catalytic properties of a Pd_6Cl_{12} cluster can be different from those of a $Pd_3(CH_3COO)_6$ cluster or those of mononuclear Pd^{2+} species. In this respect the different catalytic activity of low- and high-temperature forms of $PdCl_2$ in the isomerization of 1-hexene must be mentioned.[10]

Experimental Section

Palladium acetate was prepared by a literature method.[8] Electronic absorption spectra and reflectance spectra were recorded on a Beckman DK-2A spectrophotometer. The mass spectrum was recorded on a Varian Mat 112 mass spectrometer at 70 eV and 150 °C.

X-ray powder spectra were obtained with a Philips diffractometer equipped with a pulse discriminator and driven by a General Automation minicomputer. Internal calibration was made with silicon (ASTM). Molecular weight determinations in benzene have been carried out by F. Pascher Laboratory, Bonn, West Germany.

Preparation of Pd_6Cl_{12}. To a solution of $Pd_3(CH_3COO)_6$ in glacial acetic acid (about 0.05 M) was added the calculated quantity (2 equiv) of concentrated HCl at room temperature. The resulting brown fine precipitate was separated by centrifugation, washed with acetic acid, and dried in vacuo over NaOH. The yields of Pd_6Cl_{12} are nearly quantitative.

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Registry No. Pd_6Cl_{12}, 12268-04-1; $PdCl_2$, 7647-10-1; palladium diacetate, 3375-31-3.

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(10) Moiseev, I. I.; Grigor'ev, A. A. *Dokl. Akad. Nauk SSSR* **1968**, *178*, 132.

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Thermal and Photochemical Reactivity of Fe and Fe_2 toward CH_4 in Low-Temperature Matrices

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Diiron, but not iron atoms in their ground electronic states, has been reported to react with methane at cryogenic temperatures, to form species of the type CH_3Fe_2H, structure unknown.[1] This proposal was based on Mössbauer and infrared spectroscopic studies. Subsequently, the nonobservation of a resonance Raman spectrum for Fe_2 in solid CH_4 was considered to be consistent with the idea of a special kind of reactivity associated with the diiron moiety,[2] and analogies with the dissociative chemisorption of CH_4 on bulk iron,[3] involving at least two iron sites have been envisaged.[1] Reactivity patterns of a similar type have also been suspected for Fe/Fe_2 in solid N_2, as determined by Mössbauer, infrared,[4] and optical spectroscopy, $Fe_2(N_2)_n$ complexes being formed, with Fe atoms remaining unreactive.[2] Evidence for the coexistence of Fe atoms and Fe_2 molecules in solid rare gas matrices was originally established by Barrett et al.[5a] using Mössbauer spectroscopy and subsequently observed by De Vore et al.[5b] using optical spectroscopy.

Montano et al. have recently reported matrix EXAFS data for the $Fe/Fe_2/Ar$ system that shed considerable light on the local environment of Fe atoms as well as a value of 2.02 ± 0.13 Å for the bond length of Fe_2 entrapped in the fccub lattice of solid Ne.[6] On the basis of Mössbauer spectroscopy, Montano[7] has assigned a $^7\Sigma_g$ term for the ground electronic state of Fe_2 in solid Ar, with vibrational constant $\omega_e = 300.26$ cm^{-1} and dissociation energy $D_e = 1.2$ eV being obtained by DiLella et al.[2] from an analysis of the corresponding resonance Raman spectrum.

Reactions of a number of photoexcited metal atoms[8,9] and metal clusters[10] with methane and higher alkanes[11] under cryogenic conditions have recently been discovered. In particular, the infrared spectrum of Fe/CH_4 matrices subjected to either broad-band[8] or narrow-band[12] irradiation at $\lambda > 330$ nm and $\lambda = 300$ nm, respectively, showed the production of a new species assigned to CH_3FeH. The latter excitation corresponded to a $(3d^74p^1, {}^5D_4 \leftarrow 3d^64s^2, {}^5D_4)$ resonance line of atomic iron.[13] Because of the open-shell electronic configurations of atomic[13] and diatomic[7] iron, the Fe/Fe_2 matrix system offers an opportunity for probing ground- and excited-state selectivity and reactivity patterns with CH and CC bonds of saturated hydrocarbons that are not readily accessible with Cu/Cu_2.[9,10]

In this note we wish to report that under the conditions of our experiments Fe_2 could be coisolated with Fe atoms in solid CH_4 at 10–12 K and was found to neither react thermally (10–50 K) nor react photochemically (400–580 nm) with CH_4, in contrast to the observations of earlier studies.[1] On the other hand, Fe atoms photoexcited at 300 nm are highly reactive toward CH_4 at 12 K, leading to the oxidative-addition product CH_3FeH.[8,12]

The optical spectra of matrix entrapped Fe atoms and Fe atoms coisolated with Fe_2 in solid Kr are illustrated in Figure 1B,C. Gas- to matrix-phase correlations for the observed Fe atomic resonance lines can be seen from an examination of Figure 1A,B. The gas-phase spectrum (only spin- and dipole-allowed transitions shown) is represented by sticks (Figure 1A), the wavelengths, heights, and notation of which are in accord with the energies, oscillator strengths, and Russell–Saunders electronic state assignments, respectively, suggested from earlier studies.[13] The three most prominant visible bands of Fe_2 in Kr occur at 418, 474, and 532 nm, close to the wavelengths observed for Fe_2 in solid Ar, 414.5, 474.0, and 544.8 nm in previous investigations.[2,5] Partially resolved vibronic structure is best seen on the 474-nm absorption of Fe_2

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(1) P. H. Barrett, N. Pasternak, and R. G. Pearson, *J. Am. Chem. Soc.*, **101**, 222 (1979).

(2) M. Moskovits and D. P. DiLella, *J. Chem. Phys.*, **73**, 4917 (1980). Dr. Moskovits agrees that his inability to observe a resonance Raman spectrum for Fe_2 in CH_4 matrices at 12 K most probably originates from electronic quenching or energy-transfer effects rather than chemical quenching of Fe_2 by CH_4 (personal communication).

(3) J. R. Anderson, Ed., "Chemisorption and Reactions on Metallic Films", Vol. 2, Academic Press, New York, 1971 (and references cited therein).

(4) P. Barrett and P. Montano, *Ber. Bunsenges. Phys. Chem.*, **82**, 30 (1978); *J. Chem. Soc., Faraday Trans. 2*, **73**, 378 (1977).

(5) T. K. McNab, H. Micklitz, and P. H. Barrett, *Phys. Rev. B*, **4**, 3787 (1971); H. Micklitz and P. H. Barrett, *Phys. Rev. Lett.*, **28**, 1547 (1972); (b) T. C. DeVore, A. Ewing, H. F. Franzen, and V. Calder, *Chem. Phys. Lett.*, **35**, 78 (1975).

(6) P. A. Montano and G. K. Shenoy, *Solid State Commun.*, **35**, 53 (1980); H. Purdum, P. A. Montano, G. K. Shenoy, and T. Morrison, *Phys. Rev. B*, **25**, 4412 (1982).

(7) P. A. Montano, *Symp. Faraday Soc.*, **14** (1980).

(8) W. E. Billups, J. L. Margrave, M. M. Konarski, and R. H. Hague, *J. Am. Chem. Soc.*, **102**, 7393 (1980).

(9) G. A. Ozin, D. F. McIntosh, S. A. Mitchell, and J. Garcia-Prieto, *J. Am. Chem. Soc.*, **103**, 1574 (1981).

(10) G. A. Ozin, S. A. Mitchell, and J. Garcia-Prieto, *Angew. Chem. Suppl.*, 798 (1982).

(11) G. A. Ozin, S. A. Mitchell, and J. Garcia-Prieto, *Angew. Chem. Suppl.*, 369 (1982).

(12) G. A. Ozin and J. G. McCaffrey, *J. Am. Chem. Soc.*, **104**, 7351 (1982).

(13) D. H. W. Carstens, W. Brashear, D. R. Eslinger, and D. M. Gruen, *Appl. Spectrosc.*, **26**, 184 (1972); C. Moore, *Natl. Bur. Stand.* (*U.S.*) *Circ. No. 467*, **1** (1949), **2** (1952), **3** (1958).

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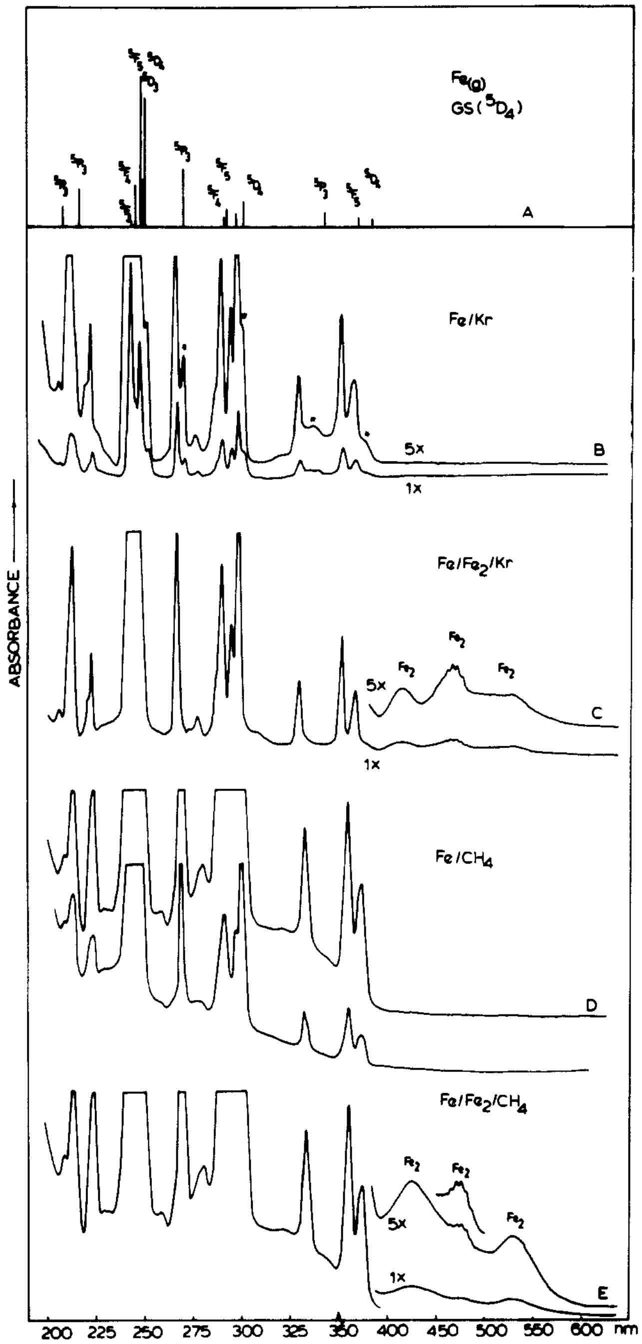

Figure 1. UV-visible spectra of (A) gaseous Fe atoms,[13] (B) Fe atoms isolated in solid Kr (1/10^4) at 10–12 K, (C) Fe atoms and Fe$_2$ dimers coisolated in solid Kr (1/10^3) at 10–12 K and annealed at 20 K, (D) Fe atoms isolated in solid CH$_4$ (1/10^4) at 10–12 K, (E) Fe atoms and Fe$_2$ dimers coisolated in solid CH$_4$ (1/10^3) at 10–12 K. (Lines marked with an asterisk in part B are ascribed to Fe atoms isolated in thermally unstable (secondary) trapping sites in the lattice of solid Kr.)

($\omega_e \sim 230$ cm^{-1}), in close agreement with earlier matrix studies.[2,5] Photoexcitation into the most intense UV lines of Fe atoms in Kr leads only to slight bleaching of the atomic lines with concomitant agglomeration to Fe$_2$ to only a minor extent. These effects should be contrasted with the extreme sensitivity of the Cu,[14] Ag,[15] and Rh[16] rare-gas matrix systems with respect to metal atom photoaggregation. In addition, narrow-band irradiation into each of the visible bands of Fe$_2$ in Kr matrices causes only minor perturbations to the optical spectra of Fe and Fe$_2$, with very little indication of photofragmentation of Fe$_2$ to Fe atoms in contrast to that observed in the Cu$_2$,[14,17] Ag$_2$,[17,18] Cr$_2$,[19] Mo$_2$,[19] and Rh$_2$[16] rare-gas matrix systems. These kinds of Fe/Fe$_2$/rare-gas solid photochemical experiments served as a necessary prelude to our investigations of Fe/Fe$_2$/CH$_4$ matrices, which are described below.

The optical spectra of Fe atoms deposited with CH$_4$ at 10–12 K under conditions that favored the generation of Fe and Fe/Fe$_2$ composites (Fe/CH$_4$ $\cong$ 1/10^4 and 1/10^3, respectively) are depicted in Figure 1D,E. Correlation of the Fe atomic resonance lines between the gas phase, rare-gas solids, and solid methane is clear from Figure 1. Of particular note is the observation of three well-defined absorptions at 425, 475, and 528 nm in Figure 1E, under matrix preparation conditions which are conducive to the production of substantial concentrations of Fe$_2$. These three absorptions occur at energies very close to the similar bands ascribed to Fe$_2$ in Ar and Kr solids. Noteworthy also is the observation of partially resolved vibronic structure ($\omega_e \sim 230$ cm^{-1}) on the 475-nm band in solid CH$_4$, which should be compared with the vibrational spacings ($\omega_e \sim$ 220–230 cm^{-1}) observed on the 474-nm bands of Fe$_2$ in solid Ar and Kr. From these results there can be little doubt that Fe and Fe$_2$ can be coisolated in 10–12 K CH$_4$ matrices. Similar Fe/CH$_4$ $\cong$ 1/10^4 and 1/10^3 deposits prepared at 10–12 K were examined by infrared spectroscopy in the 4000–200-cm^{-1} wavelength range. No absorptions other than those attributable to methane were observed in a series of six different experiments.

Narrow-band irradiation into the intense 300-nm (3d^{7}4p^1, $^5D_4 \leftarrow$ 3d^{6}4s^2, $^5D_4$) atomic resonance line of Fe atoms in CH$_4$ under high dispersion (1/10^4) conditions caused rapid bleaching of all Fe atom bands with concomitant growth of a weak, broad absorption around 415–420 nm, corresponding to CH$_3$FeH.[12] The corresponding infrared experiments[12] clearly demonstrated the production of the CH$_3$FeH insertion product absorbing strongly at 2921, 2888, 2869, 1650, 1148, 1145, 547, 544, 519, 300, and 293 cm^{-1}, which is in accord with the original observations of Billups et al.[8] Similar UV-visible and infrared experiments were conducted under lower dispersion conditions (Fe/CH$_4$ $\cong$ 1/10^3), which promoted the coisolation of Fe/Fe$_2$ in CH$_4$ as described above. Under these circumstances, the photoreactivity of Fe$_2$ toward CH$_4$ could be investigated by performing selective irradiations at 425, 475, and 528 nm, which correspond to the band maxima of Fe$_2$ in solid CH$_4$. Only minor perturbations of the optical spectra of Fe$_2$ in CH$_4$ were observed following photochemical treatment of the above type (signaling site interconversions and thermal annealing effects but not chemical reaction). Confirmation of the photoinertness of Fe$_2$ toward CH$_4$ stemmed from the analogous infrared experiments, in which no absorptions other than those ascribable to methane were detected in the 4000–200-cm^{-1} range, in agreement with earlier observations.[8]

The thermal reactivity of Fe$_2$ with respect to CH$_4$ was also examined in the accessible cryogenic range 10–50 K. Up to the temperature that the methane actually sublimed away from the sample window (around 50 K) no new infrared or optical bands ascribable to an Fe atom, Fe$_2$ dimer, or Fe$_n$ cluster CH$_4$ reaction product were ever observed.

Collectively, these observations for Fe/Fe$_2$/CH$_4$ matrices force one to the inescapable conclusion that diiron does not

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(14) G. A. Ozin, S. A. Mitchell, and J. Garcia-Prieto, *J. Phys. Chem.*, **86**, 473 (1982).

(15) J. Farrell, S. A. Mitchell, G. Kenny-Wallace, and G. A. Ozin, *J. Am. Chem. Soc.*, **102**, 7702 (1980).

(16) G. A. Ozin and A. J. Lee Hanlan, *Inorg. Chem.*, **18**, 1781 (1979).

(17) G. A. Ozin, H. Huber, D. McIntosh, S. A. Mitchell, J. G. Norman, Jr., and L. Noodleman, *J. Am. Chem. Soc.*, **101**, 3504 (1979).

(18) J. Farrell, S. A. Mitchell, G. Kenny-Wallace, and G. A. Ozin, *J. Am. Chem. Soc.*, **103**, 6030 (1981).

(19) G. A. Ozin, *J. Mol. Catal.*, **3**, 195 (1977).

react with CH_4 on deposition, or during subsequent thermal annealing (10–50 K), or following photoexcitation into any of its visible absorptions (400–580 nm). In contrast, 300 nm photoexcited Fe atoms do react with CH_4 at 12 K to yield CH_3FeH, whereas ground-state Fe atoms are inert toward CH_4 up to 50 K.

We believe that the nonobservation of Mössbauer and resonance Raman spectra of Fe_2 in solid CH_4, compared to the case of solid rare gases[1,2] in earlier studies, could well be traced to differences in the experimental conditions required to produce detectable amounts of Fe_2 in CH_4 and/or to electronic quenching or energy-transfer effects and that the infrared spectra reported by Pearson et al.[1] might have originated from back-streaming of methane into the furnace region and subsequent trace cracking of CH_4 on the high-temperature source possibly followed by reaction of fragments such as CH_3, CH_2, CH, C, and H with Fe/Fe_2[20] during the matrix deposition.

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Registry No. Fe_2, 12596-01-9; Fe, 7439-89-6; CH_4, 74-82-8; CH_3FeH, 83615-51-4.

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(20) R. Hague and J. Margrave at Rice University have also found that Fe_2 is nonreactive toward CH_4 at 12 K (private communication). Recent unpublished research by R. Pearson and P. Barrett also appears to support the view that it is Fe atoms and not Fe_2 that react with CH_4 (private communication).

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Magnetic Behavior of Tetranuclear Copper(II) Complexes. An Explanation in Terms of the Isotropic Heisenberg Model

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Complexes such as chloro(2-(diethylamino)ethanolato)copper(II),[1] (acetylacetone)(*o*-hydroxyanil)copper(II),[2] $Cu_2Br_4(C_5H_5N)_2$,[3] $Fe_4Cl_3(OMe)_9$,[4,5] and $Fe(C_6H_5COO)(OMe)_2$[6] exhibit magnetic behavior that has been modeled successfully by an isotropic Heisenberg Hamiltonian involving more than one coupling constant, *J*. The purpose of this work is to show that such a model also provides a satisfactory explanation for the magnetism of a number of tetranuclear copper(II) complexes of the form $Cu_4OX_6L_4$, where X represents a chloride or bromide ion and L a Lewis base ligand, many of which show a maximum in the magnetic moment as a function of temperature. The structure of several of these tetranuclear complexes has been shown to be based on a $(CuL)_4$ tetrahedron with an oxygen atom at the center and edge-bridging halides.[7-9]

Table I. Fits to the Heisenberg Model Using Data from Wong[12]

complex	J_1, cm^{-1}	J_2, cm^{-1}	X	g	FIT[a]
$(NMe_4)_4(Cu_4OCl_{10})$[b]	200	−135	0.94	2.10	0.068
$(NMe_4)_4(Cu_4OCl_6)Br_4$[b]	220	−148	0.96	2.07	0.068
$Cu_4OBr_6(py)_4$	45	−28	0.94	2.21	0.038
$Cu_4OCl_6(pyo)_4$	210	−106	~0	2.14	0.031
$Cu_4OCl_6(tmu)_4$	190	−97	~0	2.04	0.09[c]
$Cu_4OCl_6(Me_2SO)_4$	280	−141	~0	2.11	0.029
$Cu_4OBr_6(Me_2SO)_4$	195	−98.8	~0	2.25	0.027

[a] FIT = rms deviation of the calculated from the experimental moments. [b] These data may be affected by a monomeric impurity. [c] Neither the orbital degeneracy model nor the Heisenberg model gives good fits to these data.

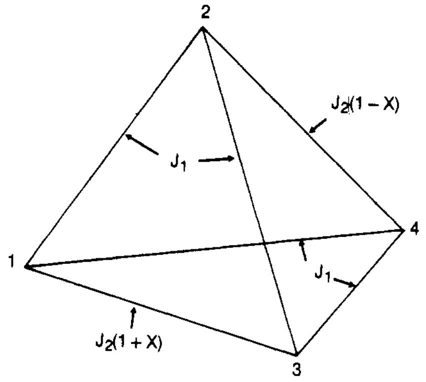

Figure 1. Coupling constants of the copper tetrahedron.

The experimental results tested are those of Lines,[10] Hatfield,[11] Dickinson,[7] and Wong.[12] The data of Wong et al.[12] are the most recent and extensive and are considered in detail.

When considering magnetic exchange in polyatomic systems it is usual to assume the following: (1) all coupling constants *J* are equal; (2) the ground state is an orbital singlet; (3) intercluster interactions are negligible. The magnetic behavior can often be explained if these assumptions are retained; removing them complicates the model and causes ambiguity in any fits to experimental results. For the tetranuclear complexes under consideration here, no explanation retaining all the above assumptions is possible. Previous models have removed assumptions 2 and 3,[10,13] but not assumption 1, though models with several *J*'s have previously been used successfully for effectively antiferromagnetic systems.[1]

The experimental data for these complexes have been successfully fitted to an orbitally degenerate ground state model by Lines et al.[10] However, as noted by Wong et al.,[12] copper complexes in which orbital effects are important in magnetic exchange are rare and thus on this model the tetranuclear copper(II) complexes seem anomalous. The intercluster exchange model,[10] though it fits the experimental data almost as well as the orbitally degenerate model, frequently invokes an intercluster exchange parameter that is larger than is physically reasonable—large enough to cause long-range ordering effects that are not observed experimentally. Thus some doubt exists about the validity of both these earlier models.

In the present work it is shown that a pairwise antiferromagnetic distortion of a ferromagnetic tetrahedron can re-

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(1) Hall, J. W.; Estes, W. E.; Estes, E. D.; Scaringe, R. P.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 1572.

(2) Hatfield, W. E.; Inman, G. W. *Inorg. Chem.* **1969**, *8*, 1376.

(3) Swank, D. D.; Willett, R. D. *Inorg. Chem.* **1980**, *19*, 2321.

(4) Kakos, G. A. Winter, G. *Aust. J. Chem.* **1969**, *22*, 97.

(5) Abbreviations used in this work: Me, methyl; py, pyridine, pyo, pyridine *N*-oxide; tmu, tetramethylurea; Me_2SO, dimethyl sulfoxide; 3-quin, 3-quinuclidinone.

(6) Kokot, E.; Mockler, G. M.; Sefton, G. L. *Aust. J. Chem.* **1975**, *28*, 299.

(7) Dickinson, R. C.; Helm, F. T.; Baker, W. A.; Black, T. D.; Watson, W. H. *Inorg. Chem.* **1977**, *16*, 1530.

(8) Bertrand, J. A.; Kelley, J. A. *Inorg. Chem.* **1969**, *8*, 1982.

(9) Bertrand, J. A. *Inorg. Chem.* **1967**, *6*, 495.

(10) Lines, M. E.; Ginsberg, A. P.; Martin, R. L.; Sherwood, R. C. *J. Chem. Phys.* **1972**, *57*, 1.

(11) Barnes, J. A.; Inman, G. W.; Hatfield, W. E. *Inorg. Chem.* **1971**, *10*, 1725.

(12) Wong, H.; tom Dieck, H.; O'Connor, C. J.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1980**, 786.

(13) Ginsberg, A. G.; Lines, M. E. *Inorg. Chem.* **1972**, *11*, 2289.

0020-1669/83/1322-1399$01.50/0