

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and
subscription information:

<http://www.tandfonline.com/loi/gmcl17>

A Novel Ferromagnet: $\text{Ca}_{14}\text{MnBi}_{11}$

Traci Y. Kuromoto^a, Susan M. Kauzlarich^a & David J. Webb^b

^a Departments of Chemistry, University of California, Davis,
California, 95616

^b Physics University of California, Davis, California, 95616
Version of record first published: 22 Sep 2006.

To cite this article: Traci Y. Kuromoto, Susan M. Kauzlarich & David J. Webb (1990): A Novel Ferromagnet: $\text{Ca}_{14}\text{MnBi}_{11}$, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 181:1, 349-357

To link to this article: <http://dx.doi.org/10.1080/00268949008036019>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

A NOVEL FERROMAGNET: $\text{Ca}_{14}\text{MnBi}_{11}$

TRACI Y. KUROMOTO*, SUSAN M. KAUZLARICH* and DAVID J. WEBB*

Departments of Chemistry* and Physics+
University of California
Davis, California 95616

Magnetic susceptibility and electrical resistivity measurements have been made on the Zintl compound, $\text{Ca}_{14}\text{MnBi}_{11}$, for temperatures between 6 K and 300 K. The magnetic data are consistent with high spin Mn^{+3} for $T > 100$ K and a ferromagnetic transition is observed at ~ 56 K. Although the Mn^{+3} ion has four unpaired spins in the paramagnetic regime, the ferromagnetic moment is considerably reduced. Resistivity data also display a transition at approximately 56 K.

INTRODUCTION

Contrary to what the name implies, a large number of intermetallic compounds may be described as stoichiometric salts.¹ These structures are made up of electropositive elements that donate their electrons to the electronegative elements which in turn uses them to form bonds. The structures can then be described as a combination of cations and polyatomic anionic units. A wide variety of main group ternary compounds fit this description and are referred to as Zintl phases after the original researcher.^{1,2} The Zintl concept has been successfully extended to ternary transition metal chalcogenides and pnictides.^{3,4} We have prepared a new series of ternary transition metal Zintl compounds, $\text{A}_{14}\text{MnX}_{11}$ ($\text{A}=\text{Ca}, \text{Sr}$ and $\text{X}=\text{As}, \text{Sb}, \text{Bi}$),^{4,5} which are isostructural to the main group Zintl compounds, $\text{Ca}_{14}\text{GaAs}_{11}$ ⁶ and $\text{Ca}_{14}\text{AlSb}_{11}$ ⁷. Although these new transition metal Zintl compounds are all ferromagnets, we will limit our discussion to the compound most completely characterized to date: $\text{Ca}_{14}\text{MnBi}_{11}$.⁴

EXPERIMENTAL SECTION

Synthesis

$\text{Ca}_{14}\text{MnBi}_{11}$ was prepared by the reaction of the elements Ca and Bi in stoichiometric quantities with a four-fold excess of Mn powder. The crystalline calcium dendrites (99.997%) and Bismuth needles (99.999%) were obtained from Anderson Physics Lab. Manganese flakes, obtained from Johnson Matthey, were etched with 5% HNO_3 /methanol, transferred into a nitrogen filled dry box, and ground into a powder. The reactants and products were handled in a nitrogen filled dry box. The reaction was carried out in a tantalum container that was sealed with a helium arc welder and then jacketed in a silica ampoule under $\sim 1/5$ atm. of argon.

The silica ampoule with its contents were slowly heated to 1250°C and held for 2 hours, then quickly cooled. The product consisted of large black pieces of air sensitive material which had a metallic luster. Crystals for X-ray diffraction were obtained by heating the reaction at 1350°C for one hour and quickly cooling. A yield of $>95\%$ was estimated based on powder X-ray diffraction.

Characterization

X-ray powder diffraction data was obtained with a focusing Guinier camera (Enraf-Nonius) equipped with a silicon monochromator to give $\text{Cu K}\alpha_1$ radiation. Silicon (99.99999+%, Johnson Matthey) was included as an internal standard, the five lines being fitted to known diffraction angles by a non-linear least squares function. The sample was mixed with $\sim 10\%$ silicon and was mounted between two pieces of transparent tape and transferred from a drybox to the camera. The powder camera was then evacuated (10^{-4} torr) in order to maintain the sample integrity. A calculated powder pattern was obtained using the single crystal structure data. $\text{Ca}_{14}\text{MnBi}_{11}$ crystallizes in the tetragonal space group $I4_1/acd$ with lattice constants, $a = 17.002(6)$ and $c = 22.422(7)$ ($Z=8$).

Low-temperature powder diffraction patterns were obtained for $\text{Ca}_{14}\text{MnBi}_{11}$ by using a CTI closed-cycle helium refrigerator mounted on a Siemens powder diffractometer. The sample was loaded in a drybox and maintained with a vacuum pump. X-ray scans were taken in the range $20 \leq 2\theta \leq 35$ at 8, 50, 70, and 300 K at scan rates of 0.01 deg s^{-1} .

Magnetic Susceptibilities

Measurements were made on a Quantum Design SQUID magnetometer. Magnetization versus temperature measurements were made over the temperature range 6-300 K at a field of 1500 Oe. Magnetization versus magnetic field measurements were done at fields of -20 kOe to 20 kOe at 10 K. Measurements were made on both crystals and powder samples. The crystals were separated from the reaction product and sealed under vacuum ($\sim 10^{-6}$ torr) in a thin wall fused silica holder. The powders were prepared in a similar fashion and resulted in data identical to the crystals.

Resistivity

AC resistivity measurements were made using the standard four probe method. Leads were attached to the polycrystalline sample using indium contacts in a specially designed sample holder for air sensitive compounds. The samples could be mounted and attached to leads in the dry box and were protected from air by an O-ring seal. The holder was made out of OFHC copper to ensure good thermal contact and could be mounted on the cold head of a CTI closed cycled helium refrigerator for temperature control. Measurements were made at low frequency (~ 24 Hz) from 300 K down to 10 K allowing the sample to equilibrate at each temperature point.

RESULTS AND DISCUSSION

Structure

$\text{Ca}_{14}\text{MnBi}_{11}$ is isostructural with the main-group Zintl compounds, $\text{Ca}_{14}\text{GaAs}_{11}$ and $\text{Ca}_{14}\text{AlSb}_{11}$. It consists of MnBi_4 tetrahedra, linear Bi_3 chains and isolated Bi and Ca atoms. All the Mn-Bi distances in the MnBi_4 tetrahedron are the same, 2.814(1) Å, and the tetrahedron is distorted with angles 105.4(1)° and 118.0(1)°. The Mn-Bi distance is typical for many Mn-Bi compounds.⁸ All these structures have an unusual three-atom linear chain, in which the Bi-Bi distance⁴ is 3.336(2) Å compared to 3.196 Å for the Sb chain⁷ and 2.967 Å for the As chain.⁶ The other Bi...Bi distances are significantly larger than observed in the three-atom chain (> 4.50 Å). The closest Ca^{2+} ...Bi distances are ~ 3.2 -3.5 Å. An important feature to note is that the closest Mn...Mn distance is ~ 11 Å. A view of the polyatomic anions in $\text{Ca}_{14}\text{MnBi}_{11}$ is shown in Figure 1 (important distances and angles are

labeled) and a perspective view of the unit cell down the c axis is shown in Figure 2. The MnBi_4 tetrahedra alternate with Bi_3 linear chains along the c axis, with the chains stacking perpendicular with respect to one another. The linear chains also alternate with the tetrahedra along the a and b axes but are colinear with these axes. If the Zintl concept is used to rationalize the bonding observed in this structure type, $\text{A}_{14}\text{MnX}_{11}$, the formal oxidation state of the Mn ion can be obtained. The analysis is identical to the main group analogues². An oxidation state of 2+ is assigned to the alkaline earth atoms and the isolated pnictide atoms are given an oxidation state of 3-, thus satisfying their octet. The charge on the three atom linear unit can be obtained using the VSEPR model:⁹ the central atom has three lone pairs in the equatorial position similar to XeF_2 ¹⁰ and the two terminal atoms have complete octets, thus the three atom chain has a formal charge of 7-. Therefore, in one formula unit, there are fourteen Ca^{2+} cations, four Bi^{3-} anions and one Bi_3^{7-} , leaving a charge of 9- on the tetrahedral MnBi_4 unit. The Bi atoms in the tetrahedral unit can be assigned an oxidation state of 3-, thus, Mn is a 3+ ion (d^4). Therefore the structure of this compound can be described as being made up of $\text{Mn}^{\text{III}}\text{Bi}_4^{9-}$ tetrahedra, Bi_3^{7-} linear chains, and isolated Bi^{3-} and Ca^{2+} ions.

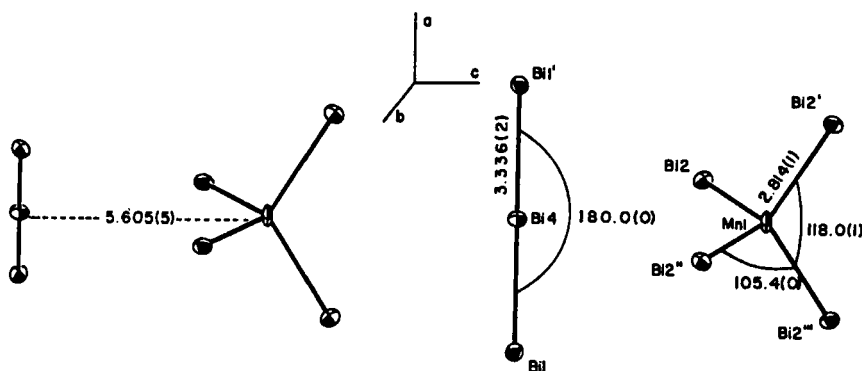


FIGURE 1. Thermal ellipsoid (70% probability) plot of the polyatomic anionic units.

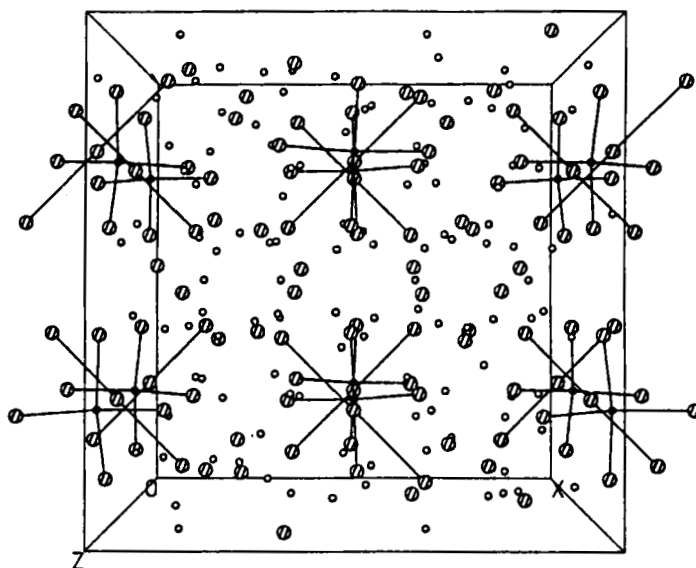


FIGURE 2. Perspective view of the unit cell down the c axis. Dark circles are Mn, open circles are Ca, and striped circles are Bi.

Magnetic and Transportation Measurements

The magnetization at $H=1500$ Oe is shown as a function of temperature in Figure 3. The low temperature state is a ferromagnet with a Curie temperature of ~ 56 K. Such a high transition temperature is surprising considering the fact that the magnetic ions are so far apart (~ 11 Å). χ_m for $T > 100$ K can be fit to the Curie-Weiss equation ($\chi_m = \frac{C}{T-\theta} + \chi_0$) with the results $C=2.86(7)$, $\theta=50(1)$, and

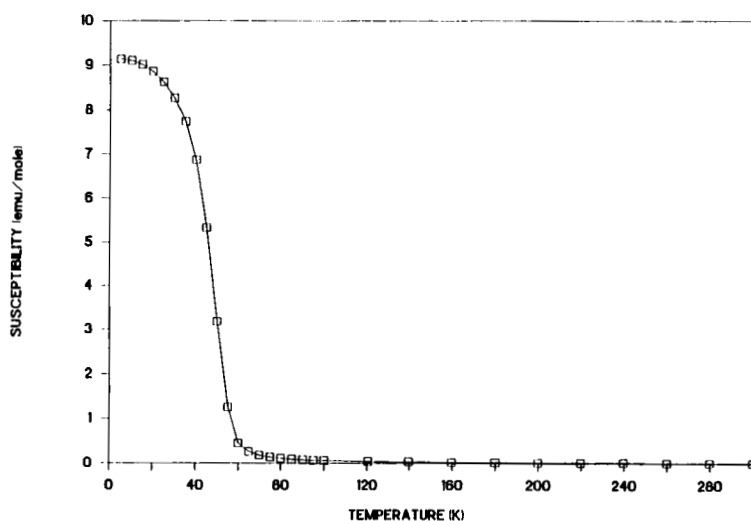


FIGURE 3. Variation of χ_m with temperature at a magnetic field of 1500 Oe.

$\chi_0 = 1.7(3) \times 10^{-3}$. If χ_m is corrected for the diamagnetic susceptibilities of Ca^{+2} , Bi and Mn^{+3} , the results for C and θ remain the same and χ_0 becomes negligible ($10^{-4} \text{ cm}^3/\text{mol}$). A plot of $(\chi_m - \chi_{\text{dia}})^{-1}$ versus temperature ($T > 100 \text{ K}$) is shown in Figure 4. The experimentally determined effective Bohr magneton number $p = 4.8(1) \mu_B$ was calculated from the Curie constant and is consistent with the spin only value for four unpaired electrons ($4.9 \mu_B$). This is in good agreement with the assignment of +3 for the oxidation state of the Mn atoms and is consistent with the bonding scheme outline above. To our knowledge, this is the first example of Mn^{3+} with tetrahedral geometry. The slight distortion of the Mn^{3+} tetrahedron to D_{2d} symmetry results in a stable high spin d^4 configuration. Although it can be argued that this is a Jahn Teller effect, a small distortion (107.4° and 114°)^{6,7} is also observed in the Al and Ga analogues. This indicates that it may be due to anion-anion repulsion¹¹ between the central Bi atom in the Bi_3^{7-} linear chain and the terminal Bi atoms in the MnBi_4 tetrahedron.

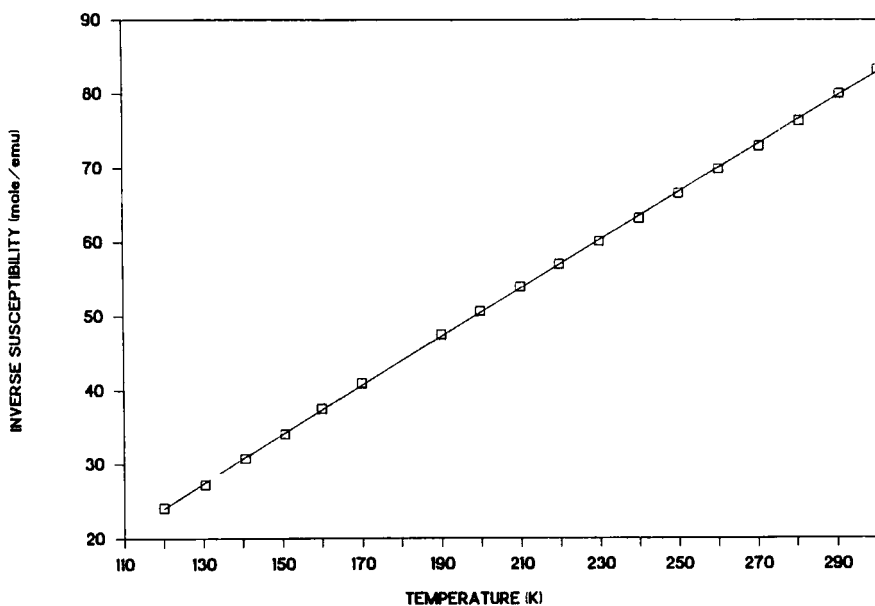


FIGURE 4. Temperature dependence of $(\chi_m - \chi_{\text{dia}})^{-1}$ between 120 and 300 K. The solid curve is obtained from the Curie-Weiss equation.

The ferromagnetic moment can be estimated from the hysteresis curve shown in Figure 5. A moment of $2.3 - 2.5 \mu_B/\text{Mn}$ is obtained by extrapolating the high field linear region to zero field. It appears that complete saturation is not obtained at 10 K even at 20 kOe. The moment is significantly less than the spin only value of $4 \mu_B/\text{Mn}$ that one would expect for four unpaired spins. Given the high temperature results which imply a local moment, there are two possible explanations for the low moment observed in the ferromagnetic state. One possibility is a structural transformation which would alter the crystal field around Mn^{+3} , changing the electronic configuration from high spin to low spin. This would result in a moment of $2 \mu_B/\text{Mn}$. The other possibility is that the compound is metallic and that there is coupling between the conduction electrons and the local moments. This would result in a reduced effective moment at low temperatures.

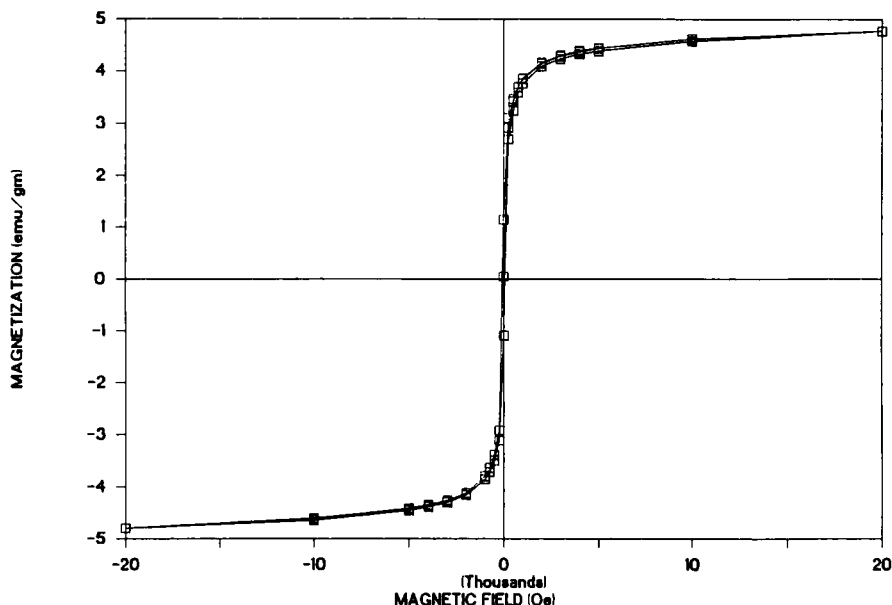


FIGURE 5. The hysteresis plot of $\text{Ca}_{14}\text{MnBi}_{11}$ at 10 K.

In order to understand the ferromagnetic transition in this compound, temperature dependent powder X-ray diffraction and resistivity data were taken from 300 K to 10 K. No significant structural changes were observed in the powder X-ray diffraction at or below the transition temperature. This rules out a high spin to low spin transformation. A plot of $\rho(T)/\rho(300 \text{ K})$ versus T is given in Figure 6. The data show that the compound is a metal and that a change in slope occurs at the Curie temperature. The resistivity at room temperature is on the order

of $10^{-4} \Omega\text{-cm}$, indicating that $\text{Ca}_{14}\text{MnBi}_{11}$ is a fairly good metal ($\rho_{\text{Cu(RT)}} = 10^{-6} \Omega\text{-cm}$). The presence of conduction electrons implies that the ferromagnetic moment is reduced by coupling between the conduction electrons and the local moments. In addition, the drop in resistivity at the Curie temperature shows that its magnitude at high temperature is mostly due to spin disorder scattering of the conduction electrons from the local moments. The change in slope to more conducting behavior at the Curie temperature is characteristic of a metallic ferromagnet.

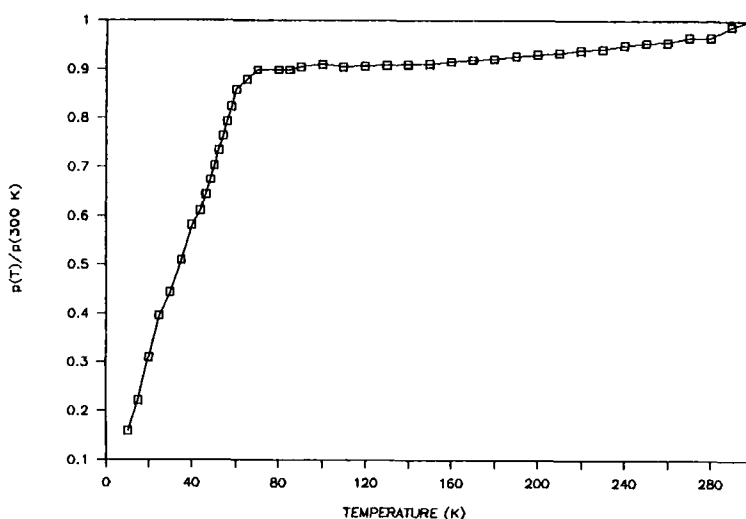


FIGURE 6. Temperature dependence of resistivity of $\text{Ca}_{14}\text{MnBi}_{11}$.

The magnetic data ($T > 100 \text{ K}$) indicate that the Zintl concept may be used to describe the bonding within this structure. However, the resistivity data indicate that a metallic component to the bonding is also present. Studies of heat capacity and thermopower on both the main group and transition metal compounds in this series is underway and will provide greater insight towards understanding the properties of these materials.

ACKNOWLEDGEMENTS

This research was supported in part by the Petroleum Research Fund administered by the American Chemical Society. We thank Professor Robert N. Shelton for use

of the magnetometer, resistivity apparatus and X-ray powder diffractometer, and Peter Klavins for useful discussion.

REFERENCES

1. H. Schäfer, B. Eisenmann and W. Müller, Angew. Chem.Int. Ed. Engl., **12**, 694 (1973).
2. (a) H. Schäfer and B. Eisenmann, Reviews in Inorganic Chemistry, **3**, 29 (1981). (b) H. Schäfer, Ann.Rev. Mater. Sci., **15**,1 (1985). (c) H. Schäfer, J. Solid State Chem., **57**, 97 (1985).
3. (a) W. Bronger, Pure & Appl. Chem., **57**, 1363 (1985). (b) W. Bronger, Angew. Chem. Int. Ed. Engl., **20**, 52 (1981).
4. S. M. Kauzlarich, T. Y. Kuromoto, and M. M. Olmstead, J. Am. Chem. Soc., **111**, 8041 (1989).
5. T. Y. Kuromoto, S. M. Kauzlarich and D. J. Webb, unpublished research.
6. S. M. Kauzlarich, M. M. Thomas, and M. M. Olmstead, paper in preparation.
7. G. Cordier, H. Schäfer and M. Stelter, Z. Anorg. Allg. Chem., **519**, 183 (1984).
8. (a) In CaMnBi_2 , the Mn-Bi distance is 2.874(4): E. Brechtel, G. Cordier and H. Schäfer, Z. Naturforsch., **35b**, 1 (1980). (b) In $\text{Ca}_9\text{Mn}_4\text{Bi}_9$, there are several Mn-Bi distances ranging from 2.817(6) to 2.974(11): E. Brechtel, G. Cordier, and H. Schäfer, Z. Naturforsch., **34b**, 1229 (1979). (c) In CaMn_2Bi_2 , the Mn-Bi distance is 2.781(1): G. Cordier and H. Schäfer, Z. Naturforsch., **31b**, 1459 (1976).
9. (a) A. G. McKenna and J. F. McKenna, J. Chem. Educ., **61**,771 (1984). (b) R. J. Gillespie, J. Chem. Educ., **40**, 295 (1963). (c) N. V. Sidwick and H. M. Powell, Proc. Roy. Soc., **A176**, 153 (1940).
10. (a) R. E. Rundle, J. Am. Chem. Soc., **85**, 112 (1963). (b) R.J. Gillespie in Noble Gas Compounds, edited by H. H. Hyman, (The University of Chicago Press, Chicago, IL, 1963), p. 333.
11. (a) J. K. Burdett, T. Hughbanks, G. J. Miller, J. W. Richardson, Jr., and J. V. Smith, J. Am. Chem. Soc., **109**, 3639 (1987). (b) J. K. Burdett, Inorg. Chem., **24**, 2244 (1985).