Pentadentate thioether-oxime macrocyclic and quasi-macrocyclic complexes of copper(II) and nickel(II)

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Abstract

A series of new pentadentate thioether-oximes (TtoxH2, MeTtoxH2, OdtoxH2) were synthesized along with their Ni(II) and Cu(II) complexes. BF2−-bridging is accomplished by reaction of the H-bonded oxime complex with BF3·OEt2, though when Cu(BF4)2 is used as the Cu(II) salt, direct macrocyclization occurs during the metal complexation reaction. Crystallographic studies reveal: [Cu(TtoxH)]ClO4 has a N2S3 square-pyramidal geometry, with an H-bond forming a quasi-macrocycle. In [Cu(OdtoxH)](ClO4)[Cu(OdtoxH2)](ClO4)2, while retaining the same overall geometry as [Cu(TtoxH)]ClO4, half of the cations are singly deprotonated and the remaining half retain both their protons. In addition, there is an unexpected interaction involving a perchlorate oxygen and the dimethylene bridges between the ligand’s ether oxygen and thioether sulfurs. [Ni(OdtoxBF2)]ClO4·H2O has an N2S2O2 octahedral geometry. The ligand occupies the equatorial plane and one of the apical positions; the coordination sphere is completed by a water oxygen. Cyclic voltammetry and rotating disk electrode (RDE) polarography reveal that N2S3 donor sets stabilize both Ni(III) and Ni(I), whereas the Cu(II) complexes stabilize only Cu(I). The copper complexes show axial ESR spectra typical of tetragonal Cu(II). Nitrogen superhyperfine structure is observed in both the room temperature fluid and 77 K cryogenic glass spectra. Macrocyclization by BF2+ enforces the in-plane geometry around the metal ion. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Macrocycle; Crystal structures; Oxime; Copper complexes; Nickel complexes; Electrochemistry; Polarography

1. Introduction

In 1905, Chugaev discovered the vicinal dioxime metal complex bis-dimethylglioximatonickel(II) [1], initiating an area of coordination chemistry which has been widely explored during the past century. The first vic-oxime quasi-macrocyclic complexes were prepared by Uhlig and Friedrich [2]. Since that time, several N4 and N2S2 quasi-macrocyclic and BF2-macrocyclized oximes have been synthesized [3–7]. Recently a copper–oxime complex was used to oxidize anthracene [8], while metal-containing oxime complexes are utilized in medicine as well; technetium(V)- and copper(II)-containing vic-oximes currently are used as cerebral and myocardial perfusion imaging agents [9–14]. This area was also recently reviewed [15,16]. The ability of sulfur- and nitrogen-based donors to stabilize reduced and oxidized forms of Cu(II) and Ni(II), respectively, has sparked interest in their role in bioinorganic systems. Interest continues in the combined effects of thioether sulfur with imino nitrogen on the redox chemistry of Cu(II) and Ni(II). We report here the synthesis, structure and electronic properties of Ni(II)- and Cu(II)-oxime complexes with N2S3 and N2S2O donor arrays, as well as the properties of the BF2-macrocyclized complexes, some of which exhibit the ability of stabilizing both Ni(I) and Ni(III) in the same ligand framework. It was found that the direct reaction of Cu(BF4)2 with the dioxime ligands produced the BF2+ -macrocyclized products.

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2. Experimental

Reagents (Aldrich, Fluka, GFS) were generally used as received. Acetonitrile for electrochemistry was distilled off P₂O₅ under N₂. 3-Chloro-2-propanone oxime and 3-chlorobutanone oxime were prepared according to literature procedures [7,17]. Proton NMR spectra were obtained on a Bruker AM250 spectrometer using CDCl₃ as solvent with TMS as internal standard. Electronic spectra were recorded on a Perkin–Elmer Lambda-3 spectrophotometer (solution) or on a Perkin–Elmer 330 spectrophotometer, equipped with an integrating sphere for diffuse reflectance. Electrochemical measurements were carried out with a Bioanalytical Systems (BAS-100A) electrochemical analyzer. The three-electrode assembly comprised the working electrode, an Ag⁺ (0.01 M, 0.1 M NEt₄ClO₄, MeCN)/Ag reference electrode, and a Pt-mesh auxiliary electrode. The working electrode was a Pt wire for voltammetry and a Pt disk for rotating electrode polarography (for which E₁/₂ is defined as the potential at which i = iₐ/₂ [18]. The supporting electrolyte was 0.1–0.2 M NEt₄ClO₄, and solutions were approximately 1 mM in complex. ESR spectra were obtained on a Varian E-12 X-band instrument calibrated near g = 2 with diphenylpicrylhydrazyl radical; g-values are ±0.005 (gᵣ) and ±0.01 (gₛ); isotropic g-values (gᵣ) are ±0.005. ESR spectra were simulated (to second order in the resonance fields) on a Macintosh G3 platform using software derived from the work of Lozos et al. [19]. Elemental microanalyses were performed by Robertson–Microlit Laboratories (Madison, NJ) or by the University of Pennsylvania Microanalytical Laboratory. Mass spectra were obtained on a VG-ZABHF high resolution double focusing instrument using 2-nitrobenzyl alcohol as the matrix for FAB mode.

2.1. Syntheses

2.1.1. 4,7,10-Trithiatridecane-2,12-dione dioxime (TtoxH₂)

Under an atmosphere of N₂, Na metal (0.69 g, 30 mmol) was dissolved in absolute ethanol (20 ml). Bis(2-mercaptoethyl) sulfide (2.3 g, 15 mmol) was added, followed by NaBH₄ (0.33 g, 3 mmol). The mixture was heated to boiling on a steam bath and allowed to cool to room temperature (r.t). An ethanol solution (15 ml) of 3-chloro-2-propanone oxime (3.21 g, 30 mmol) 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 20 ml of diethyl ether and 30 ml of water. Three such ether extracts were combined and dried over anhydrous Na₂SO₄. Ether removal (rotary evaporator) afforded a viscous pale yellow oil. Yield: 3.36 g (76%). FAB MS: M + H = 297; ¹H NMR: δ 2.0 (s, 6H), 2.7 (m, 8H), 3.3 (s, 4H), 9.9 (s, 2H).

2.1.2. 4,10-Dithia-7-oxatridecane-2,12-dione dioxime (OdtoxH₂)

The procedure followed was as above, 2-mercaptoethyl ether (2.07 g, 15 mmol) being used instead of 2-mercaptoethyl sulfide. Yield: 3.90 g (93%). FAB MS: M + H = 325; ¹H NMR: δ 1.4 (2d, 6H), 1.9 (s, 6H), 2.6 (m, 8H), 3.7 (qd, 2H), 9.6 (s, 2H).

2.1.3. 3,11-Dimethyl-4,7,10-trithiatridecane-2,12-dione dioxime (MeTtoxH₂)

The procedure followed was as for TtoxH₂, but using 3-chlorobutanone oxime (3.63 g, 30 mmol) instead of 3-chloro-2-propanone oxime. Yield: 3.94 g (81%). FAB MS: M + H = 325; ¹H NMR: δ 2.0 (s, 6H), 2.7 (m, 8H), 3.2 (s, 4H), 3.6 (m, 4H), 9.9 (s, 2H).

2.1.4. [Ni(TtoxH)ClO₄]H₂O

To a stirred solution of TtoxH₂ (2 g, 7.3 mmol) in MeOH (20 ml), was added a solution of Ni(ClO₄)₂·6H₂O (2.67 g, 7.3 mmol) in MeOH (10 ml), to give a lilac solution. A methanolic solution (15 ml) of NaOAc·3H₂O (0.99 g, 7.3 mmol) was then added. After 10 min a powdery lilac precipitate formed, which was filtered off, washed with MeOH (2 × 5 ml) and recrystallized from hot 2:1 MeOH–Me₂CO. Yield: 1.86 g (52%) of lilac microprisms. Anal. Calc. for C₁₀H₁₉Cl·CuN₂O₆S₃: C, 26.2; H, 4.65; N, 6.15. Found: C, 25.4; H, 4.73; N, 6.00%. FAB MS: (M – ClO₄)⁺: 337.

2.1.5. [Ni(OdtoxH)]ClO₄·H₂O

For 5.0 mmol (1.40 g) of ligand: Yield, 1.33 g (58%) of lilac microprisms. Anal. Calc. for C₁₀H₁₉ClN₂·NiO₂S₂·H₂O: C, 26.4; H, 4.65; N, 6.15. Found: C, 25.4; H, 4.98; N, 6.04%. FAB MS: (M – ClO₄)⁺: 372.

2.1.6. [Ni(MeTtoxH)]ClO₄·H₂O

For 1 mmol (0.32 g) of ligand: Yield, 0.28 g (56%). Recrystallized from hot 1:3 MeOH–MeNO₂ of purple–black single rhombic crystals. Anal. Calc for C₁₂H₂₃ClN₂·NiO₂S₂·H₂O: C, 29.0; H, 4.66; N, 5.63. Found: C, 28.8; H, 5.14; N, 5.71%. FAB MS: (M – ClO₄)⁺: 381.

2.1.7. [Cu(TtoxH)]ClO₄

For 2 mmol (0.59 g) of ligand: Yield, 0.54 g (59%) (Purple–black solid). Recrystallized from hot 1:1 MeOH–MeNO₂ of purple–black single rhombic crystals. Anal. Calc for C₁₅H₁₉Cl·CuN₂O₆S₃: C, 26.2; H, 4.18; N, 6.11. Found: C, 25.3; H, 4.13; N, 6.00%. FAB MS: (M – ClO₄ + H)⁺: 359.
2.1.8. [Cu(OdtoxH)][ClO₄]·[Cu(OdtoxH₂)][ClO₄]₂
For 2 mmol (0.56 g) of ligand: Yield, 0.84 g (85%). Recrystallized from hot 1:1 MeOH–MeNO₂ of purple–black single rhombic crystals. Anal. Calc. for C₁₀H₁₇.₅Cl₁.₅Cu₂N₂O₉S₂·C: 24.4; H, 3.99; N, 5.69. Found: C, 24.5; H, 3.90; N, 5.69%. FAB MS: (M – ClO₄ + H)⁺: 343.

2.1.9. [Cu(MeTtoxH)][ClO₄]·[Cu(MeTtoxH₂)][ClO₄]₂
For 4.1 mmol (0.73 g) of ligand: Yield, 1.51 g (76%) (purple–black solid). Recrystallized from hot 1:1 MeOH–MeNO₂ of purple–black rhombic crystals. Anal. Calc. for C₁₂H₂₅Cl₁.₅CuN₂O₉S₂·C: 26.8; H, 4.41; N, 5.00. Found: C, 26.9; H, 4.30; N, 4.99%. FAB MS: (M – ClO₄)⁺: 343.

2.1.10. [Ni(TtoxBF₂)][ClO₄]·0.5CH₂OH
To [Ni(TtoxBF₄)]ClO₄·H₂O (0.472 g, 1.0 mmol) in 20 ml of boiling MeCN, were added 1.0 mmol (0.10 g, 0.138 ml) of triethylamine and 1.0 mmol (0.14 g, 0.125 ml) of boron trifluoride diethyl etherate. The solution was heated to the boil on a steam bath followed by the addition of triethylamine (0.10 g, 0.138 ml, 1 mmol) to give a dark blue solution. The solution volume was reduced to 10 ml and the solution was concentrated down on a steam bath. The residue was dissolved in 10 ml of water and the resulting lilac solution was cooled with ice to precipitate a lilac solid, which was filtered off, washed with cold H₂O (3×5 ml) and recrystallized from hot 1:1 MeOH–MeCN (v:v) of purple rhombic crystals. Yield: 0.15 g (15%) of purple rhombic single crystals. Anal. Calc. for C₁₀H₁₉.₅Cl₁.₅CuN₂O₉S₂·CH₂OH: C, 24.7; H, 3.94; N, 5.41%. FAB MS: (M – ClO₄)⁺: 343.

2.1.11. [Ni(OdtoxBF₂)][ClO₄]·2H₂O
A solution of [Ni(OdtoxBF₂)]ClO₄·H₂O (0.456 g, 1 mmol) was dissolved in MeCN (20 ml), the solution was heated to the boil on a steam bath followed by the addition of triethylamine (0.10 g, 0.138 ml, 1 mmol) and boron trifluoride diethyl etherate (0.14 g, 0.125 ml, 1 mmol). The solution volume was reduced to 10 ml (steam bath), the solution was cooled on ice to precipitate a lilac solid, which was filtered off and washed with MeCN (2×3 ml) and Et₂O (5 ml) and dried over anhydrous CaCl₂ in vacuo. Recrystallized from hot 1:1 MeOH–MeNO₂ as lilac microcrystalline prisms. Yield: 0.35 g (70%). Anal. Calc. for C₁₀H₁₈BF₂Cl₁.₅CuN₂O₉S₂·2H₂O: C, 23.0; H, 4.25; N, 5.37. Found: C, 23.9; H, 4.35; N, 5.36%. FAB MS: (M – ClO₄)⁺: 385.

2.1.12. [Cu(TtoxBF₃)]BF₄
TtoxBF₃ (0.7 g, 2.36 mmol) was dissolved in MeOH (20 ml). With stirring, a methanolic solution of Cu(BF₄)₂ (2.36 mmol) was slowly added to give a dark green solution which immediately precipitated a dark purple solid. The mixture was stirred for 25 min, after which the solution was concentrated down on a steam bath to half the volume. The resulting solid was filtered off, washed with MeOH (3×5 ml) and recrystallized from hot MeCN. Yield: 0.40 g (34.3%) of purple rhombic shaped microcrystals. Anal. Calc. for C₁₀H₁₈BF₂·BF₄·Cu·N₂O₉S₂·C: 24.3; H, 4.36; N, 5.68. Found: C, 24.4; H, 4.36; N, 5.57%. FAB MS: (M – BF₄)⁺: 406, (M – BF₂–BF₄)⁺: 343.

2.1.13. [Cu(OdtoxBF₃)]BF₄·0.5H₂O
Same general procedure as above, for 2.0 mmol (0.56 g) of ligand: Yield: 0.15 g (15%) of purple rhombic microcrystals. Anal. Calc. for C₁₀H₁₈BF₂Cl₁.₅CuN₂O₉S₂·0.5H₂O: C, 27.8; H, 4.34; N, 5.76. Found: C, 27.6; H, 4.34; N, 5.64%. FAB MS: (M – BF₄)⁺: 390, (M – BF₂–BF₄)⁺: 343.

2.1.14. [Cu(MeTtoxBF₃)]BF₄
For 1 mmol (0.32 g) of ligand. Recrystallized from hot 1:1 MeOH–Me₂CO of purple rhombs. Yield: 0.47 g (91%). Anal. Calc. for C₁₂H₂₂BF₂CuN₂O₉S₂·C, 27.6; H, 4.25; N, 5.37. Found: C, 27.8; H, 4.54; N, 5.41%. FAB MS: (M – BF₄)⁺: 434, (M – BF₂–BF₄)⁺: 387. Caution! The perchlorate salts used in this study are potentially explosive and should be prepared only in small quantities. [Cu(MeTtoxBF₃)]ClO₄ proved to be mechanically sensitive, so due caution in its preparation and handling should be observed.

2.1.15. X-ray data collection
X-ray data for [Cu(TtoxH)]ClO₄ and [Cu(OdtoxH)]ClO₄·[Cu(OdtoxH₂)][ClO₄]₂ were collected on a Siemens P4S diffractometer and refined according to previously published procedures [7].

For [Cu(TtoxH)]ClO₄ a total of 1929 reflections were collected (−7 ≤ h ≤ 0, −18 ≤ k ≤ 0, −28 ≤ l ≤ 0) in the range of 2.90 to 27.50°, with all being unique (Rint = 0%). The empirically derived transmission coefficient ranged from 0.654 to 0.899. Disorder in the methylene linkages between S1 and S2 was resolved by constraining the bond distances and solving for the relative occupancies which gave the best fit to the diffraction data. The two positions for the methylene carbons have occupancies of 0.732 and 0.268, respectively.

For [Cu(OdtoxH)]ClO₄·[Cu(OdtoxH₂)][ClO₄]₂ a total of 2555 reflections were collected (−18 ≤ h ≤ 18, −15 ≤ k ≤ 0, −17 ≤ l ≤ 15) in the range of 2.39 to 28.50°, with 2457 being unique (Rint = 2.15%). The empirically derived transmission coefficient ranged from 0.1567 to 0.2961. The labile OdtoxH proton is effectively distributed over symmetry-equivalent sites, and thus could not be located in the refinement.

X-ray data for [Ni(OdtoxBF₃)]ClO₄·2H₂O was collected on a Siemens SMART CCD diffractometer sys-
3. Results and discussion

Due to their insolubility in methanol, Cu(II) complexes of OdtoxH₂ and MeTtoxH₂ tend to form compounds that are made up of 1:1 mixtures of non-deprotonated and singly-deprotonated complexes. This insolubility tends to inhibit further deprotonation, which would otherwise lead to the completely quasi-macrocyclized, singly deprotonated products. Attempts to macrocyclize [Ni(MeTtoxH)]⁺ with BF₂⁺ produced only starting material, while attempts to induce reaction of excess NaBF₄ with [Ni(TtoxH)]ClO₄ in methanol, in order to macrocyclize via a direct reaction with BF₄⁻ produced only the metathesis product [Ni(TtoxH)]BF₄.

3.1. Synthesis of Cu–BF₂⁺-macrocyclized oximes

It was found that when Cu(BF₄)₂ is used as the Cu²⁺ salt, one is able to obtain in rather good yield, the BF₂⁺-macrocyclized 6-oxime. It is interesting to note that this reaction does not occur in the case of the Ni(II) oximes, which we attribute to the greater acidity of the copper(II) oxime promoting oximate nucleophile formation. The only other known example of the reaction of BF₄⁻ with hydrogen-bonded oximes requires the addition of an equimolar amount of NaBF₄ to the reaction mixture and refluxing conditions for ~18 hours [21]. The reaction described here is a factor of approximately 10³ times faster and requires neither the addition of excess BF₄⁻ nor refluxing conditions (Fig. 1, Table 1).

### Table 1

Crystallographic data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>Formula weight</th>
<th>Crystal system</th>
<th>Crystal size (mm)</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>V (Å³)</th>
<th>Z</th>
<th>(\rho_{calc}) (g cm⁻³)</th>
<th>F(000)</th>
<th>(\mu) (mm⁻¹)</th>
<th>(\lambda) (Mo Kα) (Å)</th>
<th>T (K)</th>
<th>R 💥, (R_w) 💫, b</th>
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<td>[Cu(TtoxH)]ClO₄</td>
<td>C₁₀H₁₉N₂O₆CuS₃</td>
<td>458.44</td>
<td>monoclinic</td>
<td>0.06 × 0.47 × 0.17</td>
<td>Pbcm</td>
<td>5.4075(17)</td>
<td>14.043(4)</td>
<td>21.650(6)</td>
<td>90</td>
<td>1644.0(8)</td>
<td>4</td>
<td>1.852</td>
<td>940</td>
<td>1.901</td>
<td>0.71073</td>
<td>293(2)</td>
<td>0.0426; 0.0837</td>
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<tr>
<td>[Cu(OdtoxH)]ClO₄</td>
<td>C₁₀H₁₉.5Cl₁.5N₂O₉CuS₃</td>
<td>524.70</td>
<td>monoclinic</td>
<td>0.30 × 0.88 × 0.50</td>
<td>C2/m</td>
<td>11.448(2)</td>
<td>12.693(2)</td>
<td>113.376(14)</td>
<td></td>
<td>1850.9(6)</td>
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<td>1.668</td>
<td>0.71073</td>
<td>293(2)</td>
<td>0.0529; 0.1386</td>
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<td>[Cu(OdtoxH₂)]ClO₄</td>
<td>C₁₀H₂₂BClF₂N₂NiO₉S₂</td>
<td>521.39</td>
<td>monoclinic</td>
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<tr>
<td>[Cu(TtoxH)]ClO₄·[Cu(OdtoxH₂)]ClO₄</td>
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<tr>
<td>[Ni(OdtoxBF₂)]ClO₄·2H₂O</td>
<td>C₁₀H₂₂BClF₂N₂NiO₉S₂</td>
<td>1.833</td>
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\(\rho_{calc}\) = \(\Sigma|F_o| - |F_c|\)/\(\Sigma|F_o|\),
\(R_w = [\Sigma\omega(|F_o| - |F_c|)^2]/\Sigma\omega(F_o^2)^{1/2}\).

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Fig. 1. Ligands treated in this paper.
3.2. Description of the structure of \([\text{Cu(TtoxH)}]\)ClO$_4$

An ORTEP projection is shown in Fig. 2, while selected bond distances and angles are given in Table 2. The X-ray structure reveals an almost perfect square pyramidal N$_2$S$_3$ coordination environment ($\tau = 0.06$) [22]. The Cu(II) in each quasi-macrocyclic unit is coordinated by two cis-thioether sulfur and two cis-oxime nitrogen donors in the basal plane and by the ligand's central thioether sulfur in the apical position. The equatorial Cu–S (2.335 Å) distances are identical to that of the only other structurally characterized thioether–oxime complex of Cu(II) (2.33 Å) in the literature [23]. The Cu–N(oxime) (2.00 Å) distances are typical for compounds of this nature [24–26]. A single proton bridging the two oxime oxygens closes off the equatorial chelate ring, which is typical for metal complexes with two oximes in a cis-conformation. The O···O separation (2.429 Å) is consistent with H-bonded oxime O···O distances found in other vic-dioxime complexes [6,27]. The axial Cu–S distance (2.482 Å) is considerably longer than those in the equatorial plane, but typical for Jahn–Teller elongated axial thioether donors [28].

3.3. Description of the structure of \([\text{Cu(OdtoxH)}]\)[ClO$_4$] \([\text{Cu(OdtoxH)$_2$)}][\text{ClO$_4$}]$_2$

An ORTEP projection is shown in Fig. 3 and a representation of the unit cell, showing the intramolecular interactions is shown in Fig. 4; selected bond distances and angles are in Table 3. The X-ray structure reveals a square pyramidal N$_2$S$_2$O coordination environment ($\tau = 0.07$), the overall coordination mode be-

![Fig. 2. ORTEP projection of the [Cu(TtoxH)]$^+$ cation in [Cu(TtoxH)]ClO$_4$.](image)

![Fig. 3. ORTEP projection of [Cu(OdtoxH)]ClO$_4$ in [Cu(OdtoxH)]-[ClO$_4$][Cu(OdtoxH)$_2$)][ClO$_4$]$_2$.](image)

![Fig. 4. ab Projection of the unit cell for [Cu(OdtoxH)]-[ClO$_4$][Cu(OdtoxH)$_2$)][ClO$_4$]$_2$ showing the tetramolecular cluster involving two bridging perchlorates and two [Cu(OdtoxH)]$^+$ cations.](image)
bridges between the ligand’s ether oxygen and thioether involving a perchlorate oxygen and the dimethylene perchlorate O(11) is located directly above each CuN2S2 plane, weakly bound at 2.524 Å from the copper(II).

In addition, there is an unexpected interaction involving a perchlorate oxygen and the dimethylene bridges between the ligand’s ether oxygen and thioether sulfur. The 2 equiv. perchlorate O(12) act as H-bond acceptors with respect to the two methylene protons of the C(4) atoms adjacent to the thioether sulfurs. The two C–H groups are directed toward the two O’s, the H···O distance being 2.463 Å and the C–H···O angle 160.6°. H-bonding interactions involving hydrocarbons are not so common, but the distances are in the range of 2.4–3.0 Å [30–33]. Consequently, there exist tetratomic clusters involving two bridging perchlorates and two complex cations, linked in a cyclic structure by two Cu···OCIO4 interactions and two pairs of C–H···OCIO4 hydrogen bonds.

### 3.4. Description of the structure of [Ni(OdtoxBF2)]ClO4·2H2O

An ORTEP projection is shown in Fig. 5, with selected bond distances and angles given in Table 4. The macrocyclic structure shows a distorted octahedral geometry around Ni(II), with each Ni(II) coordinated by two cis-thioether sulfur and two cis-oxime nitrogen donors, and by the ether oxygen in an axial position. The overall disposition of the ligand around the nickel is the same as the above described Cu(II) complexes. The remaining apical site in the octahedral coordination sphere is occupied by a water oxygen. The ligand is macrocyclized by the BF2+ group, which bridges the two cis-oxime oxygens. The equatorial Ni–S (2.402, 2.400 Å) distances are longer by ~0.24 Å and the Ni–N (2.045, 2.034 Å) distance are ~0.14 Å longer compared to those found in [Ni(Dtox)][ClO4], but are quite similar to those found in [Ni(Dtox)(Dhox)]2+ form. The oxime O–B bond lengths (1.475, 1.460 Å) are comparable with those found in molecules such as [Ni(Cyclops)I][34], while the axial ether O–Ni distance (2.126 Å) is slightly larger than the axial water O–Ni distance (2.044 Å).

![Fig. 5. ORTEP projection of the [Ni(OdtoxBF2)]ClO4·2H2O cation in [Ni(OdtoxBF2)]ClO4.](image-url)
### Table 5
Electronic absorption spectra

<table>
<thead>
<tr>
<th>Complex</th>
<th>Medium</th>
<th>( \lambda ) (nm) (( \epsilon ) (M(^{-1}) cm(^{-1})))</th>
<th>10 Dq (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(TtoxH)}]\text{ClO}_4\cdot1.2\text{H}_2\text{O})</td>
<td>CH(_3)CN</td>
<td>991 sh (15), 870 (26), 515 (24)</td>
<td>11943</td>
</tr>
<tr>
<td>solid state</td>
<td></td>
<td>955 sh, 880, 540</td>
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<td>([\text{Ni(TtoxBF}_2\text{)}]\text{ClO}_4\cdot0.5\text{CH}_3\text{OH})</td>
<td>CH(_3)CN</td>
<td>971 sh (18), 868 (30), 520 (23)</td>
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<td>964 sh (24), 895 (30), 528 (20)</td>
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<td>935 sh, 900, 545</td>
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<td>985 (6.9), 874 (6.8), 740 (10), 539 (28)</td>
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<td>984 (7.7), 861 (8.0), 792 (8.1), 542 (17)</td>
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<tr>
<td>([\text{Ni(MeTtoxH)}]\text{ClO}_4\cdot\text{H}_2\text{O})</td>
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<td>1002 (13), 862 (30), 512 (27)</td>
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<td>978 sh (12), 834 (26), 528 (23)</td>
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<td>([\text{Cu(TtoxH)}]\text{ClO}_4)</td>
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<td>906 (79), 550 (458), 419 (345), 341 (562)</td>
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<td>CH(_3)NO(_2)</td>
<td>882 (84), 551 (532), 399 (1781)</td>
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<td>DMF</td>
<td>814 sh (40), 550 sh (228), 429 (993), 332 (1375)</td>
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<td>945, 570, 380 sh</td>
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<td>solid state</td>
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<td>960, 600, 370 sh</td>
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<td>CH(_3)CN</td>
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<td>DMF</td>
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<td>([\text{Cu(MeTtoxH)}]\text{ClO}_4\cdot\text{H}_2\text{O})</td>
<td>CH(_3)CN</td>
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<td>DMF</td>
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<td>CH(_3)CN</td>
<td>865 (122), 570 (309), 349 (1120)</td>
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<td>CH(_3)NO(_2)</td>
<td>863 (190), 570 (325), 392 (1907)</td>
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<td>DMF</td>
<td>874 (84), 572 (208), 348 (1723)</td>
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<td>solid state</td>
<td></td>
<td>910, 570, 370</td>
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<tr>
<td>Cu(CF(_3)SO(_3))(_2)</td>
<td>DMF</td>
<td>809 (30), 265 (2553)</td>
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</table>

\(a\) Solid-state data from diffuse reflectance in MgCO\(_3\) matrix.

\(b\) Insoluble in MeNO\(_2\)

\(c\) \(n_2\) values in nickel solid state spectra are obscured by instrument artifacts.

\(d\) 10 Dq values for solution spectra were calculated according to Hancock’s method [32].

### 3.5.Electronic spectra

The spectroscopic data are summarized in Table 5.

#### 3.5.1. Nickel(II) complexes

Three d–d transitions are generally observed for hexacoordinate Ni(II) (\(3\)T\(_{2g}\) \(\leftrightarrow\) \(3\)A\(_{2g}\), \(3\)T\(_{1g}(F)\) \(\leftrightarrow\) \(3\)A\(_{2g}\), and \(3\)T\(_{1g}(P)\) \(\leftrightarrow\) \(3\)A\(_{2g}\)). With donor atoms from row-3 and beyond, the Ni(II) spectra become less straightforward to interpret. Generally, it is known that only two d–d transitions are observed when thioether donors are present, the highest energy band (\(3\)T\(_{1g}(P)\) \(\leftrightarrow\) \(3\)A\(_{2g}\)) becoming obscured by the charge-transfer processes (\(\sim 400\) nm) [35]. Two other problems are often encountered in Ni(II)–thioether and nitrogen containing systems which are interrelated: (a) The mathematical relation-
ships involving spectral transitions and the ligand field parameters break down if there are row-3 donors in the coordination sphere [36]; (b) the lowest energy band ($^3T_{2g} \leftrightarrow ^3A_{2g}$) often exhibits a double-humped shape due to mixing with a close-lying spin-forbidden transition ($^3E_g \leftrightarrow ^1A_{2g}$) through spin-orbit coupling [37,38]. These problems make it difficult to obtain values for 10 $D_q$ as well as Hancock and coworkers have attempted to tackle the problem of determining 10 $D_q$ by ‘deconvoluting’ the low energy spin-allowed (10 $D_q$) from the spin-forbidden transition and the method has been used to interpret the spectra of other hexacoordinate Ni(II) systems with thioether and nitrogen donors [36,39]. In the nickel complexes discussed in this study, only the first two d–d transitions ($v_1$, $v_2$) are observed. The transition $v_1$ is split into a double-humped peak, which can be interpreted as indicated above, but attempts to calculate the Racah B parameter produced values which were physically unrealistic for those reasons. The values obtained for 10 $D_q$ (10 400–13 500 cm$^{-1}$) are reasonable for pseudo-octahedral high-spin Ni(II) complexes with strong in-plane fields [7,40,41]. The values of 10 $D_q$ are larger for those compounds which possess an axial thioether relative to those with ether axial donors. This difference is due to the larger ligand field strength of thioether donors compared to ether donors [38].

### 3.5.2. Copper(II) complexes

Optical spectral data for the Cu(II) complexes are given in Table 5. The spectra are generally consistent with Cu(II) with $N,S$-coordination. The complexes exhibit two ligand-field bands. For those compounds with axial sulfur donors, one ligand-field band is centered around 570 nm, and the other, less intense band around 890 nm on average. Replacing the axial S(thioether) by O(ether) shifts the ligand field bands to around 418–600 nm. This shift is consistent with a lower ligand field induced by oxygen donors compared to sulfur donors, within a pentacoordinate Cu(II) complex with strongly interacting in-plane donors [40]. The bands between 329 and 429 nm are due to S→Cu(II) charge transfer [42,43].

Two sulfur LMCT bands are observed in the complexes where a proton resides on one or both oximes (in CH$_3$CN or DMF only), whereas in the BF$_2$ complexes, only one sulfur LMCT band is evident. Aoi et al. noted that acetonylitrile or DMF coordination tends to shift charge transfer bands to longer wavelengths [44]. ESR evidence also supports the conclusion that solvents may displace endogenous ligand donors from their positions as seen in the solid state structure (vide infra).

### 3.6. Electrochemistry

A synopsis of the electrochemical data is given in Table 6 (Fig. 5). Fig. 6 shows a cyclic voltammo-
The stabilization of both Ni(I) and Ni(III) by the same ligand is quite uncommon. Studies of Ni(II) complexes for which reversible or quasi-reversible Ni\(^{2+}/\text{Ni}^{3+}\), and Ni\(^{2+}/\text{Ni}\) couples are observed commonly show differences between these two waves (\(E_{\text{oxid}} - E_{\text{red}}\)) varying from 1.8 to 2.6 V [39,40,61–63]. In the nickel complexes reported here only those with three thioether donors show both Ni\(^{3+}/\text{Ni}^{2+}\) and Ni\(^{2+}/\text{Ni}\) processes. The differences between the oxidation and reduction waves vary from 1.88 V for [Ni(MeTtoxH)]-ClO\(_4\)\(_2\)\(\cdot\)H\(_2\)O (1.92 V for [Ni(TtoxH)]ClO\(_4\)\(_2\)\(\cdot\)H\(_2\)O) to 2.2 V for [Ni(TtoxBF\(_2\))]ClO\(_4\)\(_0.5\)CH\(_3\)OH.

The copper complexes exhibit only a reduction wave, at quite negative (the H-bonded oximes) to slightly negative potentials (BF\(_2\)^+ -bridged oximes). Most of the reductions are irreversible, as the Cu(I) forms are unstable toward conversion to Cu(0) which tends to plate out on the electrode surface. Those complexes which exhibit quasi-reversible reductions both have three thioether donors and also are macrocyclized by BF\(_2\)^+ ([Cu(TtoxBF\(_2\))]BF\(_4\) and [Cu(MeTtoxBF\(_2\))]BF\(_4\)). The effect of the BF\(_2\)^+ bridge is fairly constant for all of the compounds: replacing the oxime-H by BF\(_2\)^+ stabilizes Cu(I) by about 700–900 mV relative to oxime-H. This effect is unexpectedly large compared with what has previously been observed for [Cu(PreH)]\(^+\) and [Cu(cyclops)]\(^+\) [3] possibly due to the combined structural and electronic effect of thioether donors and the electron withdrawing ability of the BF\(_2\)^+.

3.7. Electron spin resonance

The EPR spin-Hamiltonian parameters for the copper(II) complexes are given in Table 7. An example of the ambient temperature and 77 K solution spectra are given in Fig. 7. The EPR parameters, particularly the \(A_i\) and \(g_{||}\)-values of the Cu(II) complexes, are notably similar to each other and rather independent of axial donor type. As these values are controlled principally by the equatorial plane donors, this indicates a commonality in the detailed equatorial stereochemistry as well as of equatorial donor type. All the values of \(g_{||} > g_\perp\) indicate a d\(_{x^2-y^2}\) ground state, which is typical for tetragonal copper complexes. As a result of the strong equatorial donor dominance, the complexes exhibit axial spectra in all but one case (solid state spectrum of [Cu(TtoxBF\(_2\))]BF\(_4\)). It has been advanced that interpretability in terms of structure is vitiated by exchange interactions when axial spectra with \(g_{\text{min}} > 2.04\) are observed, this is particularly so when \(G < 4\) [64,65]. However, within the limits of our data analyses (including simulations) these sulfur-containing coordination spheres frequently elicit \(G\)-values ranging from 2.04 to 4.2 even in solution, so we conclude that exchange interactions are not necessarily obscurative for the neat powders of these compounds unless \(G < 2.04\)
The lack of rhombic splitting in most of the spectra coincides with weak axial donors for the square pyramidal structures, as revealed by the X-ray crystallographic studies of [Cu(MeTtoxH)_2]ClO_4 and [Cu(OdtoxH)_2](ClO_4)_2. The large values of \( A_{g \perp} \) as well as the relatively lower values of \( (g_\parallel)^2 \) also betoken tetragonal stereochemistry in solution and most of the solids [67]. Further evidence for the persistence of tetragonal coordination over a wide temperature range in solution is provided by the similarity between the \( g_\parallel \) values near 295 K and the \( g_{\perp} \) values at 77 K. In addition, the majority of the Cu(II) complexes exhibit nitrogen superfine features in both the cryogenic glass and in the room temperature fluid spectra, indicating that the geometric relationships amongst the Cu and N-orbitals are preserved over this wide range of conditions. The five nitrogen superfine lines observed mirror the two nitrogen donors, the coupling constants being similar to those of other tetragonal Cu(II) complexes with N:S donor sets [68].

The replacement of the oxime proton by BF_2 seems to have little effect on the values of \( A_{g \parallel} \) or \( A_\perp \) as occurs in some Cu(II) BF_2 macrocyclized oximes [3,69]. The Table 7

| Complex | Medium | \( g_\parallel \) | \( 10^4 \times |A_{g \parallel}| \) (cm\(^{-1}\)) | \( 10^4 \times |A_{g(N)}| \) (cm\(^{-1}\)) | \( g_\| \) | \( 10^4 \times |A_\| \) (cm\(^{-1}\)) | \( g_\perp \) | \( 10^4 \times |A_\perp| \) (cm\(^{-1}\)) | \( 10^4 \times |A_{g(N)}| \) (cm\(^{-1}\)) |
|---------|--------|----------------|----------------|----------------|---------|----------------|---------|----------------|----------------|
| [Cu(TtoxH)]ClO_4 | DMF solid | 2.050 | 77 | 12 | 2.163 | 200 | 2.08 | 16 | 18 |
| [Cu(TtoxBF_2)]BF_4 | DMF solid | 2.057 | 77 | 2.17 | 2.167 | 212 | 2.06 | 9 | 18 |
| [Cu(OdtoxH)_2](ClO_4)_2 | DMF solid | 2.060 | 80 | 11 | 2.170 | 219 | 2.07 | 10 | 18 |
| [Cu(OdtoxH)]ClO_4 | DMF solid | 2.074 | 77 | 2.17 | 2.210 | 232 | 2.07 | 6 | 18 |
| [Cu(MeTtoxH)](ClO_4)_2 | DMF solid | 2.057 | 80 | 13 | 2.196 | 155 | 2.08 | 8 | 20 |
| [Cu(MeTtoxBF_2)]BF_4 | DMF solid | 2.057 | 80 | 17 | 2.165 | 208 | 2.06 | 16 | 15 |

Fig. 7. ESR spectra of [Cu(MeTtoxH)]BF_4. (a) 10% BuOH–DMF (g = 2.05). (b) DMF. (c) 77 K. (d) Room temperature (295 K) fluid spectrum (9.44 GHz). (e) 77 K cryogenic glass spectrum (9.147 GHz)

(a) 10% BuOH–DMF was used as solvent for ambient-T isotropic as well as 77 K cryogenic spectra (spectra were identical in pure DMF, but the addition of 10% BuOH provided superior glassing properties). Solid state spectra were obtained from neat powders at 77 K.

b Copper hyperfine coupling parameter.

c \( g_\perp \), \( A_\perp \) from RT fluid spectra; \( g_\| \), \( A_\| \) from 77 K, \( g_\perp \) value obtained via simulation; \( A_\perp \) via 3\( A_\| \) = \( A_\| + 2A_\perp \). \( g_\| \) \( \pm 0.005; 10^4 \) \( A_\| \pm 3; g_\perp \pm 0.01.

d No N-shf observed.
BF$_2^+$-macrocyclization does however seem to play a structural role; replacement of an H-bonded oxime linkage by a covalently bridged BF$_2^+$ oxime causes the donor atoms to become closer to Cu(II), and as a consequence increases the interaction between Cu(II) and the axial donor. This effect is evidenced by the large decrease in $|A_x|$ upon macrocyclization [70]. In [Cu(TioxBF$_2$)]BF$_4$ the axial thioether sulfur is brought sufficiently close to the metal to manifest itself as a rhombic distortion in the powder spectrum (rhombicity index $R = 0.6$) [71]. The absence of rhombic features in the cryogenic spectra provides evidence for weaker axial coordination. Further evidence for a solvent coordination role is provided by the presence of a minor species at $g_\| \sim 2.6$ ($A_\| \sim 155$) in those compounds without the BF$_2^+$ bridge. The minor species, which is not Cu(DMF)$_n^{2+}$, is attributed to a [Cu(L)(DMF)$_x$] adduct, and is also observed in the optical spectra of these complexes (vide supra).

4. Conclusions

Addition of a fifth donor atom to thioether-oxime ligands transforms the nickel(II) chelates from $S = 0$ to $S = 1$ systems. However, variation of this donor atom generally has little further effect upon the electronic properties of the Ni(II) and Cu(II) complexes. When the fifth donor atom in the ligand is thioether sulfur, the resulting nickel complexes are capable of supporting Ni(I) and Ni(III). For copper, the redox chemistry generally has little further effect upon the electronic, magnetic and structural properties of the Ni(II) and Cu(II) complexes. When the resulting nickel complexes are capable of supporting M(I); this effect is most evident for the Cu(II) complexes. By understanding what role a fifth donor atom has upon the structure and reactivity of thioether oxime complexes, we hope to be further understand what effect ligand differences have upon the electronic, magnetic and structural properties of thioether-oxime complexes.

5. Supplementary material

Listings of atomic coordinates, anisotropic thermal parameters, $F_{obs}$ and $F_{calc}$, views of unit cell contents (40 pages), as well as cif files of the structures are available upon request from the authors.

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References