

Copper(II) complexes of tetradentate thioether-oxime ligands

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Received 5 March 2005; accepted 26 April 2005

Available online 13 June 2005

Abstract

Two dinuclear copper(II) thioether-oxime complexes ($[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ and $[\text{Cu}(\text{DtudH})_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$) have been synthesized. $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ reacted with excess $\text{BF}_3 \cdot \text{OEt}_2$ to yield $[\text{Cu}(\text{Thyclops})]\text{ClO}_4$, a BF_2^+ -macrocyclized di-oxime. $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ and $[\text{Cu}(\text{DtudH})_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$ are the first representatives of copper(II) thioether oximes which exhibit the classical out-of-plane oximate oxygen-metal dimer structure. $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ and $[\text{Cu}(\text{Thyclops})]\text{ClO}_4$ have been structurally characterized by single-crystal X-ray diffraction. The geometry about each copper(II) in $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ is a distorted square pyramid ($\tau = 0.14$). The average copper–nitrogen(oxime) bond length is 1.984 Å longer (~ 0.03 Å) than the average copper–nitrogen(oxime) bonds in copper(II) bis-glyoximates. The geometry of $[\text{Cu}(\text{Thyclops})]\text{ClO}_4$ reveals an almost perfect square pyramid ($\tau = 0.03$) of $\text{N}_2\text{S}_2\text{O}$ donors. Solution, cryogenic glass, and powder ESR spectra show a typical axial pattern, except for the powder spectrum of $[\text{Cu}(\text{DtudH})_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$ which displays a small rhombic distortion. Variable-temperature magnetic susceptibility measurements indicate very weak ferromagnetic interactions in $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$, where $J = +0.52 \text{ cm}^{-1}$ and very weak antiferromagnetic interactions in $[\text{Cu}(\text{DtudH})_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$, where $J = -0.59 \text{ cm}^{-1}$. Electrochemical measurements reveal that the mixed thioether-oxime coordination environment tends to stabilize Cu(II), as all electrochemical reductions are quasi-reversible or irreversible. $[\text{Cu}(\text{Thyclops})]\text{ClO}_4$ is more oxidizing than $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ by 0.14 V.

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Keywords: Thioether-oxime; Copper; Magnetochemistry; Electrochemistry; Crystal structure

1. Introduction

The coordination chemistry of copper(II) with oxime-containing ligands has been extensively studied. Vicinal (*vic*-) dioximes, including copper(II) complexes have received considerable attention as model compounds for many important biological processes [1–3]. Oxime metal complexes possess biological activity [4] as well as semi-conducting properties [5]. Due to the bridging ability of

the oxime moiety, copper(II) oxime complexes have been synthesized with nuclearities varying from monomeric to tetrameric and beyond [6–9,17]. Most dimeric copper(II) complexes of di-oxime ligands bridge in an out-of-plane fashion, where one oximate oxygen from one complex bridges to the adjacent copper(II) and vice versa. Out-of-plane bridging is generally responsible for the ferromagnetic interactions observed in these complexes, such as $[\text{Cu}(\text{dmg})_2]$ [10]. Recently, a large number of papers have appeared in the literature dealing with the synthesis, structure and magnetic properties of oxime-containing complexes [11–14]. One of the main

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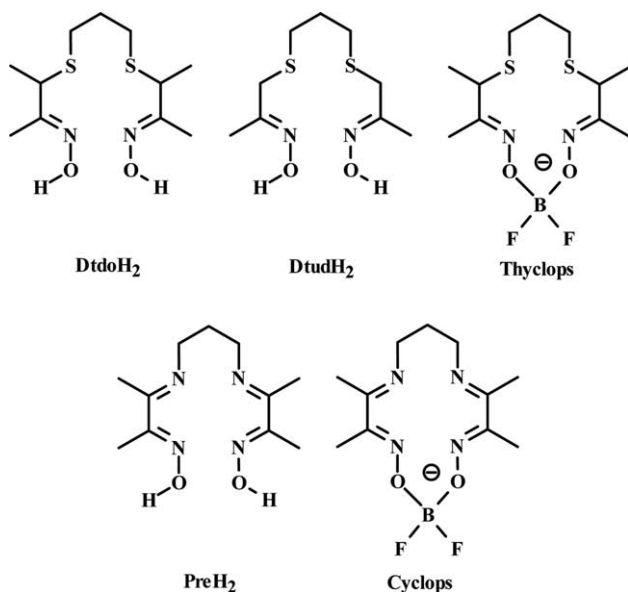


Chart 1. Ligands treated in this paper.

reasons for the current interest in oxime metal complexes is the ability of oximes (oximates) to coordinate in different modalities to metals as well as the easy tunability of their properties by alteration of the ligand substituents [15,16]. In this paper we report the synthesis and structures and physical properties of two dimeric copper(II) complexes of tetradentate thioether-dioxime ligands (Chart 1) as well as a BF_2^- -macrocyclized complex, $[\text{Cu}(\text{thyclops})]\text{ClO}_4$.

2. Experimental

Commercially available reagents (from Aldrich and Fisher) were used without further purification. Acetonitrile for electrochemistry was distilled off P_4O_{10} under N_2 . Electrochemistry, ESR and optical spectra were carried out as previously described [17]. Elemental microanalyses were performed by the University of Pennsylvania Microanalytical Laboratory. FAB-mass spectra were obtained on a VG-ZABHF instrument using 2-nitrobenzyl alcohol as the matrix (M is the complex cation). Variable temperature magnetic data (2–300 K) were obtained with a Quantum Design MPMS5S SQUID magnetometer employing an applied field of 1 T and a gradient field of 10 T m^{-1} . Calibrations were carried out with $\text{Co}[\text{Hg}(\text{SCN})_4]$. Susceptibility data were corrected for diamagnetism using Pascal's constants [18]. Data were analyzed using SAS Insitute's JMP 3.1 or Excel 2000 using the Solver Add-in. Initial estimates were obtained through quadratic extrapolation. Fitting iterations (1000 max.) utilized a quasi-Newton search algorithm. 3-Chloro-2-butanone oxime [17], chloro-2-propanone oxime [19] and $[\text{Cu}(\text{PreH})_2(\text{ClO}_4)_2]$ [27] were prepared according to literature procedures. A

standardized 1 mM methanolic solution of $\text{Cu}(\text{ClO}_4)_2$ was used to prepare the complexes.

2.1. Synthesis of ligands

4,8-dithia-3,9-dimethylundecane-2,10-dione dioxime (DtdoH₂). Under an atmosphere of N_2 , Na metal (120 mmol, 2.76 g) was dissolved in absolute ethanol (50 mL). 1,3-propanedithiol (60 mmol, 6.50 g) was added, followed by NaBH_4 (0.1 eq/mol dithiol) (6 mmol, 0.66 g). The mixture was heated to boiling on a steam bath and allowed to cool to room temperature. An ethanol solution (25 mL) of 3-chloro-2-butanone oxime (120 mmol, 14.6 g) was slowly added with stirring. The mixture was allowed to stir overnight. The ethanol was evaporated off (steam bath) and the residue was partitioned between 40 mL of diethyl ether and 60 mL water. Three such ether extracts were combined and dried over anhydrous Na_2SO_4 . Ether removal (rotary evaporator) afforded a white solid which was recrystallized from 95% ethanol. Yield, 16.5 g (98.8%). FAB-MS: 279, $[\text{MH}]^+$, 85%. $^1\text{H NMR}$ ($\text{DMSO-}d_6$) δ 1.1 (t, 4H), 1.4 (d, 6H), 1.8 (s, 6H), 3.4 (q, 2), 3.6 (m, 2), 10.0 (s, 2H).

4,8-dithiaundecane-2,10-dione dioxime (DtudH₂) [2]. The procedure for the synthesis of *DtdoH₂* was followed using 1,3-propanedithiol (50 mmol, 5.34 g) and chloro-2-propanone oxime (100 mmol, 10.7 g). Recrystallization from 95% ethanol yielded 11.14 g (89%) of white solid. FAB-MS (NaBr added): 251 $[\text{MH}]^+$, 80%, 273 $[\text{MNa}]^+$, 25%, 178 $[\text{M} - \text{C}_3\text{H}_5\text{NOH}]^+$, 45%. $^1\text{H NMR}$ (CDCl_3): δ 2.0 (s, 6H), 2.2 (s, 4H), 2.4 (t, 2H), 3.2 (s, 4H), 9.4 (s, 2H).

2.2. $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$

DtdoH₂ (3 mmol, 0.870 g) was dissolved in MeOH (20 mL) with stirring and a methanolic solution of $\text{Cu}(\text{ClO}_4)_2$ (3 mmol) was added. After the addition of a solution (MeOH, 5 mL) of sodium acetate (3 mmol, 0.246 g) a purple precipitate formed. The solid was collected via vacuum filtration, washed with MeOH ($2 \times 5 \text{ mL}$) and dried in air. Recrystallization from hot MeOH gave purple rhombs. Yield 0.82 g (62.1%). *Anal.* Calc for $\text{C}_{11}\text{H}_{21}\text{ClCuN}_2\text{O}_6\text{S}_2$: C, 30.0; H, 4.81; N, 6.36. Found: C, 30.1; H, 4.70; N, 6.36%. FAB-MS: $(\text{M})^+$: 340.

2.3. $[\text{Cu}(\text{DtudH})_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$

DtudH₂ (3 mmol, 0.768 g) was dissolved in MeOH (20 mL) with stirring and a methanolic solution of $\text{Cu}(\text{ClO}_4)_2$ (3 mmol) was added. After the addition of a solution (MeOH, 5 mL) of sodium acetate (3 mmol, 0.246 g) a purple precipitate formed. The solid was collected via vacuum filtration and washed with MeOH ($2 \times 5 \text{ mL}$) and dried in air. Recrystallization from hot MeOH gave purple microcrystals. Yield 1.15 g (86.3%).

Anal. Calc. for $C_9H_{17}ClCuN_2O_6S_2 \cdot CH_3OH$: C, 27.0; H, 4.76; N, 6.30. Found: C, 27.0; H, 4.61; N, 6.64%. FAB-MS: (MH)⁺: 313.

2.4. [Cu(Thyclops)]ClO₄

[Cu(DtdoH)]ClO₄ (3 mmol, 0.438 g) was dissolved in MeCN (3 mL) under an atmosphere of N₂. With stirring, triethylamine (1 mmol, 0.14 mL) was added followed by BF₃ · OEt₂ (2 mmol, 0.25 mL). The mixture was stirred for 15 min to give a deep purple solution. The acetonitrile was removed via rotary evaporation and isopropanol (10 mL) was added. The resulting solid was collected by vacuum filtration and recrystallized from 1:1 hot isopropanol/methanol. Yield 0.30 g (61%) of purple prisms. *Anal. Calc.* for C₁₁H₂₀BClCuF₂N₂O₆S₂: C, 27.1; H, 4.13; N, 5.74. Found: C, 27.0; H, 4.21; N, 5.53%. FAB-MS: (M)⁺: 388.

Caution: Although the complexes reported do not appear to be mechanically sensitive, perchlorate complexes should be treated with due caution.

2.5. X-ray data collection

X-ray data for [Cu(DtdoH)]₂(ClO₄)₂ and [Cu(Thyclops)]ClO₄ were collected on a Siemens P4S diffractometer and refined according to published procedures [19]. Crystallographic data are given in Table 1.

For [Cu(DtdoH)]₂(ClO₄)₂ a total of 4446 reflections were collected ($0 \leq h \leq 9$, $0 \leq k \leq 27$, $-15 \leq l \leq 15$) in the range of 2.63–27.50°, with 4143 being unique ($R_{\text{int}} = 2.39\%$).

For [Cu(Thyclops)]ClO₄ a total of 4488 reflections were collected ($-19 \leq h \leq 17$, $0 \leq k \leq 12$, $0 \leq l \leq 17$)

in the range of 2.52 to 27.49°, with 4307 being unique ($R_{\text{int}} = 1.23\%$). The structure of [Cu(DtdoH)]₂(ClO₄)₂ and [Cu(Thyclops)]ClO₄ were solved by direct methods. Both structures were refined by full least-squares methods based on F^2 to R values [20]. Hydrogens were included in structure factor calculations in calculated positions and refined using a riding model. ORTEP diagrams were created with ORTEP-3 ver.1.08 [21]. Thermal ellipsoids are displayed at the 20% probability level for clarity, and hydrogen atoms are shown as spheres of arbitrary size.

3. Results and discussion

3.1. The reaction of BF₂⁺ and [Cu(DtudH)]₂(ClO₄)₂

Attempts to –BF₂⁺ macrocyclize [Cu(DtudH)]₂(ClO₄)₂ yielded only oily products which defied purification. Attempts to –BF₂⁺ bridge via the hydrolysis reaction of BF₄[–] to BF₂⁺ [17] yielded only the metathesis product, [Cu(DtudH)]₂(BF₄)₂.

3.2. Description of the structure of [Cu(DtdoH)]₂(ClO₄)₂

An ORTEP diagram is shown in Fig. 1 and selected bond distances and angles are given in Table 2. The structure is composed of two quasi-macrocyclic units (proton bridging between the two oxime oxygens (2.528 Å)) joined by two Cu–O(oximate) bonds (one from each ligand) at 2.293 Å, which is quite common for *cis*-oxime copper(II) complexes. The geometry at

Table 1
Crystallographic data

	[Cu(DtdoH)] ₂ (ClO ₄) ₂	[Cu(Thyclops)]ClO ₄
Formula	C ₁₁ H ₂₁ ClCuN ₂ O ₆ S ₂	C ₁₁ H ₂₀ BClCuF ₂ N ₂ O ₆ S ₂
Fw	440.41	488.21
Crystal system	monoclinic	monoclinic
Crystal size (mm)	0.15 × 0.54 × 0.21	0.15 × 0.83 × 0.43
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	7.4566(9)	15.0454(11)
<i>b</i> (Å)	20.947(2)	9.9656(8)
<i>c</i> (Å)	11.8939(13)	13.7135(10)
β (°)	103.792(9)	113.933(5)
<i>V</i> (Å ³)	1804.2(3)	1879.4(2)
<i>Z</i>	4	4
ρ _{calc} (g cm ^{–3})	1.621	1.725
<i>F</i> (000)	908	996
μ (mm ^{–1})	1.618	1.576
λ(Mo Kα) (Å)	0.71073	0.71073
<i>T</i> (K)	293(2)	293(2)
<i>R</i> ^a , <i>R</i> _w ^b	0.0453; 0.1161	0.0358; 0.0890

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]$$

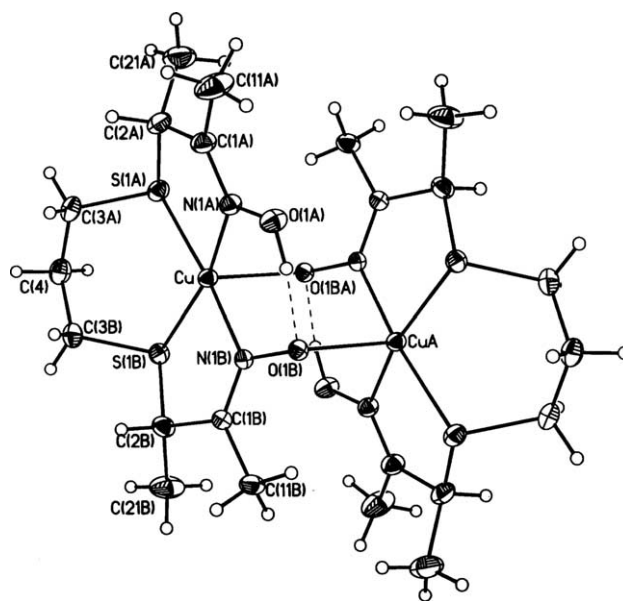


Fig. 1. ORTEP diagram of [Cu(DtdoH)]⁺ dimer structure in [Cu(DtdoH)]₂(ClO₄)₂.

Table 2
Selected bond lengths (Å) and angles (°) for [Cu(DtdoH)]₂(ClO₄)₂

Bond lengths			
Cu–N(1B)	1.973(3)	Cu–N(1A)	1.996(3)
Cu–S(1B)	2.2778(9)	Cu–O(1B)#1	2.293(2)
Cu–S(1A)	2.2957(10)	S(1A)–C(2A)	1.837(4)
S(1A)–C(3A)	1.838(4)	S(1B)–C(3B)	1.817(4)
O(1B)–Cu#1	2.293(2)	O(1B)–N(1B)	1.372(3)
Bond angles			
N(1B)–Cu–N(1A)	98.13(11)	N(1B)–Cu–S(1B)	83.85(8)
N(1A)–Cu–S(1B)	165.88(9)	N(1B)–Cu–O(1B)#1	89.03(9)
N(1A)–Cu–O(1B)#1	96.67(10)	S(1B)–Cu–O(1B)#1	97.34(6)
N(1B)–Cu–S(1A)	174.42(8)	N(1A)–Cu–S(1A)	83.61(9)
S(1B)–Cu–S(1A)	93.18(4)	O(1B)#1–Cu–S(1A)	96.05(6)
C(2A)–S(1A)–C(3A)	101.59(19)	C(2A)–S(1A)–Cu	99.26(13)
C(3A)–S(1A)–Cu	107.40(14)	C(3B)–S(1B)–C(2B)	102.08(19)
(3B)–S(1B)–Cu	105.88(14)	C(2B)–S(1B)–Cu	97.83(11)

each copper(II) (monomer unit) can be described as a distorted square pyramid ($\tau = 0.14$) [22], with the bases of the square pyramids (the two C₂NSCu rings) twisted by 26.9°. The overall geometry of [Cu(DtdoH)]₂(ClO₄)₂ is quite similar to that of [Cu(dmgH)]₂ [23], where $\tau = 0.13$ and the two five-membered C₂N₂Cu rings are twisted by 23.2° with respect to each other. The basal plane contains two S(thioether) donors and two N(oxime) donors coordinated to the Cu at typical average distances (2.287 Å) and (1.984 Å), respectively [4b,24]. Although the overall structure of [Cu(DtdoH)]₂(ClO₄)₂ is very similar to that of [Cu(dmgH)]₂, the subtle differences result in differences in magnetochemical properties (vide infra).

3.3. Description of the structure of [Cu(Thyclops)]ClO₄

An ORTEP diagram is shown in Fig. 2 and selected bond distances and angles are given in Table 3. The X-ray structure reveals an almost perfect square pyramidal N₂S₂O coordination environment ($\tau = 0.027$). The apical position is occupied by an O(perchlorate) (2.211 Å) and is typically elongated due to Jahn–Teller distortion. The *cis*-oximes are macrocyclized by a –BF₂⁺ group and the resulting O–B bond distances (1.47 Å) as well as S(thioether) (2.295 Å) and N(oxime) (1.980 Å) distances are typical for –BF₂⁺ macrocyclized thioether-oxime copper(II) complexes [17]. The hydrogen atoms of C(1B) are disordered over two equivalent positions.

3.4. Electronic spectra

Optical spectral data are given in Table 4. The electronic spectra show two bands in the visible region. The fairly intense ($\epsilon = 1.5\text{--}3.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) higher energy band (between 350–425 nm) is assigned as thioether sulfur-to-copper(II) charge-transfer [25]; more

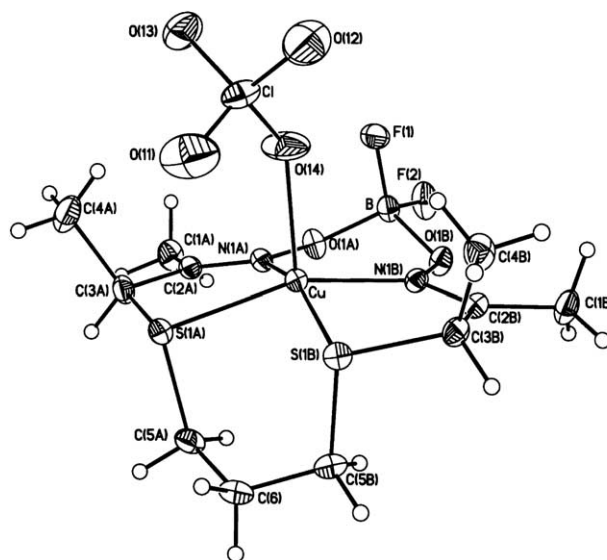


Fig. 2. ORTEP diagram of [Cu(Thyclops)]⁺ cation in [Cu(Thyclops)]ClO₄.

Table 3
Selected bond lengths (Å) and angles (°) for [Cu(Thyclops)]ClO₄

Bond lengths			
Cu–N(1B)	1.977(2)	Cu–N(1A)	1.981(2)
Cu–O(14)#1	2.211(3)	Cu–S(1B)	2.2952(8)
Cu–S(1A)	2.2953(8)	S(1A)–C(5A)	1.833(3)
S(1B)–C(3B)	1.822(3)	S(1B)–C(5B)	1.826(3)
F(1)–B	1.378(4)	F(2)–B	1.368(4)
O(1A)–N(1A)	1.382(3)	O(1A)–B	1.475(4)
O(1B)–N(1B)	1.379(3)	O(1B)–B	1.467(4)
O(14)–Cu#2	2.211(3)	N(1A)–C(2A)	1.282(4)
N(1B)–C(2B)	1.279(4)		
Bond angles			
N(1B)–Cu–N(1A)	95.87(9)	N(1B)–Cu–O(14)#1	97.75(12)
N(1A)–Cu–O(14)#1	100.51(13)	N(1B)–Cu–S(1B)	84.87(7)
N(1A)–Cu–S(1B)	160.82(7)	O(14)#1–Cu–S(1B)	98.37(11)
N(1B)–Cu–S(1A)	159.90(7)	N(1A)–Cu–S(1A)	84.89(7)
O(14)#1–Cu–S(1A)	101.86(10)	S(1B)–Cu–S(1A)	87.97(3)
C1–O(14)–Cu#2	138.8(2)	C(2A)–N(1A)–O(1A)	114.3(2)
C(2A)–N(1A)–Cu	123.5(2)	O(1A)–N(1A)–Cu	122.00(16)
C(2B)–N(1B)–O(1B)	114.2(2)	C(2B)–N(1B)–Cu	123.4(2)

specifically, a $\sigma(\text{S}) \rightarrow d_{x^2-y^2}(\text{Cu})$ transition. The magnitude of the LMCT depends on the extent of the interaction between the σ -orbitals on the thioether-sulfur and the Cu(II) $d_{x^2-y^2}$ orbital. This orbital overlap has important consequences for attempts at modeling the high molar absorptivities of blue-copper proteins [26]. The excessive intensity of the lower energy band (between 498 and 590 nm) mitigates against assigning it as purely a $d \rightarrow d$ transition [25a]. This transition has been assigned as a $d\pi(\text{Cu})/3b_1(\text{S}) \rightarrow d_{x^2-y^2}(\text{Cu})$. According to Nikles et al. [25b], the $\text{S}(\pi) \rightarrow d_{x^2-y^2}(\text{Cu})$ transition is usually weaker than the $\text{S}(\sigma) \rightarrow d_{x^2-y^2}(\text{Cu})$ transition

Table 4
Optical spectra

Complex	Medium ^a	λ (nm (ϵ ($M^{-1} cm^{-1}$)))
[Cu(Thyclops)]ClO ₄	Solid state	590, 350 sh
	CH ₃ CN	582 (747), 385 (2290)
	CH ₃ NO ₂	546 (610)
	CH ₃ OH	570 (429), 357 (1640)
[Cu(DtdoH)] ₂ (ClO ₄) ₂	Solid state	570, 390
	CH ₃ CN	552 (1240), 425 (2090)
	CH ₃ NO ₂	500 sh (1220), 399 (3030)
	CH ₃ OH	556 (1160), 419 (2600)
[Cu(DtudH)] ₂ (ClO ₄) ₂ · 2CH ₃ OH	Solid state	600, 420
	CH ₃ CN	540 (1010), 419 (2440)
	CH ₃ NO ₂	498 sh (1140), 401 (3270)

^a Solid-spectra spectra from diffuse reflectance in MgCO₃ matrix.

and has the possibility of mixing with the $d \rightarrow d$ transition. The $Cu \leftarrow N=O$ (oxime) charge transfer, which usually occurs around 350 nm [26] is obscured by the intensity of the $S \rightarrow Cu$ LMCT band. The low energy band occurs at slightly lower energy in the thioether-oxime complexes (N_2S_2) compared to the N_4 -oxime analogs such as [Cu(Cyclops)]ClO₄ (445 nm) [27], [Cu(preH)]₂(ClO₄)₂ (490 nm) [27] and [Cu(dmgH)]₂ (477 nm) [28], due to thioether-sulfur acting as a slightly weaker ligand-field donor than imino-nitrogen.

3.5. ESR spectra

The ESR spin-Hamiltonian parameters are given in Table 5. Fig. 3 shows the 77 K solution spectrum of [Cu(Thyclops)]ClO₄ in MeOH. No $\Delta M_s = 2$ transitions were observed for [Cu(DtdoH)]₂(ClO₄)₂, as is sometimes the case for coupled Cu(II) dimers [29,30], probably due to the cleavage of the dimer in solution to a solvent-monomer. The ESR spectra of the tetradentate thioether-oxime copper(II) complexes are axial in nature, where $g_{\parallel} > g_{\perp}$ indicates a $d_{x^2-y^2}$ ground state, which is a typical occurrence for tetragonal copper(II) complexes (except for the neat powder spectrum of [Cu(DtudH)]₂-

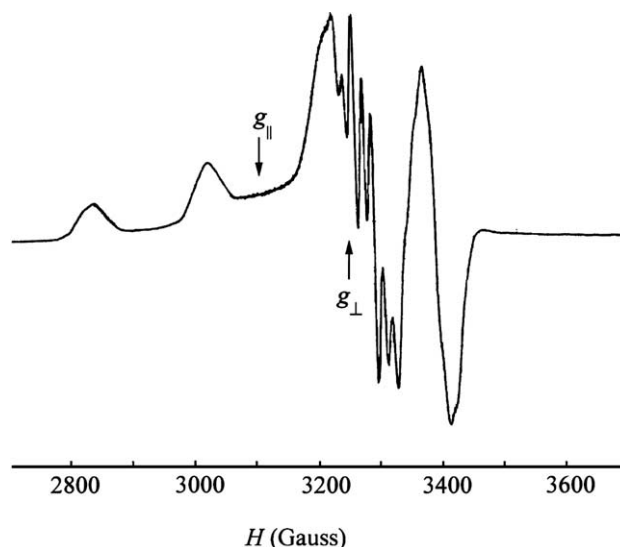


Fig. 3. 77 K Cryogenic ESR spectrum of [Cu(Thyclops)]ClO₄ in MeOH.

(ClO₄)₂ · 2CH₃OH). The g_{\parallel} -values are greatly influenced by the donor types and by the coordination geometry. Hard donors as well as distortion from planar geometries cause g_{\parallel} to increase, whereas soft donors and planar geometries cause g_{\parallel} to decrease [31]. The ESR-based gauges of coordination geometry (tetragonal vs. trigonal), namely large values of $|A_{\parallel}|$ and low values of the distortion index ($g_{\parallel} - 2/|A_{\parallel}|$) [32] are good indicators of “regular” tetragonal stereochemistry. Another important aspect of the geometry can be learned from the similarities between $\langle g \rangle$ (average g -value) and g_0 (isotropic g -value). The closer these values are to each other the more persistent a particular stereochemistry is over the temperature ranges (room temperature to 77 K) and states (RT solution, cryogenic glass, and neat solid) in which the spectra are obtained. These parameters point to tetragonal geometries for [Cu(DtdoH)]₂(ClO₄)₂ and [Cu(Thyclops)]ClO₄. The values of g_{\parallel} (between 2.09 and 2.16) all are similar to other copper-oxime complexes, which have g_{\parallel} values ranging from 2.10 to 2.19 [17,27]. Another interesting feature of many

Table 5
ESR data

Complex	Medium ^a	g_0^b	$10^4 \times A_0 $ (cm^{-1}) ^b	g_{\parallel}^b	$10^4 \times A_{\parallel} $ (cm^{-1}) ^b	g_{\perp}^b	$10^4 \times A_{\perp} $ (cm^{-1}) ^b	$10^4 \times A(N) $ (cm^{-1}) ^b
[Cu(Thyclops)]ClO ₄	MeOH	2.03	81	2.10	196	2.01	23	17
	Solid			2.09		2.01		
[Cu(DtdoH)] ₂ (ClO ₄) ₂	MeOH	2.07	76	2.14	185	2.07	22	17
	Solid			2.13		2.04		
[Cu(DtudH)] ₂ (ClO ₄) ₂ · 2CH ₃ OH	MeOH	2.07	77	2.16	171	2.03	30	18
	Solid			$g_1 = 2.15$	$g_2 = 2.10$	$g_3 = 2.03$		

^a MeOH was used as the solvent for ambient-T isotropic and 77 K cryogenic spectra.

^b g_0 , A_0 are from RT fluid spectra; g_{\parallel} , A_{\parallel} and g_{\perp} are from 77 K spectra g_{\perp} value obtained via simulation; A_{\perp} via $3A_0 = A_{\parallel} + 2A_{\perp}$ and $g_{\parallel} \pm 0.005$; $10^4 A \pm 3$; $g_{\perp} \pm 0$.

copper(II) oximes is the appearance of nitrogen super-hyperfine lines in the g_{\perp} region, which generally mirror the number of nitrogen donors ($2nI + 1$, where $I = 1$ for nitrogen and n is the number of nitrogen donors) [17,27]. The small g_{\parallel} values are consistent with thioether-sulfur being present in the coordination environment [31,33,34]. The above distortion indices for all three complexes are rather low and betoken tetragonal symmetry: 5.1 for $[\text{Cu}(\text{Thyclops})]\text{ClO}_4$ and 7.6 for $[\text{Cu}(\text{DtdoH})]_2(\text{ClO}_4)_2$. These conclusions are reinforced by the geometries observed in the crystal structures of these two complexes (vide supra). The large value observed in $[\text{Cu}(\text{DtudH})]_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ (9.4) also manifests itself as rhombic spectrum ($R = 0.71$) in the neat powder [35], which signals lower symmetry in the coordination sphere. The lower symmetry observed in the ESR spectrum of $[\text{Cu}(\text{DtudH})]_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ is also evidenced by the magnetic properties of this complex, which are different from that of $[\text{Cu}(\text{DtdoH})]_2(\text{ClO}_4)_2$ (vide infra).

3.6. Magnetochemistry

Magnetic data for the tetradentate thioether-oxime complexes, as well as for other complexes with similar axial/equatorial bridging modes are provided in Table 6. Very weak ferromagnetic coupling dominates the magnetism of these complexes. The variable temperature magnetic susceptibility data for $[\text{Cu}(\text{DtdoH})]_2(\text{ClO}_4)_2$ (Fig. 4), $[\text{Cu}(\text{DtudH})]_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ and $[\text{Cu}(\text{PreH})]_2(\text{ClO}_4)_2$ were fit using the modified Bleaney–Bowers equation [36,37], which is based on the isotropic exchange Hamiltonian ($H = -2J\hat{S}_1 \cdot \hat{S}_2$).

$$\chi_m = \frac{2Ng^2\beta^2}{kT} \frac{1}{3 + e^{-2J/kT}} + N\alpha, \quad (1)$$

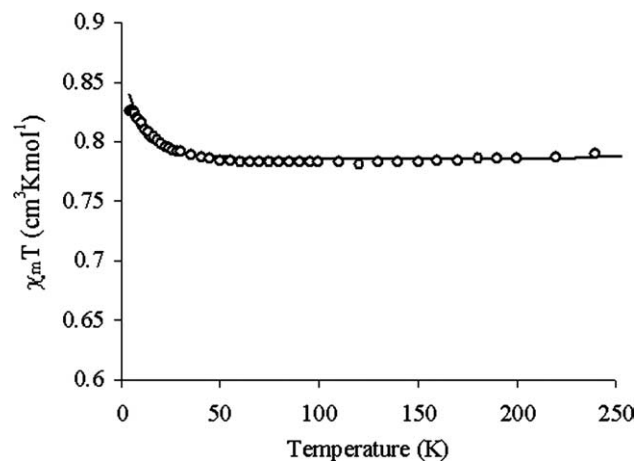


Fig. 4. Variable temperature magnetism for $[\text{Cu}(\text{DtdoH})]_2(\text{ClO}_4)_2$.

where $N\alpha$ [38] is the temperature independent paramagnetism and J is the exchange integral.

The magnetic data for $[\text{Cu}(\text{DtdoH})]_2(\text{ClO}_4)_2$ was fit with $J = +0.52 \pm 0.02 \text{ cm}^{-1}$, $g = 2.038 \pm 0.001$ and $N\alpha = 1.07 \times 10^{-5} \pm 4 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ (Fig. 4), whereas the data for $[\text{Cu}(\text{PreH})]_2(\text{ClO}_4)_2$ was fit with $J = +0.80 \pm 0.02 \text{ cm}^{-1}$, $g = 2.030 \pm 0.002$ and $N\alpha = 0$ [38]. The out-of-plane bonding in $[\text{Cu}(\text{DtdoH})]_2(\text{ClO}_4)_2$ and $[\text{Cu}(\text{PreH})]_2(\text{ClO}_4)_2$, common in *vic*-dioxime copper(II) complexes [39,40,47,48] generally leads to very weak ferromagnetic coupling. The ferromagnetism is primarily due to the approximate orthogonality of the $d_{x^2-y^2}$ orbitals on adjacent Cu(II) ions. A magnetostructural correlation has been developed which shows the dependence of the magnitude and sign of the coupling to the angle of the out-of-plane O(oxime)–Cu bond (α) and the Cu–O(axial) distance (R) [47,48].

The correlation shows that as the values of α and R decrease, the overlap between the magnetic orbitals

Table 6
Magnetochemical and structural data

Complex	J (cm^{-1})	$10^{-3} \times \text{GOF}^i$	Cu–Cu (\AA)	Cu–O (\AA)	α ($^\circ$)	R (\AA)	Reference
$[\text{Cu}(\text{DtdoH})]_2(\text{ClO}_4)_2$	+0.54	1.42	3.96	2.29	109	2.29	This work
$[\text{Cu}(\text{DtudH})]_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$	–0.59	2.75	–	–	–	–	This work
$[\text{Cu}(\text{preH})]_2(\text{ClO}_4)_2^{\text{a,b}}$	+0.80	1.15	–	2.50	–	–	This work
$[\text{Cu}(\text{Hbdmg})]_2(\text{ClO}_4)_2^{\text{c}}$	–0.85 ^h	–	3.91	2.27	108	2.27	[47]
$[\text{Cu}(\text{Hchd})]_2^{\text{d}}$	+1.55 ^h	–	3.83	2.24	106	2.24	[47]
$[\text{Cu}(\text{Hdeg})]_2^{\text{e}}$	+0.50 ^h	–	3.90	2.26	106	2.26	[47]
$[\text{Cu}(\text{Hdmg})]_2^{\text{f}}$	+4.6 ^h	–	3.85	2.30 ^g	103	2.30	[47]

^a Structurally characterized as perrhenate salt which is monomeric [46].

^b $\text{preH}_2 = 3,9$ -dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime.

^c $\text{H}_2\text{bdmg} = 3,10$ -dimethyl-4,9-diazadodeca-3,9-diene-2,11-dione dioxime.

^d $\text{H}_2\text{chd} = \text{cyclohexane-1,2-dione dioxime}$.

^e $\text{H}_2\text{deg} = \text{diethylglyoxime}$.

^f $\text{H}_2\text{dmg} = \text{dimethylglyoxime}$.

^g $[\text{Cu}(\text{dmg})_2]$ X-ray structure from Vacigo and Zambonelli [23].

^h J -values adjusted to a singlet–triplet gap of $2J$.

ⁱ GOF (Goodness of fit), $R^2 = \frac{\sum (\chi T_{\text{obs}} - \chi T_{\text{calc}})^2}{\sum \chi T_{\text{obs}}^2}$.

of the copper(II) ions decreases, generally leading to ferromagnetic interactions. For $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ ($\alpha = 109.1^\circ$ and $R = 2.293 \text{ \AA}$) the very small ferromagnetic exchange integral ($+0.54 \text{ cm}^{-1}$) is consistent with this correlation. Size and electronic effects of the thioether donors may also play an important role in modulating the magnetic interactions in copper(II) thioether-oxime dimers. In $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ the average Cu–N(oxime) distance is 1.984 \AA , whereas in $[\text{Cu}(\text{Hbdmg})_2(\text{ClO}_4)_2]$ the average Cu–N(oxime) distance is 1.974 \AA [47]. The average Cu–N(oxime) distance amongst the three copper(II) alkylglyoxime (H_2chd , H_2deg , H_2dmg) complexes examined by Cervera et al. [47] was 1.956 \AA . The increase in the Cu–N(oxime) distance ($\sim 0.03 \text{ \AA}$ longer) may partial account for differences in coupling found in $[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$ compared to the Cu(II) alkylglyoximes.

The variable temperature data of $[\text{Cu}(\text{DtudH})_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$ was fit with $J = -0.59 \pm 0.03 \text{ cm}^{-1}$, $g = 2.016 \pm 0.001$ and $N\alpha = 5.17 \times 10^{-4} \pm 6 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. Although $N\alpha$ is higher than usual (normally ca. $10^{-5} \text{ cm}^3 \text{ mol}^{-1}$), even larger ($N\alpha > 5 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$) temperature independent paramagnetic contributions have been reported [49,50]. The small antiferromagnetic coupling present in $[\text{Cu}(\text{DtudH})_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$ distinguishes it from other Cu(II) *vic*-dioximes. This observation correlates with the ESR data (vide supra) which suggested that this complex is more trigonally distorted than the other complexes. X-ray diffraction studies could provide insight into the exact nature of the distortion. Repeated attempts to obtain single crystals of $[\text{Cu}(\text{DtudH})_2]^{2+}$, as both the perchlorate and tetrafluoroborate salts only resulted in microcrystalline solids which effloresced solvent on standing.

3.7. Electrochemistry

The electrochemical data are summarized in Table 7. The reductions of the tetradentate thioether-oxime copper(II) complexes are all quasireversible/irreversible, thus lending credibility to the idea that such coordination environments tend to stabilize copper(II) relative to copper(I). Anionic ligands tend to support copper(II),

as has been noted for a variety of sulfur-, nitrogen- and oxygen-donor ligands [41,42]. That $[\text{Cu}(\text{Cyclops})]^+$ ($E_{1/2} = -0.40 \text{ V}$ vs. SCE) is more oxidizing than $[\text{Cu}(\text{Thyclops})]^+$ by about 0.53 V , is a somewhat unexpected result, as thioether donors generally yield copper complexes whose $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ potentials are higher than those of the corresponding nitrogen-ligated systems [43]. However, an additional factor to be considered is that the conjugated tetraimine moiety in $[\text{Cu}(\text{Cyclops})]^+$ offers an unusual delocalization of the electron added upon reduction, so that there is significant radical-dianion character for the ligand [51,52]. The same trend in relative $E_{1/2}$'s also holds for $[\text{Cu}(\text{DtdoH})]^+$, and $[\text{Cu}(\text{DtudH})]^+$, which are again harder to reduce by ca. 0.5 V relative to their N_4 analogs [27]. Replacing H^+ by BF_2^+ shifts the Cu(II)/Cu(I) reduction in a positive direction (by 0.14 V for $[\text{Cu}(\text{Thyclops})]^+$ vs. $[\text{Cu}(\text{DtdoH})]^+$). This effect is of the same order of magnitude observed for $[\text{Cu}(\text{Cyclops})]^+$ vs. $[\text{Cu}(\text{PreH})]^+$ (0.23 V) [27] and is interpreted as an indicator of a greater electron-withdrawing nature for the BF_2^+ -group compared to a proton. Saturation of the $[\text{Cu}(\text{Thyclops})]^+$ solution with CO gas causes the quasi-reversible voltammetry of $[\text{Cu}(\text{Thyclops})]^+$ to become irreversible ($E_{p,c}$ shifts cathodically by 89 mV at $v = 100 \text{ mV s}^{-1}$), suggesting the formation of a Cu(I)–CO adduct which is kinetically unstable toward conversion to non-electroactive species.

4. Supplementary material

Crystallographic data (excluding structure factors) for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 265453 and 265454. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc@cam.ac.uk).

Acknowledgement

M.J.P. thanks La Salle University for current support and Drexel University for past support. A.W.A. thanks Drexel University for support.

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Table 7
Electrochemical data

Complex	$E_{1/2}$ (V) ^a	$10^8 D\eta$ (g cm s^{-2}) ^b
$[\text{Cu}(\text{Thyclops})]\text{ClO}_4$	–1.23	3.24
$[\text{Cu}(\text{DtdoH})_2(\text{ClO}_4)_2]$	–1.37 ^c	1.58
$[\text{Cu}(\text{DtudH})_2(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}]$	–1.50 ^c	1.45

^a $E_{1/2}$ vs. Ag^+ (0.01 M, 0.1 M NEt_4ClO_4 , CH_3CN)/ Ag . This electrode is at ca. $+0.540 \text{ V}$ vs. the SHE. All electrochemistry was performed in CH_3CN with 0.1 M NEt_4ClO_4 supporting electrolyte.

^b η (0.1 M TEAP in CH_3CN) = $0.00380 \text{ g cm}^{-1} \text{ s}^{-1}$ at 298 K.

^c $E_{1/2}$ and $D\eta$ obtained from RDE polarogram, estimate of $D\eta$ obtained according to Levich [44] and Adams [45].

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