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### An Electron-Deficient Thallium Zintl-Metal Carbonylate: Structure and Bonding of $[\text{Et}_4\text{N}]_6[\text{Ti}_6\text{Fe}_{10}(\text{CO})_{36}]$

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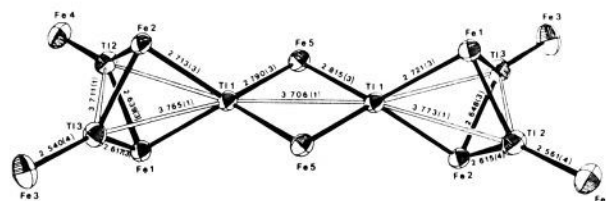
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Cluster anions of the heavy main-group elements are well-known except for those of group 13 where the high degree of electron deficiency inhibits cluster bonding.<sup>1</sup> Those elements can, however, be incorporated into more electron-rich, heteroelement clusters such as  $[\text{Ti}_2\text{Te}_2]^{2-}$ ,<sup>2</sup>  $[\text{TiSn}_3]^{3-}$ ,<sup>3</sup> and  $[\text{TiSn}_3]^{3-}$ . Thallium interacts with transition-metal carbonyls to form traditional complexes such as  $\text{TiCo}(\text{CO})_4$ ,<sup>4</sup>  $[\text{Ti}(\text{Co}(\text{CO})_4)_3]^{3-}$ ,<sup>5</sup>  $[\text{Ti}(\text{Mn}(\text{CO})_5)_3]^{6-}$  and  $[\text{Ti}(\text{Co}(\text{CO})_4)_4]^{7-}$ . A report of  $\text{Ti}_2\text{Fe}_3(\text{CO})_{12}$ ,<sup>8</sup> which has not been structurally characterized, has appeared. This latter report coupled with our recent discovery of  $[\text{Et}_4\text{N}]_2[\text{Bi}_4\text{Fe}_4(\text{CO})_{13}]^9$  suggested that the Ti-Fe system might yield some examples of unusual bonding situations.

When  $\text{Fe}(\text{CO})_5/\text{KOH}/\text{MeOH}$  solutions are treated with thallium salts, deep yellow-brown solutions result from which an anionic metal carbonyl complex can be isolated and is proposed to be  $[\text{Et}_4\text{N}][\text{Ti}(\text{Fe}(\text{CO})_4)_2]^{10}$  (**1**), which may be structurally related to the known  $[\text{M}(\text{Fe}(\text{CO})_4)_2]^{2-}$  ions ( $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ ).<sup>11</sup> When methanol solutions of this complex stand at room temperature black crystals, **2**, deposit slowly which will not redissolve in methanol. On the basis of analyses, spectroscopic data and X-ray analysis, **2** is shown to be  $[\text{Et}_4\text{N}]_4[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})[\mu\text{-}$



**Figure 1.** ORTEP diagram of  $[\text{Ti}_6\text{Fe}_{10}(\text{CO})_{36}]^{6-}$  with carbonyl ligands omitted for clarity. Three carbonyls are associated with each of the iron atoms Fe1, Fe1', Fe2, and Fe2' while the other irons are ligated by four carbonyls each.

$\text{Ti}[\text{Fe}(\text{CO})_4]_2]_2$ , an aggregate of **1** produced by loss of CO. Details of the structure of **2**, which is structurally similar to Burlitch's recently reported  $\text{Co}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-ZnCo}(\text{CO})_4)_2$ , will appear elsewhere.<sup>13</sup> An X-ray diffraction study of crystals of a minor product showed it to be the highly unusual cluster compound **3** which can be viewed as a derivative of **2** in which the  $\mu\text{-CO}$ 's are replaced by  $[\mu\text{-TiFe}(\text{CO})_4]^-$ . The structure and bonding of this complex whose formula is  $[\text{Et}_4\text{N}]_6[\text{Ti}_6\text{Fe}_{10}(\text{CO})_{36}]$  is the subject of this paper. The Ti-Fe framework is shown in Figure 1.<sup>14</sup> Bond distances and angles are given in Table I.

The structure is composed of two thallium triangles held together asymmetrically by two  $\mu_3\text{-Fe}(\text{CO})_3$  moieties without any apparent bonding between the irons ( $d_{\text{Fe-Fe}} = 3.087(5)$  Å). The triangles are connected by two  $\text{Fe}(\text{CO})_4$  bridges. Terminal, trigonal-bipyramidal  $\text{Fe}(\text{CO})_4$  groups are attached to Ti2, Ti2', Ti3, and Ti3', and all metals, with the exception of the  $\mu_3\text{-Fe}$ 's, are coplanar.

For purposes of understanding the bonding in **3**, it is useful to consider it to be a dimer of  $\text{Ti}_3[\mu_3\text{-Fe}(\text{CO})_3]_2[\text{Fe}(\text{CO})_4]_3^{3-}$  (**4**). On the basis of electron counting rules for cluster compounds,<sup>15</sup> a *closo* trigonal-bipyramidal cluster should possess 12 skeletal electrons. In **4**, two electrons on each Ti atom are utilized for dative bonds to the  $\text{FeL}_4$  units. This leaves 10 electrons for cluster bonding and the cluster is electron deficient by Wade's electron counting rules which presuppose the existence of Ti-Ti bonding. The Ti-Ti distances in Figure 1, however, fall nicely in the range of Ti-Ti nonbonded contacts for other structures.<sup>2,16</sup> This is consistent with extended Hückel molecular orbital calculations<sup>17</sup> on **4** which gave a very small Ti-Ti overlap population of 0.025. Localized bonding in the  $\text{Ti}_3[\mu_3\text{-Fe}(\text{CO})_3]_2$  fragment would also require 12 skeletal electrons for two-center two-electron bonding. The cluster may still be considered to be deficient by two electrons per monomeric **4**.

How does this molecule accommodate the electron deficiency? Our calculations on **4** give five occupied levels of  $e''$ ,  $e'$ , and  $a_1'$  symmetry which are associated with Ti- $\text{FeL}_3$  cluster bonding along with three occupied Ti- $\text{FeL}_4$  bonding orbitals of  $a_1'$  and  $e'$  symmetry.<sup>18</sup> All eight molecular orbitals lie at moderate energies.

- (1) Corbett, J. D. *Prog. Inorg. Chem.* **1976**, *21*, 129.
- (2) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2627.
- (3) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 2804.
- (4) Hieber, W.; Teller, U. Z. *Anorg. Allg. Chem.* **1942**, *249*, 43.
- (5) Patmore, D. J.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5*, 1586.
- (6) Hsieh, A. T. T.; Mays, M. J. *J. Organomet. Chem.* **1970**, *22*, 29.
- (7) Robinson, W. R.; Schussler, D. P. *J. Organomet. Chem.* **1971**, *30*, C5.
- (8) Hieber, W.; Gruber, J.; Lux, F. Z. *Anorg. Allg. Chem.* **1959**, *300*, 275.
- (9) Whitmire, K. H.; Churchill, M. R.; Fetting, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1056.

(10) Pentacarbonyl iron (0.68 g) was added to 0.69 g of KOH dissolved in MeOH. To this was added 0.73 g of  $\text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ . After it was filtered, the solution was treated with aqueous  $[\text{Et}_4\text{N}]\text{Br}$  to precipitate  $[\text{Et}_4\text{N}][\text{Ti}(\text{Fe}(\text{CO})_4)_2]$ , which was washed with water and dried under vacuum. IR ( $\text{MeOH}, \text{cm}^{-1}$ ) 1983 m, 1912 s. Anal. Calcd.: N, 2.09; Fe, 16.65; Ti, 30.47. Found: N, 1.86; Fe, 15.10; Ti, 30.50. <sup>13</sup>C NMR (ppm relative to  $\text{Me}_4\text{Si}$ ) 218.0 (carbonyl), 53.3 and 7.6 ( $\text{Et}_4\text{N}^+$ ).

(11) (a) Pierpont, C. G.; Sosinsky, B. A.; Shong, R. G. *Inorg. Chem.* **1982**, *21*, 3247. (b) Sosinsky, B. A.; Shong, R. G.; Fitzgerald, B. J.; Norem, N.; O'Rourke, C. *Inorg. Chem.* **1983**, *22*, 3124.

(12) (a) IR ( $\text{CH}_3\text{CN}, \text{cm}^{-1}$ ) 1987 s, 1968 m, sh, 1958 s, 1920 s, sh, 1910 s, 1895 m, sh, 1740 w. Anal. Calcd. for  $[\text{Et}_4\text{N}]_2[\text{Ti}_2\text{Fe}_4(\text{CO})_{13}]$ : N, 2.13; Ti, 31.13; Fe, 17.02. Found: N, 1.89; Ti, 30.01; Fe, 17.84. (b) X-ray analysis: Rheingold, A. L.; Whitmire, K. H., manuscript in preparation.

(13) Burlitch, J. M.; Hayes, S. E.; Lemley, J. T. *Organometallics* **1985**, *4*, 167.

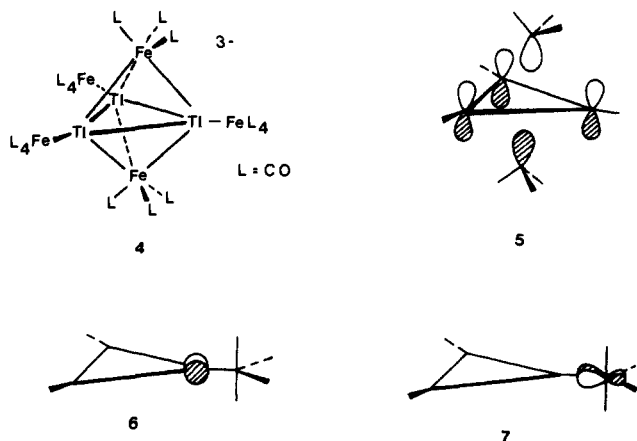
(14) Crystal data:  $\text{C}_{52}\text{H}_{40}\text{Fe}_{10}\text{N}_2\text{O}_{36}\text{Ti}_6$ ,  $M = 3053.5$ , monoclinic, space group =  $P2_1/n$ ,  $a = 12.266(5)$  Å,  $b = 20.545(3)$  Å,  $c = 22.892(6)$  Å;  $\gamma = 93.24(3)^\circ$ ,  $V = 5759.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.06$  g/cm<sup>3</sup>. 7489 intensities were measured on a Nonius CAD4 automated diffractometer using  $\text{Mo K}\alpha_1$  radiation of which 3079 were classed as observed. The structure was solved by heavy-atom techniques. Refinement of scale factor, secondary extinction parameters, positional parameters, and anisotropic thermal parameters for Ti and Fe and isotropic thermal parameters for O, N, C converged at  $R = 0.040$  and  $R_w = 0.040$  for all observed reflections.

(15) (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P. *Nature (London)*, *Phys. Sci.* **1972**, *236*, 99. (c) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 422-439. (d) Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1251.

(16) (a) Klepp, K. O.; Eulenberger, G. Z. *Naturforsch.*, *B* **1984**, *39*, 705. (b) Eulenberger, G. Z. *Kristallogr.* **1977**, *145*, 427. (c) Klepp, K. O. *Monatsh. Chem.* **1984**, *115*, 1133. (d) Dahl, L. F.; Davis, G. L.; Wampler, D. L.; West, R. J. *Inorg. Nucl. Chem.* **1962**, *24*, 357.

(17) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3179, 3489; **1962**, *37*, 2872. (c) Ammeter, J. H.; Burgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. A description of the parameters used in these calculations will be reported elsewhere.

The LUMO of **4** shown in **5** is also Tl-FeL<sub>3</sub> bonding. It is of



$a_2''$  symmetry and lies at much higher energy than the other eight valence molecular orbitals (the HOMO-LUMO gap was computed to be 2.3 eV).<sup>19</sup>

What, then, is the electronic basis for forming a dimeric structure from **4** and, furthermore, in what region of the dimer does the electron deficiency reside; i.e., is it retained in the Tl<sub>3</sub>(μ<sub>3</sub>-Fe(CO)<sub>3</sub>)<sub>2</sub> fragment or is it associated with the Tl<sub>2</sub>(μ<sub>2</sub>-Fe(CO)<sub>4</sub>)<sub>2</sub> portion of the molecule? In order for dimerization to occur, one of the terminal FeL<sub>4</sub> units of **4** must pseudorotate so that the thallium is coordinated at an equatorial rather than an axial position, but the electronic details of this new configuration are not significantly different from those for **4**. There are two ways to view formation of the dimer. Along with the dative, two-electron Tl-FeL<sub>4</sub> bond, one has an empty p orbital on Tl, **6**, and a filled d orbital on the FeL<sub>4</sub>, **7**. First, the dative Tl-FeL<sub>4</sub> bond along with **6** and **7** can combine in the dimer to yield four occupied two-center, two-electron Tl-Fe bonds. Alternatively, one could construct electron deficiency in this region of the molecule by using these four orbitals to form two three-center two-electron bonds. The extra four electrons would be placed in the two molecular orbitals of the dimer corresponding to symmetry-adapted combinations of **5**. Our computations suggest that there are four two-center two-electron bonds in the Tl-bridging FeL<sub>4</sub> region. The two LUMO's of the dimer are clearly identified as combinations of **5**. The electron deficiency, therefore, appears to be in the Tl-FeL<sub>3</sub> portion of the molecule.

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**Registry No.** **1**, 104337-74-8; **3**, 104337-76-0; **4**, 104351-50-0; Fe(CO)<sub>5</sub>, 13463-40-6; Tl, 7440-28-0; Fe, 7439-89-6.

**Supplementary Material Available:** Tables of bond distances and angles, crystallographic data collection parameters, atom coordinates, and isotropic and anisotropic thermal parameters and an ORTEP diagram of the full anion showing all carbonyl ligands (10 pages); structure factor tables (11 pages). Ordering information is given on any current masthead page.

(18) The FeL<sub>4</sub> groups in **4** are assumed to have C<sub>3v</sub> symmetry; thus, the maximum symmetry of **4** is C<sub>3v</sub>. The C<sub>3v</sub> FeL<sub>4</sub> group is, however, a conical fragment, thus, the apparent symmetry is D<sub>3h</sub> and we have used symmetry labels which conform to this.

(19) The L<sub>3</sub>Fe--FeL<sub>3</sub> bonding counterpart of **4** (a<sub>1</sub>' symmetry) is filled; thus one might propose that there should be a single bond between the two FeL<sub>3</sub> groups; however, the total overlap population between these two iron atoms is only 0.041 and the long distance argues strongly against this hypothesis.

## EXAFS Studies of the B<sub>2</sub> Subunit of the Ribonucleotide Reductase from *E. coli*

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Ribonucleotide reductases catalyze the conversion of ribonucleotides to deoxyribonucleotides and thus play a key role in regulating DNA biosynthesis.<sup>1</sup> The enzyme from *E. coli* consists of two subunits<sup>2</sup> designated B<sub>1</sub> (M<sub>r</sub> = 170 000)<sup>3</sup> and B<sub>2</sub> (M<sub>r</sub> = 87 000).<sup>3</sup> B<sub>1</sub> contains the substrate binding sites and the thiols required for substrate reduction,<sup>4</sup> while B<sub>2</sub> possesses a binuclear iron site and the tyrosine radical essential for activity.<sup>5</sup> The binuclear iron site has been probed by a variety of physical techniques. The site exhibits strong antiferromagnetic coupling (J = -108 cm<sup>-1</sup>),<sup>6</sup> large Mössbauer quadrupole splittings,<sup>7</sup> and Raman vibrations characteristic of an Fe-O-Fe bridging unit.<sup>8</sup> These properties bear a striking resemblance to those of the binuclear iron cluster in methemerythrin.<sup>9,10</sup> We report here an iron K-edge EXAFS study of the B<sub>2</sub> subunit of ribonucleotide reductase from *E. coli* (B<sub>2</sub>).

Subunit B<sub>2</sub> was isolated from *E. coli* strain N6405/pSPS2, a heat-inducible overproducer,<sup>11</sup> while methemerythrin azide (metHrN<sub>3</sub>) was obtained from *Phascolopsis gouldii*.<sup>12</sup> X-ray absorption spectra were obtained at the Cornell High Energy Synchrotron Source on the C2 beam line using fluorescence detection for the proteins at 77 K;<sup>13</sup> the specific activities and the UV-visible spectra of the protein samples were unchanged after data collection. Spectra for model compounds were obtained in transmission mode. EXAFS (χ) was extracted from the X-ray absorption spectrum by standard methods.<sup>14</sup> Curve fitting employed theoretical amplitude and phase functions.<sup>15</sup>

EXAFS spectra obtained for native B<sub>2</sub> and its radical-free (hydroxyurea-treated<sup>16</sup>) form are similar. The spectrum for native

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(1) Lammers, M.; Follman, H. *Struct. Bonding (Berlin)* **1983**, *54*, 27-91. Reichard, P.; Ehrenberg, A. *Science (Washington, D.C.)* **1983**, *221*, 514-519. Thelander, L.; Reichard, P. *Annu. Rev. Biochem.* **1979**, *48*, 133-158.

(2) Thelander, L. *J. Biol. Chem.* **1973**, *248*, 4591-4601.

(3) Carlson, J.; Fuchs, J. A.; Messing, J. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 4294-4297.

(4) Thelander, L. *J. Biol. Chem.* **1974**, *249*, 4858-4862.

(5) Sjöberg, B.-M.; Reichard, P.; Graslund, A.; Ehrenberg, A. *J. Biol. Chem.* **1978**, *253*, 6863-6865. Sjöberg, B.-M.; Graslund, A. *Adv. Inorg. Biochem.* **1983**, *5*, 87-110.

(6) Petersson, L.; Graslund, A.; Ehrenberg, A.; Sjöberg, B.-M.; Reichard, P. *J. Biol. Chem.* **1980**, *255*, 6706-6712.

(7) Atkin, C. L.; Thelander, L.; Reichard, P.; Lang, G. *J. Biol. Chem.* **1973**, *248*, 7464-7472.

(8) Sjöberg, B.-M.; Loehr, T. M.; Sanders-Loehr, J. *Biochemistry* **1982**, *21*, 96-102.

(9) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618-622.

(10) Klotz, I. M.; Kurtz, D. M., Jr. *Acc. Chem. Res.* **1984**, *17*, 16-22. Wilkins, R. G.; Harrington, P. C. *Adv. Inorg. Biochem.* **1983**, *5*, 51-85.

(11) Salowe, S. P.; Stubbe, J. *J. Bacteriol.* **1986**, *165*, 363-366.

(12) Elam, W. T.; Stern, E. A.; McCallum, J. D.; Sanders-Loehr, J. *J. Am. Chem. Soc.* **1982**, *104*, 6369-6373.

(13) Roe, A. L.; Schneider, D. J.; Mayer, R. J.; Pyrz, J. W.; Widom, J.; Que, L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1676-1681.

(14) Scott, R. A. *Methods Enzymol.* **1985**, *117*, 414-459.

(15) Teo, B. K.; Lee, P. A. *J. Am. Chem. Soc.* **1979**, *101*, 2815-2832. Teo, B. K.; Antonio, M. R.; Averill, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 3751-3762.

(16) Kjoller-Larsen, I.; Sjöberg, B.-M.; Thelander, L. *Eur. J. Biochem.* **1982**, *125*, 75-81.