co(1)-N(1)	2.136 (5)		
Co(1)-N(6)	2.148 (5)	Co(1)-N(16)	2.179 (5)		
Co(1)-N(8)	2.187 (6)	Co(1)-N(14)	2.208 (6)		
Co(2)-N(5)	2.120 (6)	Co(2)-N(13)	2.146 (5)		
Co(2)-N(2)	2.148 (5)	Co(2)-N(12)	2.172 (5)		
Co(2)-N(10)	2.184 (5)	Co(2)-N(4)	2.226 (5)		
N(2)-N(3)	1.325 (6)	N(3)-N(4)	1.304 (7)		
N(6)-N(7)	1.371 (7)	N(7)-N(8)	1.289 (6)		
N(10)-N(11)	1.330 (7)	N(11)-N(12)	1.295 (7)		
N(14)-N(15)	1.340 (7)	N(15)-N(16)	1.321 (7)		
N(1)-Co(1)-N(9)	166.85 (19)	N(14)-Co(1)-N(16)	58.7 (2)		
N(6)-Co(1)-N(8)	59.60 (18)	N(5)-Co(2)-N(13)	166.96 (19)		
N(10)-Co(2)-N(12)	58.66 (18)	N(2)-Co(2)-N(4)	58.48 (18)		
N(4)-N(3)-N(2)	108.9 (5)	N(8)-N(7)-N(6)	108.2 (5)		
N(12)-N(11)-N(10)	108.7 (5)	N(16)-N(15)-N(14)	107.8 (5)		

 TABLE 3

 Selected bond distances (Å) and angles (°) for complex 2



SCH. 2. Schematic representation of the synthesis of HL, 1 and 2.

However, complex **1** is diamagnetic at 300 K, because of strong coupled interactions between copper(II) ions.

Two different exchange pathways can occur in complex 1: Cu-N-C-N-Cu and Cu-O-Cu. To explain the magnetic behavior of complex 1, its structure can consequently be reduced to a central Cu₄N₄O₄ core. The Cu-N-C-N-Cu pathway in complex 1, is assumed to have only a second-order effect on the magnetic exchange between the copper centers. The tetranuclear copper(II) complex 1 can be formally divided into two dinuclear Cu₂O₂ subunits. The interdimer coupling via nitrogen atoms is assumed to be weaker than the intradimer exchange interactions via the oxygen atoms (μ -OMe). Hence the data can be fitted on the ba-



FIG. 1. X-ray structure of complex 1 (color figure available online).

sis of the Heisenberg model $\mathbf{H} = -2JS_1 \cdot S_2$. The molar magnetic susceptibility for Cu(II)-Cu(II) units is expressed as Eq. 1.^[18]

$$\chi_{M} = \frac{N\beta^{2}g^{2}}{3kT} \left[1 + \frac{1}{3} \exp\left(-\frac{2J}{kT}\right) \right]^{-1} (1-\rho) + \frac{N\beta^{2}g^{2}}{4kT} \rho + N\alpha$$
[1]

Least-squares fitting of the experimental data led to J = -587 cm⁻¹, g = 2.1, $N\alpha = 1.1 \times 10^{-3}$ cm³mol⁻¹, and $\rho = 0.001$. 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.^[19,20] The average Cu-O-Cu bridge angle of 102° for **1** would result in an approximate *J* value of -350 cm⁻¹ according to the



SCH. 3. The possible mechanism of the formation of L'.



FIG. 2. X-ray structure of complex 2 (color figure available online).

empirical equation reported in the literature and it deviates appreciably from the experimentally determined value of -585 cm⁻¹ for complex **1**. A possible reason for the strong exchange coupling in complex **1** is that the methoxide ion, with shorter Cu-O (average 1.923 Å) distance and a larger Cu(1)-O(5)-Cu(2)# angle (102.89°) than those with the phenoxide ion, provides a better pathway for antiferromagnetic exchange coupling.^[21-23]

The magnetic behavior of complex **2** is shown in Figure 4 in the form of $\chi_M T$ versus T or $\chi_M T$ versus T. With decreasing temperature, the $\chi_M T$ value decreases rapidly in an unusual linear fashion. This behavior can be ascribed to an antiferromagnetic interaction modified by the contribution of anisotropic exchange. The value of $\chi_M T$ at 300 K, 5.16 cm³Kmol⁻¹ (6.42 μ_B), is larger than the value of 3.75 cm³Kmol⁻¹ (5.48 μ_B) of



FIG. 3. Plot of the $\chi_M T$ versus T and χ_M versus T (inset) for complex 1 at 3000 Oe. Solid line corresponds to the best fit.



FIG. 4. Plot of the $\chi_M T$ versus T and χ_M versus T (inset) for complex 2 at 2000 Oe. Solid line corresponds to the best fit.

two isolated Co^{II} ions (S = 3/2) and decreases linearly with decreasing temperature between 300–2 K, and reaches to 0.227 cm³Kmol⁻¹ at 2.0 K.

The magnetism of **2** can be well reproduced by a modified Bleaney-Bowers Eq. 2.^[24]

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

Least-squares fitting of the experimental data led to $J = -147 \text{ cm}^{-1}$, $N\alpha = 7.1 \times 10^{-3} \text{ cm}^3 \text{mol}^{-1}$, and $\rho = 0.007$. As a consequence, there are strong antiferromagnetic exchange interactions between Co(II) ions.

Electrochemical Property of Complex 2

The electrochemical property of complex 2 was measured by cyclic voltammetry in CH₃CN. As shown in Figure 5, complex



FIG. 5. CV of complex **2** in CH₃CN/0.1 mol·L⁻¹ [Bu₄N]PF₆ at 100 mV s⁻¹ scan rate.

2 shows one reversible one-electron redox wave at -0.835 V, and one irreversible oxidation at -0.193 V, which are in accord with the redox potentials of $[Co^{III}-Co^{II}]/[Co^{II}-Co^{II}]$ and $[Co^{III}-Co^{III}]/[Co^{II}-Co^{II}]$ couples, respectively.

1-[(2-methoxy)benzene]-3-[benzothiazole]triazene (HL) was synthesized by the reaction of o-anisidine and 2aminobenzothiazole, using half an equivalent of sodium nitrite. This technique is facile and gives HL in high yield (67%). HL can chelate and bridge copper or nickel centers to give two complexes 1 and 2, which reveal significant antiferromagnetic character. Currently we are exploring this area further, including the design and synthesis of new triazenes, as well as their reactivity with metals.

SUPPLEMENTARY MATERIALS

CCDC 780722 & 780723 contain the supplementary crystallographic data for complexes **1**, and **2**, respectively. These 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.

REFERENCES

- Barrett, A.G.M.; Crimmin, M.R.; Hill, M.S.; Hitchcock, P.B.; Kociok-Kohn, G.; Procopiou, P.A. Triazenide complexes of the heavier alkaline earths: Synthesis, characterization, and suitability for hydroamination catalysis. *Inorg. Chem.* 2008, 47, 7366–7376.
- Albertin, G.; Antoniutti, S.; Bedin, M.; Castro, J.; Garcia-Fontan, S. Synthesis and characterization of triazenide and triazene complexes of ruthenium and osmium. *Inorg. Chem.* 2006, 45, 3816–3825.
- Nimitsiriwat, N.; Gibson, V.C.; Marshall, E.L.; Takolpuckdee, P.; Tomov, A.K.; White, A.J.P.; Williams, D.J.; Elsegood, M.R.J.; Dale, S.H. Monoversus bis-chelate formation in triazenide and amidinate complexes of magnesium and zinc. *Inorg. Chem.* 2007, *46*, 9988–9997.
- Clark, T.; Cochrane, J.; Colson, S.F.; Malik, K.Z.; Robinson, S.T.; Steed, J.W. Amidinato and triazenido complexes of ruthenium(II): Xray crystal structure of the *N*,*N*'-diphenylformamidine fragmentation product [RuCl(NH₂Ph){PhNC(H)NPh}(Me₂SO)₂]. *Polyhedron* 2001, 20, 1875–1880.
- Guharoy, C.; Butcher, R.J.; Bhattacharya, S. Rhodium complexes of 1,3-diaryltriazenes: usual coordination, N–H bond activation and, N–N and C–N bond cleavage. *J. Organometallic Chem.* 2008, 693, 3923– 3931.
- Adams, C.J.; Baber, R.A.; Connelly, N.O.; Hardeng, P.; Hayward, O.D.; Kandiah, M.; Orpen, A.G. Iodination of triazenide-bridged rhodium and iridium complexes: oxidative additionvs. one-electron oxidation. *Dalton Trans.* 2007, 1325–1333.
- Tejel, C.; Ciriano, M.A.; Rios-Moreno, G.; Dobrinovitch, I.T.; Lahoz, F.J.; Oro, L.A.; Parra-Hake, M. Crescent-shaped rhodium(I) complexes with bis(*o*-carboxymethylphenyl)triazenide. *Inorg. Chem.* 2004, 43, 4719–4726.

- Lei, W.-J.; Tan, X.-W.; Han, L.-J.; Zhan, S.-Z.; Li, B.-T. Design, synthesis and properties of a trinuclear copper(I) cluster with a triazenide ligand. *Inorg. Chem. Commun.* 2010, 13, 1325–1328.
- Sheldrick, G.M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, Germany, 1996.
- Sheldrick, G.M. SHELXS 97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.
- Virag, A.; Meden, A.; Kocevar, M.; Polanc, S. Synthesis and characterization of new triazenide salts. J. Org. Chem. 2006, 71, 4014–4017.
- Graham, B.; Hearn, M.T.W.; Junk, P.C.; Kepert, C.M.; Mabbs, F.E.; Moubaraki, B.; Murray, K.S.; Spiccia, L. Syntheses, crystal structures, magnetic properties, and EPR spectra of tetranuclear copper(II) complexes featuring pairs of "roof-shaped" Cu₂×₂ dimers with hydroxide, methoxide, and azide bridges. *Inorg. Chem.* **2001**, *40*, 1536–1543.
- Charlot, M.F.; Jeannin, S.; Jeannin, Y.; Kahn, O.; Lucrece-Aubal, J.; Martin-Frere, J.S. Crystal structure and magnetic properties of tetrakis(cyclohexylamine)di-.mu.-hydroxo-dicopper(II) perchlorate. The first example of a roof-shaped hydroxo-bridged copper(II) dimer. *Inorg. Chem.* 1979, 18, 1675–1681.
- Charlot, M.F.; Kahn, O.; Jeannin, S.; Jeannin, Y. Exchange interaction in roof-shaped hydroxo-bridged copper(II) dimmers. *Inorg. Chem.* 1980, 19, 1410–1411.
- Rodriguez, J.G.; Parra-Hake, M.; Aguirre, G.; Ortega, F.; Walsh, P.J. Synthesis and structure of a dinuclear copper complex of a bis(bidentate)triazenide ligand. *Polyhedron* 1999, *18*, 3051–3055.
- Corbett, M.; Hoskins, B.F.; McLeod, N.J.; O'Day, B.P. Binuclear metal(II) complexes of 1,3-diphenyltriazene: the crystal and molecular structures of the nickel(II), palladium(II) and copper(II) derivatives. *Aust. J. Chem.* 1975, 28, 2377–2392.
- Corbett, M.; Hoskins, B.F. An octahedral complex containing three fourmembered chelate rings. J. Am. Chem. Soc. 1967, 89, 1530–1532.
- Mandal, S.K.; Thompson, L.K.; Newlands, M.J.; Gabe, E.J. Structural and magnetic studies on macrocyclic dicopper(II) complexes. Influence of electron-withdrawing axial ligands on spin exchange. *Inorg. Chem.* 1990, 29, 1324–1327.
- Reim, J.; Griesar, K.; Haase, W.; Krebs, B. Structure and magnetism of novel tetranuclear μ₄-oxo-bridged copper(II) complexes. *Dalton Trans*. 1995, 2649–2656.
- Thompson, L.K.; Mandal, S.K.; Tandon, S.S.; Bridson, J.N.; Park, M.K. Magnetostructural correlations in bis(μ₂-phenoxide)-bridged macrocyclic dinuclear copper(II) complexes. Influence of electron-withdrawing substituents on exchange coupling. *Inorg. Chem.* 1996, 35, 3117– 3125.
- Karlin, K.D.; Farooq, A.; Hayes, J.C.; Cohen, B.I.; Rowe, T.M.; Sinn, E.; Zubieta, J. Models for met-hemocyanin derivatives: structural and spectroscopic comparisons of analogous phenolate and X (X = OH-, OMe-, N3-, Cl-, OAc-, OBz-) doubly bridged dinuclear copper(II) complexes. *Inorg. Chem.* 1987, 26, 1271–1280.
- Oberhausen, K.J.; Richardson, J.F.; Buchanan, R.M.; McCusker, J.K.; Hendrickson, D.N.; Latour, J.M. Synthesis and characterization of dinuclear copper(II) complexes of the dinucleating ligand 2,6-biss[(bis((1-methylimidazol-2-yl)methyl)amino)methyl]-4methylphenol. *Inorg. Chem.* 1991, *30*, 1357–1365.
- Amudha, P.; Kandaswamy, M.; Govindasamy, L.; Velmurugan, D. Synthesis and characterization of new symmetrical binucleating ligands and their μphenoxo-bridged bicopper(II) complexes: structural, electrochemical, and magnetic studies. *Inorg. Chem.* 1998, *37*, 4486–4492.
- Bleaney, B.; Bowers, K.D. Anomalous paramagnetism of copper acetate. Proc. R. Soc. London, Ser. A. 1952, 214, 451–465.