Pentaborane(11) and $P(CH_3)_3$ were from our laboratory stock and were described elsewhere.[8] The ^{11}B NMR spectra were recorded on a Varian XL-300 spectrometer, the observe frequency being 96.2 MHz. Diethyl ether–boron trifluoride was used as the external standard for the ^{11}B chemical shifts.

Reaction of $B_4H_8\cdot2P(CH_3)_3$ with $P(CH_3)_3$. A 0.129-mmol sample of B_5H_{11} was taken in a 10-mm-o.d. Pyrex tube equipped with a vertical-shaped Teflon valve, and a 26.8-mmol sample of $P(CH_3)_3$ was condensed into the tube at –197 °C. The tube was then placed in a –80 °C bath, and the tube was shaken to mix the contents. A white solid was formed in the liquid $P(CH_3)_3$. As the tube was allowed to warm to –23 °C, a clear solution resulted. The $^{11}B\{^1H\}$ NMR spectrum of the solution at –30 °C indicated that the original B_5H_{11} had been converted completely to $B_4H_8\cdot2P(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$. The tube was then kept at room temperature for 38 h, after which no noncondensable gas was found in the reaction tube. The $^{11}B\{^1H\}$ spectrum of this solution showed the signals of $B_3H_5\cdot3P(CH_3)_3$ and $B_2H_4\cdot2P(CH_3)_3$, which were overlapped by the signal of $BH_3\cdot P(CH_3)_3$. No other signals were present in the spectrum. The tube was placed in a –45 °C bath to distill out the solvent $P(CH_3)_3$, and then $BH_3\cdot P(CH_3)_3$ was sublimed out from the tube by pumping at –10 °C for 30 h. The resulting white solid residue in the tube was dissolved in CH_2Cl_2, and the $^{11}B\{^1H\}$ spectrum shown in Figure 1c was recorded.

Several other experiments, in which varied amounts of B_5H_{11} (up to 0.5 mmol) and different reaction temperatures (0–45 °C) were used, gave essentially the same $B_3H_5\cdot3P(CH_3)_3$:$B_2H_4\cdot2P(CH_3)_3$ product ratios (approximately 10:7). When a reaction solution was held at 0 °C for 50 h, the reaction was not completed. It was noted that, when the final product mixture was pumped *at 0 °C* to remove $BH_3\cdot P(CH_3)_3$, the other products, $B_2H_4\cdot2P(CH_3)_3$ and $B_3H_5\cdot3P(CH_3)_3$, remained unchanged; that is, $B_3H_5\cdot3P(CH_3)_3$ was stable at 0 °C under vacuum, and its conversion into $B_6H_{10}\cdot2P(CH_3)_3$[7] did not occur at this temperature.

Acknowledgment. This work was supported by the U.S. Army Research Office. The NMR instrument was acquired with the use of instrumentation funds that were provided by the National Science Foundation and the Department of Defense.

(8) See, for example: Dodds, A. R; Kodama, G. *Inorg. Chem.* **1979**, *18*, 1465. Kameda, M.; Shimoi, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3705.
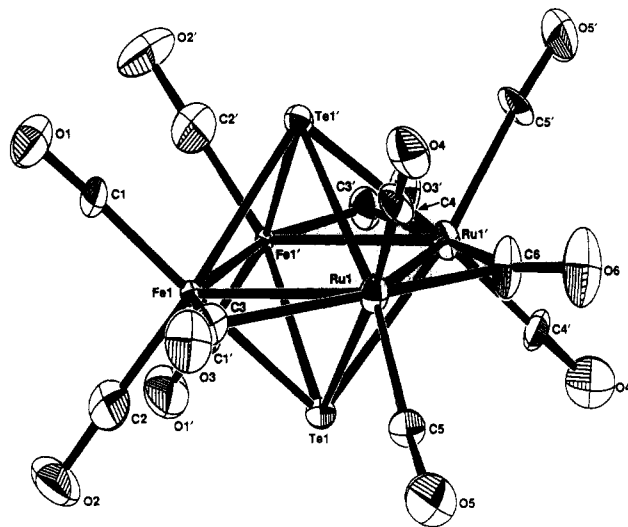

Synthesis and Characterization of $Fe_2Ru(CO)_9(\mu_3$-$Te)_2$ and $Fe_2Ru_2(CO)_{11}(\mu_4$-$Te)_2$

Pradeep Mathur,[*,1] Ipe J. Mavunkal,[1] V. Rugmini,[1] and Mary F. Mahon[2]

An important development in the area of transition-metal–non-metal cluster chemistry has been the successful use of single atom ligands (e.g. Ge, Sn, P, As, N, Bi, S, Se, and Te) for the purpose of bridging transition-metal moieties.[3] The triply bridging configuration is the most commonly observed structure type for sulfur, selenium, and tellurium in clusters. The lone pairs of electrons on the μ_3-S ligands act as Lewis donors toward coordinatively unsaturated metal fragments in numerous cluster growth reactions.[4] The trinuclear clusters $M_3(CO)_9(\mu_3$-$S)_2$ (M = Fe,

(1) Indian Institute of Technology.
(2) University of Bath.
(3) (a) Whitmire, K. H. *J. Coord. Chem.* **1988**, *17*, 95. (b) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 26. (d) Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406. (e) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

Figure 1. ORTEP drawing of $Fe_2Ru_2(CO)_{11}(\mu_4$-$Te)_2$, illustrating the atom-numbering scheme.

Ru, Os) have been among the most extensively used of all μ_3-S-containing clusters;[5] the general strategy involved has been to allow the μ_3-S-containing cluster to interact with a complex containing one or more labile groups, such as NCMe,[6] THF,[7] or C_2H_4,[8] or, alternatively, to generate a coordinatively unsaturated species by photolysis[5] in the presence of the μ_3-S-containing cluster. For instance, in the presence of UV irradiation, $Os_3(CO)_9(\mu_3$-$S)_2$ reacts with $W(CO)_5(PMe_2Ph)$ to give four mixed-metal clusters: $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3$-$S)_2$, $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3$-$S)_2$, $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3$-$S)_2$, and $Os_3O_2(CO)_{14}(PMe_2Ph)_2(\mu_3$-$S)(\mu_3$-$S)$.[9]

In recent years, tellurium has also been noted for its ability to bridge between small metal aggregates to form larger clusters. Addition of mononuclear[10] and polynuclear[11] metal carbonyl fragments occurs readily across the Te–Te bond of $Fe_2(CO)_6(\mu$-$Te_2)$. Here, we report the synthesis and characterization of two new Te-containing mixed-metal clusters: $Fe_2Ru(CO)_9(\mu_3$-$Te)_2$ (1) and $Fe_2Ru_2(CO)_{11}(\mu_4$-$Te)_2$ (2).

Room-temperature stirring of a hexane solution containing $Fe_2(CO)_6(\mu$-$Te_2)$ and $Ru(CO)_4(C_2H_4)$ for 1 h formed the cluster $Fe_2Ru(CO)_9(\mu_3$-$Te)_2$ (1), as characterized by IR spectroscopy, mass spectrometry data, and elemental analysis. The infrared spectrum of 1 in hexane solvent shows carbonyl stretching frequencies at 2088 (w) 2084 (w), 2069 (sh), 2056 (s), 2048 (s), 2041 (m), 2027 (s), 2005 (m), and 1997 (m) cm^{-1}. The mass spectrum of 1 shows the molecular ion centered at m/z 722 and peaks at m/z 694, 666, 638, 610, 582, 554, 526, 498, and 470, corresponding to the successive loss of nine carbonyl groups. There is good agreement between the computer simulated and the experimentally obtained isotopic distribution pattern for the $[Fe_2RuTe_2]^+$ ion. Elemental analysis (Calcd for $C_9O_9Te_2Fe_2Ru$: C, 14.9. Found: C, 15.2) confirms the molecular formula of 1.

(4) Adams, R. D. *Polyhedron* **1985**, *4*, 2003.
(5) (a) Adams, R. D.; Babin, J. E.; Wang, J.-G.; Wu, W. *Inorg. Chem.* **1989**, *28*, 703. (b) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1987**, *26*, 2807. (c) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4514.
(6) Adams, R. D.; Horvath, I. T.; Yang, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 1533.
(7) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 444.
(8) (a) Adams, R. D.; Hor, T. S. A.; Horvath, I. T. *Inorg. Chem.* **1984**, *23*, 4733. (b) Adams, R. D.; Babin, J. E.; Mahtab, R.; Wang, S. *Inorg. Chem.* **1986**, *25*, 1623.
(9) Adams, R. D.; Horvath, I. T.; Mathur, P. *J. Am. Chem. Soc.* **1984**, *106*, 6296.
(10) (a) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1983**, *22*, 1854. (b) Day, V. W.; Lesch, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 1290.
(11) (a) Mathur, P.; Mavunkal, I. J.; Rugmini, V. *Inorg. Chem.* **1989**, *28*, 3616. (b) Mathur, P.; Mavunkal, I. J.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 382.

The formation of **1** from $Fe_2(CO)_6(\mu\text{-}Te_2)$ and $Ru(CO)_4(C_2H_4)$ seems to be that of straightforward addition involving the cleavage of the Te–Te bond and formation of two Te–Ru and one Fe–Ru bonds. There is a net loss of one CO group. In terms of reactivity, compound **1** is similar to $Fe_3(CO)_9(\mu_3\text{-}Te)_2$. For instance, treatment of **1** with NaOMe, followed by acidification of the solution, gives $Fe_2(CO)_6(\mu\text{-}Te_2)$, and with $Pt(PPh_3)_4$, **1** reacts to form the mixed-metal compound $(CO)_6Fe_2(\mu_3\text{-}Te)_2Pt(PPh_3)_2$.

Addition of a hexane solution containing $Ru(CO)_4(C_2H_4)$ to $Fe_2Ru(CO)_9(\mu_3\text{-}Te)_2$ and room-temperature stirring yielded the mixed-metal cluster **2**. Compound **2** was separated from the unreacted **1** and $Ru_3(CO)_{12}$, which is formed in the reaction, by chromatography on silica gel TLC plates. The infrared spectrum of **2** in the carbonyl region ($\nu(CO)$, cm^{-1} (dichloromethane): 2086 (w), 2037 (s), 1993 (m), and 1825 (w, br)) indicates the presence of both terminal and bridging carbonyl groups. Platelike crystals of **2** were obtained from a dichloromethane/hexane solution at −4 °C, and an X-ray analysis was undertaken. An ORTEP diagram of the molecular structure is shown in Figure 1. The cluster consists of a planar arrangement of two iron and two ruthenium atoms, and both faces of the Fe_2Ru_2 plane are bridged by quadruply bridging tellurium ligands. The Ru–Ru bond is bridged by a carbonyl group, and the two Fe–Ru bonds contain semibridging carbonyl ligands. The structure of **2** is similar to that of the recently reported $Fe_4(CO)_{10}(\mu\text{-}(CO)(\mu_4\text{-}S)_2$, which also contains one bridging and two semibridging carbonyl ligands.[12] The Fe–Fe bond in **2** (2.867 (5) Å) is considerably longer than the Fe–Fe bonds in the structurally related $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}S)_2$ (2.489 (3)–2.605 (2) Å)[12] and $Fe_2Co_2(CO)_{11}(\mu_4\text{-}S)_2$ (2.604 (2) Å).[13] The bridged Ru–Ru bond in **2** (2.792 (4) Å) is longer than the two bridged Ru–Ru bonds (2.7330 (7), 2.7376 (8) Å) in $Ru_4(CO)_7(\mu\text{-}CO)_2(PMe_2Ph)_2(\mu_4\text{-}S)_2$ but is in fact comparable with the two unbridged bonds (2.7807 (7), 2.8147 (8) Å) in the sulfido cluster.[5c] Compound **2** contains only 62 valence electrons and so is formally electron deficient by 2 electrons, according to the 18 electron rule. It has 7 skeletal electron pairs, and thus the octahedral geometry described by the four metal and two tellurium atoms conforms to the PSEP theory.

Experimental Section

All reactions were performed under an atmosphere of pure argon by using standard Schlenk techniques. Solvents were purified, dried, and distilled under argon or nitrogen immediately before use. The compounds $Fe_2(CO)_6(\mu\text{-}Te_2)$[14] and $Ru(CO)_4(C_2H_4)$[15] were prepared by established procedures. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer as solutions in NaCl cells. Photochemical reactions were carried out in a water-cooled double-walled quartz vessel. A 125-W immersion type mercury lamp manufactured by Applied Photophysics Ltd. was used.

Preparation of $Fe_2Ru(CO)_9(\mu_3\text{-}Te)_2$ (1). A solution of $Ru_3(CO)_{12}$ (32 mg, 0.05 mmol) in hexane (90 mL) was irradiated with UV light for 10 min under a continuous purge of ethylene. The colorless solution containing $Ru(CO)_4(C_2H_4)$, thus formed, was added to $Fe_2(CO)_6(\mu\text{-}Te_2)$ (80 mg, 0.15 mmol) dissolved in a 1:1 mixture of benzene and hexane (100 mL). The mixture was stirred at room temperature for 1 h, during which time the color changed from orange to purple. Removal of solvent in vacuo and chromatography of the residue on a silica gel column using neat hexane as the eluant afforded the purple $Fe_2Ru(CO)_9(\mu_3\text{-}Te)_2$: yield = 75 mg, 73%; mp = 138 °C.

Preparation of $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (2). A hexane solution (90 mL) containing $Ru(CO)_4(C_2H_4)$, prepared from $Ru_3(CO)_{12}$ (32 mg, 0.05 mmol) by using the procedure described earlier, was added to a dichloromethane (100 mL) solution of **1** (110 mg, 0.15 mmol). The mixture was stirred for 1 h. The solvent was removed in vacuo and the residue chromatographed on a silica gel column. With hexane, trace

(12) Adams, R. D.; Babin, J. E.; Estrada, J.; Wang, J.-G.; Hall, M. B.; Low, A. A. *Polyhedron* **1989**, *8*, 1885.

(13) Vahrenkamp, H.; Wucherer, E. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 680.

(14) $Fe_2(CO)_6(\mu\text{-}Te_2)$ is known to decompose in the solid form. It is reported to form in 40% yield from $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ on treatment with NaOMe, followed by acidification. The amount to be used is therefore freshly prepared, by using the appropriate amount of $Fe_3(CO)_9(\mu_3\text{-}Te)_2$, and its solution is immediately used: Bogan, L. E.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983**, *250*, 429.

(15) Schramm, K. D.; Ibers, J. A. *Inorg. Chem.* **1980**, *19*, 2441.

Table I. Fractional Atomic Coordinates and Thermal Parameters ($\times 10^4$) for **2**

atom	x	y	z
Fe1	1711 (3)	1672 (1)	3083 (1)
Te1	4896.8 (16)	2078.3 (7)	2376.0 (6)
Ru1	1719.4 (23)	1696.6 (9)	1513.2 (8)
C1	3189 (29)	1149 (12)	3760 (10)
C2	−237 (38)	1682 (12)	3737 (13)
C3	803 (29)	748 (12)	2575 (11)
C4	2934 (28)	790 (12)	1023 (10)
C5	−733 (28)	1411 (13)	1066 (11)
C6	2500 (0)	2500 (0)	673 (13)
O1	4034 (26)	802 (10)	4191 (9)
O2	8444 (28)	1699 (12)	4174 (11)
O3	258 (28)	80 (9)	2491 (9)
O4	3633 (25)	247 (9)	737 (9)
O5	−2049 (27)	1247 (12)	771 (9)
O6	2500 (0)	2500 (0)	20 (11)

Table II. Selected Bond Lengths for **2**

Fe1–Te1	2.606 (2)	Fe1–Ru1	2.794 (2)
Fe1–C1	1.786 (18)	Fe1–C2	1.772 (25)
Fe1–C3	1.847 (19)	Fe1–Fe1	2.872 (4)
Te1–Ru1	2.737 (2)	Ru1–Ru1	2.795 (3)
Ru1–C3	2.507 (19)	Ru1–C4	1.892 (21)
Ru1–C5	1.918 (19)	Ru1–C6	2.046 (18)
Ru1–Ru1	2.795 (3)	C1–O1	1.111 (21)
C2–O2	1.19 (3)	C3–O3	1.145 (22)
C4–O4	1.117 (22)	C5–O5	1.077 (22)
C6–O6	1.16 (3)		

Table III. Bond Angles (deg) for **2**

Ru1–Fe1–Te1	60.8 (1)	C1–Fe1–Te1	88.1 (6)
C1–Fe1–Ru1	132.9 (6)	C2–Fe1–Te1	161.4 (7)
C2–Fe1–Ru1	131.2 (8)	C2–Fe1–C1	89.4 (9)
C3–Fe1–Te1	104.3 (6)	C3–Fe1–Ru1	61.5 (6)
C3–Fe1–C1	98.3 (9)	C3–Fe1–C2	94 (1)
Fe1–Te1–Fe1	66.8 (1)	Ru1–Te1–Fe1	63.0 (1)
Te1–Fe1–Te1	86.0 (1)	Te1–Ru1–Fe1	81.2 (1)
Te1–Ru1–Fe1	56.2 (1)	C3–Ru1–Fe1	40.3 (4)
C3–Ru1–Te1	85.0 (4)	C4–Ru1–Fe1	116.8 (6)
C4–Ru1–Te1	94.6 (6)	C4–Ru1–C3	89.4 (7)
C5–Ru1–Fe1	114.2 (6)	C5–Ru1–Te1	170.4 (6)
C5–Ru1–C3	87.0 (8)	C5–Ru1–C4	90.6 (8)
C6–Ru1–Fe1	137.7 (5)	C6–Ru1–Te1	93.4 (4)
C6–Ru1–C3	178.0 (6)	C6–Ru1–C4	91.9 (6)
C6–Ru1–C5	94.5 (8)	Ru1–Te1–Ru1	61.5 (1)
Ru1–C6–Ru1	86.1 (9)	O1–C1–Fe1	177 (2)
O2–C2–Fe1	179 (2)	Ru1–C3–Fe1	78.2 (6)
O3–C3–Fe1	158 (2)	O3–C3–Ru1	124 (1)
O4–C4–Ru1	179 (2)	O5–C5–Ru1	175 (2)
O6–C6–Ru1	136.9 (5)		

Table IV. Crystallographic Data for $Fe_2Ru_2(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$

chem formula	$C_{11}O_{11}Fe_2Ru_2Te_2$	space group	*Pccn*
a, Å	6.863 (3)	T, °C	20
b, Å	16.064 (3)	λ, Å	0.71069 (Mo Kα)
c, Å	17.799 (4)	ρ_{calcd}, g cm^3	2.96
V, Å^3	1962.4	μ(Mo Kα), cm^{-1}	55.32
Z	4	R	0.0522
fw	877.14		

amounts of $Ru(CO)_{12}$ and **1** were eluted. Further elution with 30:70 CH_2Cl_2/hexane gave the brown band of **2**: yield = 32 mg, 25%; mp = 120 °C dec.

X-ray Crystal Structure Determination of 2. A platelike crystal of approximate dimensions 0.25 × 0.23 × 0.1 mm was selected for data collection. Data were measured on a Hilger and Watts Y290 four-circle diffractometer in the range $2 \leq \Theta \leq 24°$. A total of 1777 reflections were collected, of which 1156 were unique with $I \geq 3\sigma(I)$. Data wre corrected for Lorentz and polarization effects and also for absorption.[16] The structure was solved by conventional Patterson methods.[17]

(16) Walker, N.; Stuart, D. DIFABS, a program to correct for absorption effects in crystals. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

Only half of the molecule was found to be unique, the second half being generated by rotation about a 2-fold axis implicit in the space group symmetry. The Ru–Ru bridging carbonyl was also seen to lie on this axis, giving both C6 and O6 half-site occupancy factors. The symmetry-generated atomic positions are indicated by primed labels in the ORTEP drawing. All atoms were allowed to vibrate anisotropically in the final stages of refinement. Final residuals after 14 cycles of full-matrix least squares were $R = 0.0522$ for unit weights. The total number of parameters varied was 128. The maximum final shift/esd was 0.003, and the maximum and minimum residual densities were 1.22 and –0.88 e Å^{-3} in the vicinity of the central metal cage. Final fractional atomic coor-

dinates and selected bond distances and angles are given in Tables I–III, respectively. Crystallographic data for **2** are given in Table IV.

A model to account for intermixing of the group 8 metals was also considered in the structure of **2**. However, no evidence was found in favor of this possibility. Analysis of the electron density at the ruthenium site did not suggest that this site was even partially occupied by an iron atom. The model exhibited poor convergence for a disorder level as low as 5%, with $R = 0.0833$ after 8 cycles of least-squares.

Supplementary Material Available: A table of anisotropic displacement parameters (Table S1) (1 page); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

(17) (a) Sheldrick, G. M. SHELX86, a computer program for crystal structure determination. University of Goettingen, 1986. (b) Sheldrick, G. M. SHELX76, a computer program for crystal structure determination. University of Cambridge, 1976.

Additions and Corrections

1984, Volume 23

Jean-Luc Vanderheyden, Alan R. Ketring, Karen Libson, Mary Jane Heeg, Lee Roecker, Philip Motz, Robert Whittle, R. C. Elder,* and Edward Deutsch*: Synthesis and Characterization of Cationic Technetium Complexes of 1,2-Bis(dimethylphosphino)ethane (DMPE). Structure Determinations of *trans*-[Tc^V(DMPE)$_2$-(OH)(O)](F$_3$CSO$_3$)$_2$, *trans*-[Tc^{III}(DMPE)$_2$Cl$_2$]F$_3$CSO$_3$, and [Tc^I-(DMPE)$_3$]$^+$ Using X-ray Diffraction, EXAFS, and ^{99}Tc NMR.

Pages 3184–3191. The correct thermodynamic information for *trans*-[Tc(DMPE)$_2$(OH)(O)]$^{2+}$ is as follows: $K_a = 6.3 \pm 0.05$; p$K_a = -(0.80 \pm 0.05)$.—Jean-Luc Vanderheyden

1990, Volume 29

Takahiko Kojima, Takeshi Usui, Tomoaki Tanase, Morio Yashiro, Sadao Yoshikawa, Reiko Kuroda, Shigenobu Yano,* and Masanobu Hidai*: Synthesis and Characterization of Cobalt(III) Complexes Containing α-Diamine and Carbinolamine Derived from α-Aminomalonate and Ethylenediamine.

Page 448. In the right column, the third sentence of the first complete paragraph should read as follows: Two resonances due to carboxyl groups of the AM^{2-} ligand were observed, one of which at 172.9 ppm could be assigned to the *uncoordinated* carboxyl group and the other of which at 183.3 ppm to the *coordinated* carboxyl group.[9c]—Takahiko Kojima

Li-June Ming, Randall B. Lauffer, and Lawrence Que, Jr.*: Proton Nuclear Magnetic Resonance Studies of Iron(II/III)–Amide Complexes. Spectroscopic Models for Non-Heme Iron Proteins.

Page 3063. In column 1, the magnetization ratios should read $(18.0 \pm 2)\%$, $(27.4 \pm 1)\%$, $(74.1 \pm 2.3)\%$, and $(80.6 \pm 3.8)\%$.—Lawrence Que, Jr.