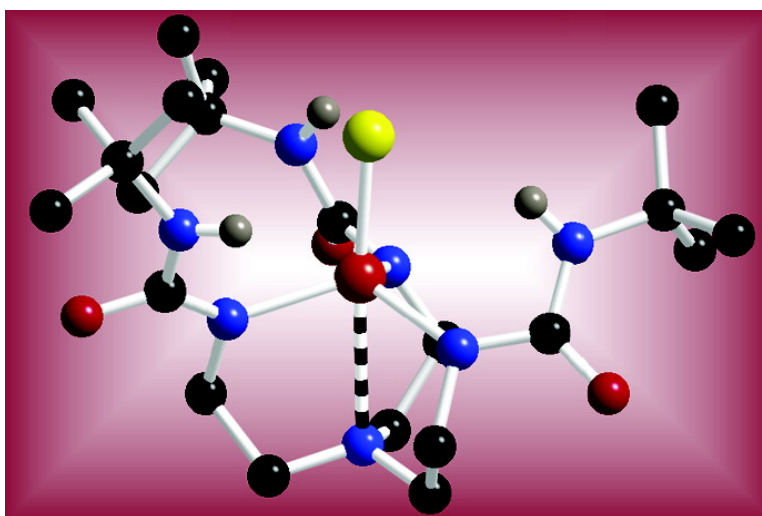


## Chalcogens as Terminal Ligands to Iron: Synthesis and Structure of Complexes with Fe–S and Fe–Se Motifs

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## Chalcogens as Terminal Ligands to Iron: Synthesis and Structure of Complexes with Fe<sup>III</sup>–S and Fe<sup>III</sup>–Se Motifs

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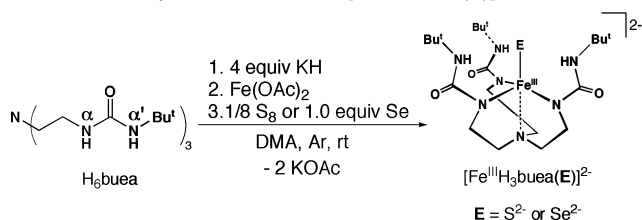
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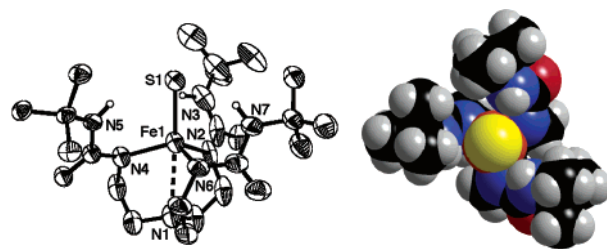
Terminal chalcogenido complexes of transition-metal ions are of interest because of their functional roles in a range of chemical processes.<sup>1</sup> This interest has led to the isolation of numerous complexes with terminal chalcogenides, almost all of which involve early transition-metal ions.<sup>1,2</sup> The scarcity of analogous complexes for the later transition-metal ions has been attributed to electronic effects of the metal ions and to the propensity of the chalcogenides, especially the heavier congeners, to bridge metal centers.<sup>2b,3</sup> This is exemplified in iron–chalcogenide chemistry, where multinuclear complexes with bridging chalcogenido ligands dominate.<sup>2b,4</sup> We showed recently that the Fe<sup>II</sup> complex of tris[(*N'*-*tert*-butylurea-ylato)-*N*-ethylene]aminato ([H<sub>3</sub>buea]<sup>3-</sup>) activates dioxygen at room temperature to afford [Fe<sup>III</sup>H<sub>3</sub>buea(O)]<sup>2-</sup>, the first structurally characterized iron complex containing a single terminal oxo ligand.<sup>5</sup> This chemistry has been extended to include other chalcogenides, and reported herein is the preparation and properties of [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> and [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup>, complexes containing terminal sulfido and selenido ligands. Our results demonstrate that Fe–S and Fe–Se units can similarly be stabilized within a hydrogen bond framework.

[Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> and [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup> were isolated using the procedures outlined in Scheme 1, which are analogous to those developed for the oxometal complexes, [M<sup>III</sup>H<sub>3</sub>buea(O)]<sup>2-</sup> (M<sup>III</sup> = Fe, Mn).<sup>5</sup> Reaction of H<sub>6</sub>buea with 4 equiv of KH in dimethylacetamide (DMA) affords [H<sub>2</sub>buea]<sup>4-</sup>; without isolation, this tetraanion was treated with 1 equiv of Fe(OAc)<sub>2</sub>. After being stirred for 1 h, the reaction mixture was allowed to react with either 1/8 equiv of S<sub>8</sub> or 1 equiv of elemental selenium,<sup>2</sup> resulting in an immediate color change from pale yellow to dark brown. Concentration of the solutions afforded dark brown powders of crude K<sub>2</sub>[Fe<sup>III</sup>H<sub>3</sub>buea(S)] and K<sub>2</sub>[Fe<sup>III</sup>H<sub>3</sub>buea(Se)] that could be readily metathesized with tetraethylammonium and tetraphenylphosphonium salts.<sup>6</sup>

### Scheme 1. Preparative Routes for [Fe<sup>III</sup>H<sub>3</sub>buea(E)]<sup>2-</sup>



Electron paramagnetic resonance (EPR) spectra show that the Fe<sup>III</sup>–S and Fe<sup>III</sup>–Se complexes are monomeric with *S* = 5/2 ground states. Frozen solutions of [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> at 77 K have X-band EPR features of *g* = 6.11 and 1.98, while those for [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup> have signals at *g* = 6.13 and 1.98. These EPR



**Figure 1.** Thermal ellipsoids plot (left) and space-filling representation (right) of [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup>. Thermal ellipsoids are drawn at the 50% probability level, and for clarity only urea hydrogens are shown. Only one of the disordered fragments for the arm containing N3 is shown.

spectra have rhombic splitting parameters *E/D* of 0.01, indicating that both complexes possess nearly axial symmetry at their Fe<sup>III</sup> centers.<sup>7</sup> The complexes gave intensely colored solutions: for instance, [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> in DMA has absorbance bands at λ<sub>max</sub>(ε<sub>M</sub>) = 575 (1300), 396 (4800), and 344 (6100) nm, which are tentatively assigned to charge-transfer transitions. Similarly, the electronic absorbance spectrum of [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup> in DMA has features at λ<sub>max</sub>(ε<sub>M</sub>) = 620 (sh), 470 (1000), and 394 (2000) nm.

X-ray diffraction measurements corroborate the similar monomeric structures of [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> and [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup> in the solid state (Table 1), which is illustrated for [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> in Figure 1.<sup>8</sup> The primary coordination spheres of the Fe<sup>III</sup> centers contain three αN<sup>-</sup> atoms and the terminal chalcogenido with average E–Fe<sup>III</sup>–αN angles of 108.0(1)° for [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> and 107.1(1)° for [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup>. The Fe1–S1 length is 2.276(4) Å in [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup>, and the Fe1–Se1 distance in [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup> is 2.355(1) Å; both distances are comparable to the distances found in complexes with Fe<sup>III</sup>–E–Fe<sup>III</sup> units (E = S<sup>2-</sup> or Se<sup>2-</sup>).<sup>9,10</sup> The apical nitrogen N1 of [H<sub>3</sub>buea]<sup>3-</sup> also interacts weakly with the iron centers at Fe1⋯N1 distances of 2.666(5) and 2.604(5) Å for [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> and [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup>.

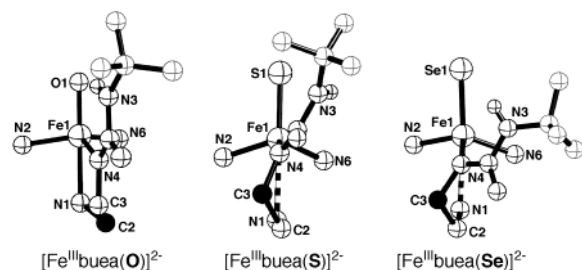
**Table 1.** Bond Lengths (Å) and Angles (deg) for [Fe<sup>III</sup>H<sub>3</sub>buea(E)]<sup>2-</sup>

E'	Fe–E'	Fe–N1	E'⋯α'N	E'–Fe–αN <sup>a</sup>	d[Fe–αN] <sup>b</sup>	ref
O <sup>2-</sup>	1.813(2)	2.276(4)	2.707(4)	102.0(1)	0.421(1)	5
S <sup>2-</sup>	2.211(1)	2.666(5)	3.377(3)	108.0(1)	0.587(1)	this work
Se <sup>2-</sup>	2.355(1)	2.604(5)	3.438(3)	107.1(1)	0.645(1)	this work

<sup>a</sup> Average values. <sup>b</sup> Displacement of the iron from the plane formed by N2, N4, and N6.

The molecular structures of [Fe<sup>III</sup>H<sub>3</sub>buea(S)]<sup>2-</sup> and [Fe<sup>III</sup>H<sub>3</sub>buea(Se)]<sup>2-</sup> differ from that of the related monomeric Fe<sup>III</sup>–O complex, [Fe<sup>III</sup>H<sub>3</sub>buea(O)]<sup>2-</sup> (Table 1). Significantly shorter Fe1–O and Fe1–N1 bonds are observed in [Fe<sup>III</sup>H<sub>3</sub>buea(O)]<sup>2-</sup> than the other two iron–chalcogenido complexes, and the iron(III) center in the oxoiron complex is situated closer to the trigonal plane formed by N2, N4, and N6. In addition, the conformations of the five-

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**Figure 2.** Portions of the molecular structures for  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{E}')^2]^-$ , illustrating the conformation of the chelate rings and placement of urea groups relative to the  $\text{Fe}^{\text{III}}-\text{E}'$  vector. For clarity, only one *tert*-butylureidoethylene arm is shown in each structure, and the out-of-plane carbon atoms are colored in black.

membered chelate rings are different: in  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{O})^2]^-$  the C2 atom is displaced on average 0.52 Å from the plane formed by the other four atoms in the ring (Figure 2). The chelate rings in  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  and  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$  have the C3 atoms out of the ring plane by more than 0.65 Å.

There are also distinct differences in the structures of the H-bond cavities around the  $\text{Fe}^{\text{III}}-\text{E}$  units, which are formed by the urea groups of  $[\text{H}_3\text{buea}]^{3-}$  (Figure 2).  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{O})^2]^-$  has an upright H-bond cavity in which the urea groups are nearly perpendicular (average angle of 86.4°) to the trigonal plane; this arrangement confines the  $\text{Fe}^{\text{III}}-\text{O}$  unit within the cavity. In contrast, the urea groups in  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  and  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$  are significantly tilted relative to the trigonal plane: on average, angles of greater than 35° from the normal are observed, resulting in bowl-like structures.<sup>11</sup> The cavities in  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  and  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$  are less constrained than those found in the oxoiron complex, resulting in greater exposure of the sulfido and selenido ligands.<sup>12</sup>

The X-ray diffraction studies also reveal the possible presence of weak intramolecular H bonds between the  $\alpha'\text{NH}$  groups and the terminal chalcogenido ligands (Figure 1). The average intramolecular  $\text{Fe}-\text{E}\cdots\text{H}\alpha'\text{N}$  distances of 3.377(3) Å in  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  and 3.438(3) Å in  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$  both suggest the formation of H bonds.<sup>13</sup> In addition, solid-state FTIR spectra of the complexes contain broadened NH signals relative to those of  $\text{H}_6\text{buea}$ , which is another indicator of H bonds. However, the chalcogenido ligands lie more than 0.7 Å above the plane formed by the  $\alpha'\text{H}$  atoms, a position not conducive for the formation of H bonds.

Even though  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  and  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$  can be isolated, they have limited stabilities, especially compared to  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{O})^2]^-$ .<sup>5</sup> In solution, the complexes' characteristic spectroscopic properties begin to diminish after 2 h; for instance, the axial EPR signals associated with the complexes (vide supra) gradually decrease, with concomitant appearance of a single feature at  $g = 4.2$ . In addition, a significant amount of an insoluble dark brown solid is produced, the formulation of which is still unknown. Similar behavior is observed in the solid state but at a slower rate. The products and mechanisms of these transformations are currently under investigation. One possible reason for the relative instabilities of  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  and  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$  is that the  $\text{Fe}^{\text{III}}-\text{E}$  units are not fully confined within their H-bond cavities, as is the case in the more stable  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{O})^2]^-$  complex.

$\text{Fe}-\text{E}-\text{X}$  ( $\text{X} = \text{metal ion}$ ) units are common motifs, especially in protein cofactors,<sup>4,9,10</sup> yet to our knowledge, iron complexes with

terminal sulfido and selenido ligands are unknown.<sup>3,4</sup> In fact, there are no reports of  $\text{M}-\text{S}$  or  $\text{M}-\text{Se}$  complexes among the late 3d transition-metal ions.<sup>2b</sup> Thus, the isolation of  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  and  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$ , with their  $\text{Fe}^{\text{III}}-\text{E}$  units, will allow structure–reactivity studies of these new metal–chalcogenido interactions to be explored.

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**Supporting Information Available:** Full synthetic and spectroscopic details of all new complexes and X-ray analyses of  $[\text{Et}_4\text{N}]_2[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})]$  and  $[\text{Et}_4\text{N}]_2[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})]$  (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) See Supporting Information for full details.
- (7) Nearly identical X-band EPR spectra were obtained for solid-state samples. Note that the frozen solution EPR spectra for the complexes contained another, minor  $S = 5/2$  component (<10%), with  $E/D$  values of >0.1.
- (8) Each complex has one disordered urea group: for  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  it is the arm containing N3 and in  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$  it is the one with N7.
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- (11) Average angles of 36° and 40° from the normal are observed for  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{S})^2]^-$  and  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{Se})^2]^-$ .
- (12) This apparent connection between chelate ring conformations and the structures of the H-bond cavities in the  $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{E}')^2]^-$  complexes is reminiscent of the relationship between deoxyribose ring conformations and the structure of DNA. See: Stryer, L. *Biochemistry*; W. H. Freeman Science: New York, 1988; p 337.
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