of the ternary lanthanide rhodium boride superconductors[43] discussed in a previous paper.[7]

(C) $Ln_6Ni_6P_{17}$. An attempt to prepare nickel analogues of LnM_4P_{12} (M = Fe, Ru, Os) led instead to products of the stoichiometry $Ln_6Ni_6P_{17}$.[48] This stoichiometry may be dissected into equal numbers of $NiP_{4/2}$ and $LnP_{2/3}P_{1/6}$ structural units by considering the nearest phosphorus neighbors of the nickel atom (P(1) in ref 48) and allocating the phosphorus atoms not within bonding distance of any nickel atom to a lanthanide atom. The phosphorus atoms of the $NiP_{4/2}$ units are bonded to one other phosphorus atom (P(2) in ref 48) but are donors of only two rather than four skeletal electrons since these phosphorus atoms are bonded to only two rather than three nickel atoms thereby being regarded as "pseudotricoordinate" excluding P–Ln bonds. Thus, in effect each phosphorus atom (P(1)) in the $NiP_{4/2}$ structural unit is using a lone pair to coordinate to the lanthanide atoms. The geometry of the nickel atom in a $NiP_{4/2}$ unit in $Ln_6Ni_6P_{17}$ is intermediate between tetrahedral with a favored 18-electron configuration and square planar with a favored 16-electron configuration. Since the lanthanides are tripositive, the actual Ni–P structural unit is $NiP_{4/2}^{3-}$ with an intermediate 17-electron configuration as follows:

neutral Ni atom	10 electrons
$^4/_2$ P atoms in PNi_2P' units: $(^4/_2)(2)$	4 electrons
–3 charge	3 electrons
total valence electrons for the nickel atom	17 electrons

Summary

This paper shows how edge-localized models suffice to account for the chemical bonding in low-coordination-number binary transition-metal polyphosphides of the stoichiometries MP_4, MP_3, and MP_2 as well as the more complicated rhenium derivatives Re_2P_5 and Re_6P_{13}. Such models explain the occurrence of direct metal–metal bonding in species such as MP_4 (M = Mn, Re, Cr, V), MP_3 (M = Tc, Re), and MP_2 (M = Co, Rh, Ir, Fe, Ru, Os) and provide simple rationalizations of their electrical properties (i.e., semiconducting versus metallic). Similar edge-localized models can be applied to ternary model polyphosphides such as $M'M_2P_{12}$ (M' = Ti, Nb, Mo, W; M = Mn, Fe) and $Ln_6Ni_6P_{17}$ (Ln = lanthanide). Application of such models to the ternary phosphide superconductors LnM_4P_{12} (Ln = lanthanide; M = Fe, Ru, Os) suggests porous delocalization similar to that found in ternary metal boride superconductors such as $LnRh_4B_4$.

(48) Braun, D. J.; Jeitschko, W. *Acta Crystallogr. B* **1978**, *B34*, 2069.

Calculation of the Theoretical Magnetic Susceptibility of the Four $S = {}^5/_2$ Spin System. Application to Tetranuclear Manganese(II) Complexes

J. Aussoleil, P. Cassoux, P. de Loth, and J.-P. Tuchagues*

The calculation of the theoretical magnetic susceptibility of the four $S = {}^5/_2$ spin system has been carried out by exact diagonalization of the effective spin Hamiltonian in the 1296 uncoupled spin states basis set. The temperature-dependent magnetic susceptibility data of more than 60 hypothetical tetranuclear manganese(II) complexes, presented as χT vs T plots, have been calculated for the first time, by varying the J, D, and g parameters within reasonable limits: $-2.5 \leq J_i \leq 0.25$ cm^{-1}; $-0.5 \leq D \leq 0.5$ cm^{-1}; $1.9 < g_i < 2.1$. Systematic variations of these parameters have shown that, within these limits, the effect of the variation of D is negligible except at low temperature, when the J values are very small. The effect of the variation of the g parameters is observable down to 10–20 K, although more pronounced in the high-temperature range. As expected, the variation of the magnetic susceptibility is strongly affected by the variation of the J parameters. On the basis of these results the experimental magnetic susceptibility data of a tetranuclear manganese(II) complex, $(C_{12}H_{14}N_3OMn^{II})_4(ClO_4)_4\cdot 2H_2O$, have been least-squares fitted with assumed S_4 or T_d symmetry, isotropic g, and $D = 0$ cm^{-1}, yielding $J_A = J_B = J = -0.51$ cm^{-1} and $g = 1.954$. The results obtained indicate that in the present case a small distortion from the T_d to the S_4 symmetry does not induce measurable differences between the two sets of exchange integrals.

Introduction

The calculation of the theoretical magnetic susceptibility, χ, of a compound in a magnetic field, H

$$\chi = -\frac{N}{H}\left(\sum_i \frac{\partial E_i}{\partial H} e^{-Ei/kT}\right) \bigg/ \left(\sum_i e^{-Ei/kT}\right) \quad (1)$$

implies the determination of all energy levels, E_i, of this compound. The most common approaches are approximated methods that deal with magnetic susceptibility at zero magnetic field.[1] In this respect, the Van Vleck method[2] is the most commonly used for fitting experimental temperature-dependent magnetic susceptibility data.

A more rigorous method based on the exact diagonalization of the effective spin Hamiltonian has been used in a few examples.[3] In that case, the results remain valid even when the zero-field splitting and exchange parameters have the same order of magnitude. However, when the number, N, of interacting magnetic centers and/or when the value of the spin, S_i, increases, the dimension of the problem

$$\prod_{i=1}^{N}(2S_i + 1)$$

becomes extremely large, resulting in lengthy calculations that are not always justified.

Recent progress in the knowledge of the water oxidation site of photosystem 2 brings a new justification for work in this di-

(1) Boudreaux, E. A.; Mulay, L. N. *Molecular Paramagnetism*; Wiley-Interscience: New York, 1976; Chapter 7.
(2) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: London, 1932.

(3) (a) Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 457–470. (b) Reem, R. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 1216–1226.

rection. This site is now known to include four manganese ions acting as a charge storage device throughout the S_0 to S_4 transitions of the Kok cycle.[4] The S_2 state of this cycle involves magnetically coupled manganese ions, and the hypothesis of a manganese tetranuclear complex has been considered[5] and supported by EPR,[6] EXAFS,[7] XANES,[8] and other spectroscopic studies.[9]

This situation has recently aroused great interest in the preparation and study of model tetranuclear complexes.[10-18] However, an extensive study of the magnetic properties of these complexes has only been attempted in one case.[10a] This is understandable for the reasons mentioned above: for the smallest spin states, i.e. four manganese(IV) atoms, the calculation of the E_i energy levels requires the diagonalization of 256 × 256 matrices, while 1296 × 1296 matrices need to be diagonalized for a four-manganese(II) system. Even for the more extensively studied Fe_4S_4 clusters, the magnetic properties have been interpreted by using a simplified Hamiltonian where only isotropic exchange and Zeeman interactions are considered.[19,20]

Fries et al.[21,22] have studied the general problem of a finite system including N spins, but their simplified treatment is valid only when isotropic exchange interactions are largely predominant, since it considers the anisotropic and Zeeman terms as perturbations of the isotropic Hamiltonian.

Thus, the problem raised by the analysis of the magnetic properties of the tetranuclear manganese site of photosystem 2,
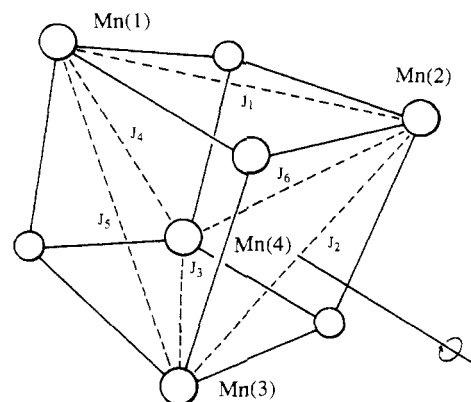
Figure 1. Manganese(II) ion-bridging ligand cubane core of a tetranuclear manganese complex with the numbering of the manganese atoms and of the J exchange integrals.
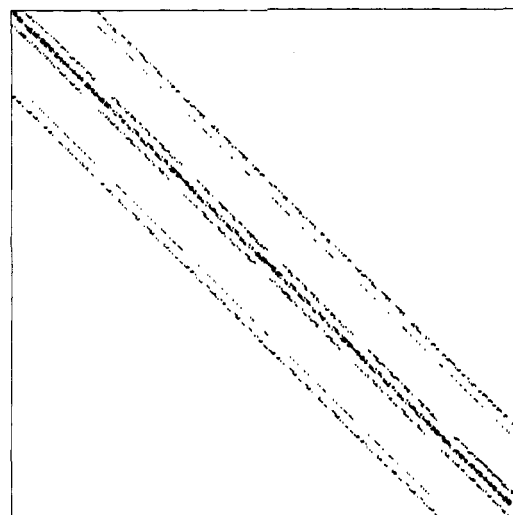
Figure 2. Location of the nonzero $\langle i,j,k,l|\mathcal{H}|I,J,K,L\rangle$ elements of the Hamiltonian energy matrix in the isotropic case, resulting in a symmetric band matrix.

at different oxidation states and with the manganese ions having most probably low-symmetry ligand environments, undoubtedly needs a more general analysis to take into account the anisotropic and Zeeman terms rigorously. Such an analysis has been performed for the S_2 state within the framework of a particular 3 Mn(III)–1 Mn(IV) hypothesis.[6b] However, it needs to be extended in order to allow estimates of the expected magnetic properties of the tetranuclear manganese site in the S_0, S_1, and S_3 states. Such a general analysis would then constitute a convenient framework for an extensive study of the magnetic properties of the different tetranuclear manganese complexes synthesized as models.[10-18]

We present in this paper the calculation of the theoretical susceptibility of the four $S = {}^5/_2$ spin system by exact diagonalization of the effective spin Hamiltonian in the uncoupled basis set obtained as product states of the 1296 individual manganese spin states $|S_i,S_{zi}\rangle$. The variations of the molar susceptibility, χ, as a function of temperature, T, have been calculated for more than 60 typical sets of J, D, and g values in order to evaluate the effect of these parameters. The results are compared with the experimental data obtained for a model tetranuclear manganese(II) complex, $(C_{12}H_{14}N_3OMn^{II})_4(ClO_4)_4 \cdot 2H_2O$.[13]

Experimental Section

Theory. The effective spin Hamiltonian[23] that we have used to describe a four $S = {}^5/_2$ spin system is given by

(4) (a) Livorness, J.; Smith, T. D. *Struct. Bonding (Berlin)* **1982**, *48*, 1–44. (b) Amesz, J. *Biochim. Biophys. Acta* **1983**, *726*, 1. (c) Govindjee; Kambara, T.; Coleman, W. *Photochem. Photobiol.* **1985**, *42*, 187–210. (d) Kambara, T.; Govindjee, *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6119–6123. (e) Brudvig, G. W.; Crabtree, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4586–4588. (f) Dismukes, G. C. *Photochem. Photobiol.* **1986**, *43*, 99–115. (g) Renger, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 643–660.

(5) Dismukes, G. C.; Siderer, Y. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 274–278.

(6) (a) de Paula, J. C.; Brudvig, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 2643–2648. (b) Beck, W. F.; de Paula, J. C.; Brudvig, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 4018–4022.

(7) (a) Yachandra, V. K.; Guiles, R. D.; McDermott, A.; Britt, R. D.; Cole, J.; Dexheimer, S. L.; Sauer, K.; Klein, M. P. *J. Phys. (Les Ulis, Fr.)* **1986**, *47*(C8), 1121–1128. (b) Guiles, R. D.; Yachandra, V. K.; McDermott, A. E.; Britt, R. D.; Dexheimer, S. L.; Sauer, K.; Klein, M. P. In *Progress in Photosynthesis Research*; Biggens, J., Ed.; M. Nijhoff: Dordrecht, The Netherlands, 1987; Vol. 1, No. 5, pp 561–568. (c) Yachandra, V. K.; Guiles, R. D.; McDermott, A. E.; Coles, J. L.; Britt, R. D.; Dexheimer, S. L.; Sauer, K.; Klein, M. P. *Biochemistry* **1987**, *26*, 5974–5981.

(8) Goodin, D. B.; Yachandra, V. K.; Britt, R. D.; Sauer, K.; Klein, M. P. *Biochim. Biophys. Acta* **1984**, *767*, 209–216.

(9) (a) Dekker, J. P.; Van Gorkom, H. S.; Wensink, J.; Ouwehand, L. *Biochim. Biophys. Acta* **1984**, *767*, 1–9. (b) Vincent, J. B.; Christou, G. *FEBS Lett.* **1986**, *207*, 250–253.

(10) (a) Smit, J. J.; Nap, G. M.; De Jongh, L. J.; Van Ooijen, J. A. C.; Reedijk, J. *Physica B+C* **1979**, *97B+C*, 365–376. (b) Ten Hoedt, R. W. M.; Reedijk, J. *Inorg. Chim. Acta* **1981**, *51*, 23–27.

(11) Horn, E.; Snow, M. R.; Zeleny, P. C. *Aust. J. Chem.* **1980**, *33*, 1659–1665.

(12) Costa, T.; Dorfman, J. R.; Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 4091–4099.

(13) (a) McKee, V.; Sheppard, W. B. *J. Chem. Soc., Chem. Commun.* **1985**, 158–159. (b) Brooker, S.; McKee, V.; Sheppard, W. B.; Pannell, L. K. *J. Chem. Soc., Dalton Trans.* **1987**, 2555–2562.

(14) Luneau, D.; Savariault, J.-M.; Cassoux, P.; Tuchagues, J.-P. *J. Chem. Soc., Dalton Trans.* **1988**, 1225–1235.

(15) Christmas, C.; Vincent, J. B.; Huffman, J. C.; Christou, G.; Chang, H. R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, *1303*–1305.

(16) Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H. R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236–238.

(17) Bashkin, J. S.; Chang, H. R.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 6502–6504.

(18) Wieghardt, K.; Bossek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328–329.

(19) Papaefthymiou, G. C.; Laskowski, E. J.; Frota-Pessôa, S.; Frankel, R. B.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 1723–1728.

(20) Whitener, M. A.; Bashkin, J. K.; Hagen, K. S.; Girerd, J.-J.; Gamp, E.; Edelstein, N.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 5607–5620.

(21) Fries, P. H.; Belorizky, E. *Nouv. J. Chim.* **1987**, *11*, 271–278.

(22) Belorizky, E.; Fries, P. H.; Gojon, E.; Latour, J. M. *Mol. Phys.* **1987**, *61*, 661–668.

(23) (a) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon Press-Oxford University Press: Oxford, U.K., 1969. (b) Owen, J.; Harris, E. A. *Electron Paramagnetic Resonance*; Geschwind, S., Ed.; Plenum Press: New York, 1972; p 445.

$$\mathcal{H} = -2\sum_{i<k}^{4} J_{ik}S_iS_k + \sum_{i=1}^{4}D_iS_{zi}{}^2 + \sum_{i=1}^{4}E_i(S_{xi}{}^2 - S_{yi}{}^2) + \beta H_z\sum_{i=1}^{4}g_{zi}S_{zi} +$$

$$\beta H_x\sum_{i=1}^{4}g_{xi}S_{xi} + \beta H_y\sum_{i=1}^{4}g_{yi}S_{yi} \quad (2)$$

where S_i and S_k are the electron spin operators, J_{ik} is the superexchange coupling constant between ions i and k, and D_i and E_i take into account the single-ion crystal field and spin–orbital contributions.[23] The symmetric and antisymmetric dipole interactions were neglected. Given the number of parameters that may be varied (four D_i, four E_i, four g_{zi}, four g_{xi}, four g_{yi}, and six J_{ij} values), axial symmetry was assumed ($E_i = 0$; $g_{zi} = g_{\parallel i}$ and $g_{xi} = g_{yi} = g_{\perp i}$) and the following sensible approximations have been also made: the four D_i terms have been considered identical for the four magnetic centers, as well as the four $g_{\parallel i}$ and the four $g_{\perp i}$ terms. For simplification purposes, the six J_{ij} terms have been written $J_1, J_2, \ldots J_6$ as shown in Figure 1. The Hamiltonian may be now written as

$$\mathcal{H} = -2(J_1S_1S_2 + J_2S_2S_3 + J_3S_3S_4 + J_4S_4S_1 + J_5S_1S_3 + J_6S_2S_4) +$$

$$D\sum_{i=1}^{4}S_{zi}{}^2 + g_{\parallel}\beta H_z\sum_{i=1}^{4}S_{zi} + g_{\perp}\beta(H_x\sum_{i=1}^{4}S_{xi} + H_y\sum_{i=1}^{4}S_{yi}) \quad (3)$$

Computational Details. The magnetic susceptibility has been calculated by using the general expression (1) quoted above. The energy levels E_i have been obtained by diagonalization of the effective spin Hamiltonian (3) in the basis set of the 1296 uncoupled spin states $|I,J,K,L\rangle$ with I, J, K, and L independently varying from ${}^5/_2$ to $-{}^5/_2$.

In the axial symmetry anisotropic case, two derived expressions of $\mathcal{H}$, one involving the $g_{\parallel}$ component and the other involving the $g_{\perp}$ component of the g tensor, have been separately used. In the isotropic case, a simplified expression of $\mathcal{H}$ involving only the $g_{\parallel}$ component can be used. It is interesting to note that the diagonalization time required in the isotropic case is reduced by a factor of ca. 7 compared to that for the axial symmetry anisotropic case.

By using scale operators, the Hamiltonian $\mathcal{H}$ can be conveniently expressed as the sum of 26 operators that include eight parameters, i.e. six J, D, and $g_{\parallel}$ (or $g_{\perp}$). These 26 operators have been applied to the 1296 spin states $|I,J,K,L\rangle$, yielding 1296×26 terms. All the matrix elements $\langle i,j,k,l|\mathcal{H}|I,J,K,L\rangle$ have then been calculated, yielding 1296×1296 elements. All nonzero elements are located in such a way (Figure 2) that symmetric band matrices are obtained with a half-width of $6^3 - 1 = 215$ in the z direction ($6^3 = 216$ in the x (or y) direction). As soon as they were generated, the elements located in one half-band plus the diagonal were stored in the central memory of the computer, i.e. 1296×216 values in the isotropic case. The 1296 eigenvalues have been calculated by using a slightly modified version of a NAG subroutine specially designed for the diagonalization of symmetric band matrices.[24] Typically, the calculation of 1296 eigenvalues in the isotropic case required 3 h of the central unit of a VAX-11/730 minicomputer. However, as the determination of the $\partial E_i/\partial H$ derivatives in eq 1 requires carrying out the calculation for three values of the field, a total of 9 h of computation time was needed for the calculation of a χ vs T variation for one set of J, D, and g parameters in the isotropic case.

The results of these calculations will be presented as χT vs T curves, as suggested by Kahn.[25] There are several different commonly used graphic representations of magnetic susceptibility data as a function of temperature: χ vs T, $1/\chi$ vs T, μ ($=2.828\chi^{1/2}T$) vs T, ... In the present case, the advantages of the χT vs T representation are (i) the variation amplitudes of the χT product exhibit the same order of magnitude for different values of the J, D, and g parameters and the resulting χT vs T curves can be clearly plotted in the same figure and easily compared and (ii) in the high-temperature range, the T factor in the χT product magnifies the gap between two curves obtained with different parameters. However, when theoretical and experimental data in the very low temperature range are compared in a fitting process, the χ vs T representation should obviously be preferred.

Synthesis. [Ba(H$_2$L)(H$_2$O)$_2$](ClO$_4$)$_2$, where L is a Schiff-base macrocycle resulting from template condensation of 2 equiv of 2,6-diacetylpyridine with 2 equiv of 1,3-diamino-2-hydroxypropane, was prepared as described in the literature.[26]

(C$_{12}$H$_{14}$N$_3$OMn^{II})$_4$(ClO$_4$)$_2$·2H$_2$O was prepared by slow interdiffusion of methanolic solutions of [Ba(H$_2$L)(H$_2$O)$_2$](ClO$_4$)$_2$ and Mn(ClO$_4$)$_2$·6H$_2$O at room temperature in an oxygen-free glovebox. The composition and structure of the resulting orange-yellow crystals were ascertained through C, H, N, Mn, and Cl elemental analysis, IR spectroscopy, and determination of the cell parameters from a least-squares fit of 25 re-
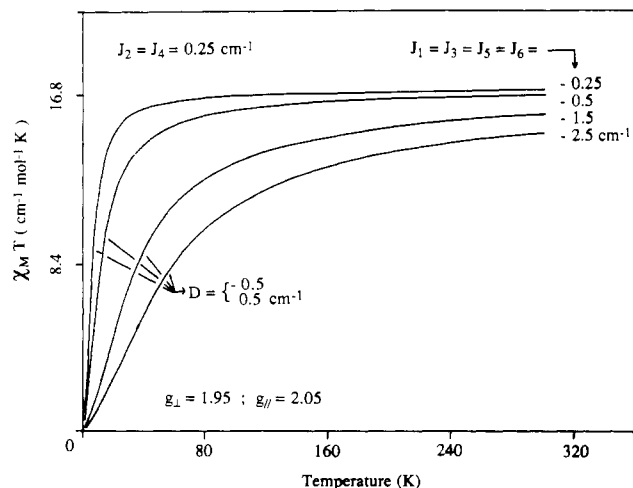

Figure 3. χT vs T plots obtained for $D = +0.5$ and -0.5 cm^{-1} with several sets of g and J parameters.

flections obtained with an Enraf-Nonius CAD4 diffractometer. All resulting data are in perfect agreement with those of the tetranuclear cubane-like complex described by McKee et al.[13]

Magnetic Susceptibility Measurements. The variable-temperature magnetic susceptibility data were obtained on polycrystalline samples (resulting from the grinding of crystals of the compound in the glovebox) with a Faraday-type magnetometer as previously described.[14]

Results and Discussion

With use of the computational scheme described above, the variations of the magnetic susceptibility as a function of temperature may be calculated for any set of arbitrary J, D, and g values. However, the underlying goal of this work being to gain a better insight into the magnetic properties of model photosynthetic manganese complexes, we had to restrict the range of variations of these parameters to reasonable values in order to avoid useless computational time.

An extended survey of the literature on mononuclear[3a] and dinuclear manganese complexes[14,27-35] and their magnetic studies provides a valuable source of information, insofar as one can assume that the J, D, and g parameters will have similar values in tetranuclear complexes. In all previously studied manganese complexes, the anisotropy of g remains quite low and, therefore, the variations of the g parameters can been restricted to the $2.0 \le g_{\parallel} \le 2.1$ and $1.9 \le g_{\perp} \le 2$ ranges, respectively. Likewise, the D terms being observed in most previous examples within the -0.5 cm$^{-1} < D < +0.5$ cm^{-1} range,[3] the variation of this parameter was also restricted within these limits in our calculations.
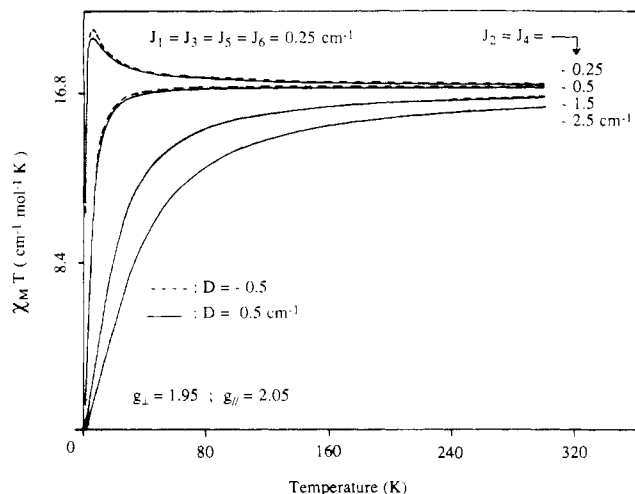
The evaluation of a plausible variation range for the J values is more difficult. The lowest J value (-4.5 cm^{-1}) reported for a dinuclear manganese complex has been determined by Wieghardt et al.[27] on the basis of experimental magnetic susceptibility data obtained in a high-temperature range, 98–293 K. Most other reported low J values, i.e. lower than -2.5 cm^{-1}, have been likewise determined from experimental data obtained at high temperature, typically between 78 and 300 K. As pointed out by Kahn,[25] the

(24) NAG Library, Numerical Algorithms Group, Ltd., Mayfield House, 256 Banbury Road, Oxford, U.K.

(25) Kahn, O. *Struct. Bonding (Berlin)* **1987**, *68*, 90–167.

(26) McKee, V.; Smith, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1645–1647.

(27) Wieghardt, K.; Bossek, U.; Bonvoisin, J.; Beauvillain, P.; Girerd, J.-J.; Nuber, B.; Weiss, J.; Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1030–1031.

(28) Lewis, J.; Mabbs, F. E.; Weigold, H. *J. Chem. Soc. A* **1968**, 1699–1703.

(29) Earnshaw, A.; King, E. A.; Larkworthy, L. *J. Chem. Soc. A* **1968**, 1048–1052.

(30) Butler, K. D.; Murray, K. S.; West, B. O. *Aust. J. Chem.* **1971**, *24*, 2249–2256.

(31) Laffey, M. A.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1982**, 313–317.

(32) Pecoraro, V. L.; Kessissoglou, D. P.; Li, X.; Butler, W. M. In *Progress in Photosynthesis Research*; Biggens, J., Ed.; M. Nijhoff: Dordrecht, The Netherlands, 1987; Vol. 1, No. 5, pp 725–728.

(33) Timken, M. D.; Marritt, W. A.; Hendrickson, D. N.; Gagné, R. A.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 4202–4208.

(34) Mabad, B.; Cassoux, P.; Tuchagues, J.-P.; Hendrickson, D. N. *Inorg. Chem.* **1986**, *25*, 1420–1431.

(35) Lambert, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683–2686.

Figure 4. χT vs T plots obtained for $D = +0.5$ cm^{-1} (—) and $D = -0.5$ cm^{-1} (---) with several sets of g and J parameters.
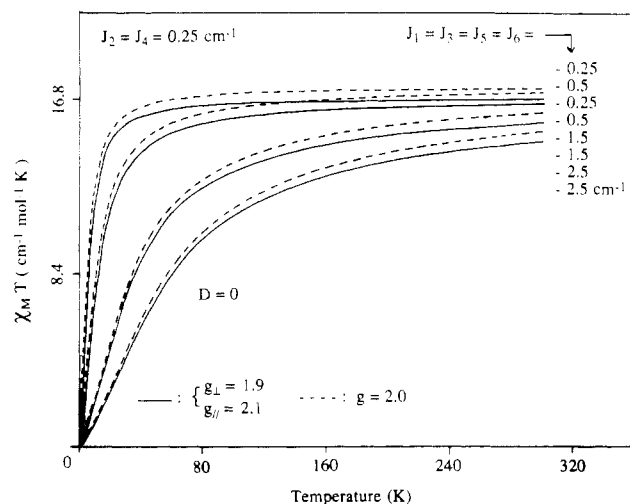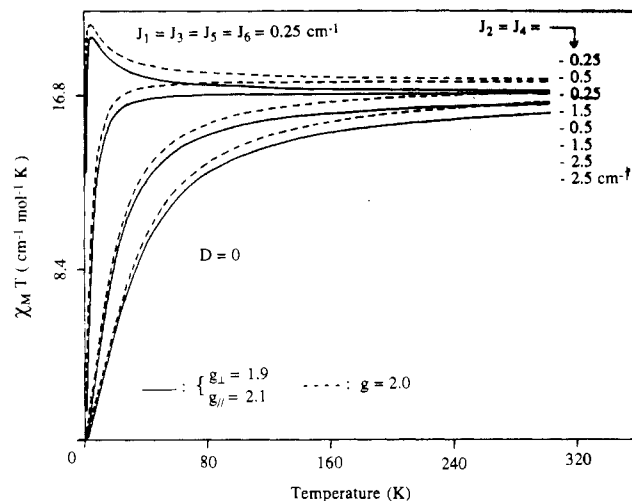

Figure 6. χT vs T plots obtained for $g_{\parallel} = 1.9$ and $g_{\perp} = 2.1$ (—) and for $g = 2.0$ (---) with $D = 0$ cm^{-1} and different sets of J parameters.

Figure 5. χT vs T plots obtained for $g_{\parallel} = 1.9$ and $g_{\perp} = 2.1$ (—) and for $g = 2.0$ (---) with $D = 0$ cm^{-1} and different sets of J parameters.

Figure 7. χT vs T plots obtained with the assumption of T_d symmetry for J varying from -2.5 to $+0.25$ cm^{-1}, $D = 0$ cm^{-1}, and $g = 2.0$.

Table I

sym	no. of indep J's	numbering of the distinct J's
T_d	1	$J_1 = J_2 = J_3 = J_4 = J_5 = J_6 = J$
S_4	2	$J_1 = J_3 = J_5 = J_6 = J_A$
		$J_2 = J_4 = J_B$
C_{2v}	3	$J_1 = J_3 = J_A$
		$J_5 = J_6 = J_C$
		$J_2 = J_4 = J_B$
C_2	4	$J_1 = J_3 \neq J_5 = J_6 \neq J_2 \neq J_4$

experimental data obtained at low temperature are more critical in determining an accurate value of J than the high-temperature data. In this respect, the most accurate J values that have been determined from low-temperature measurements (down to 4.2 K) were found higher than -2.5 cm^{-1}.[3a,31-34] The few positive J values reported for dinuclear manganese(II) complexes are lower than 0.25 cm^{-1}.[14,35] Therefore, the variation of the J values has been generally restricted in the present work to the -2.5 cm$^{-1} \leq J \leq$ 0.25 cm^{-1} range (some calculations have been performed, for checking purposes, with J values outside of this range: their results are quite far from available data obtained for tetranuclear manganese(II) complexes).
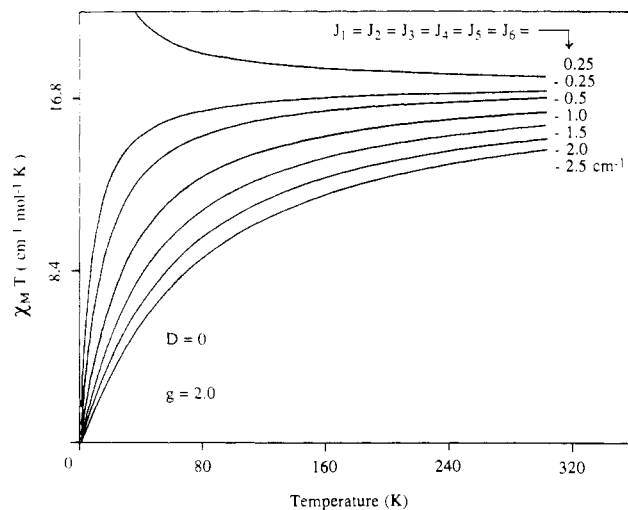
Over 60 calculations with systematic variations of the J, D, and g parameters *within their assumed range* have been carried out to evaluate the effect of these parameters.

Effect of the D Parameter. A number of calculations have been carried out for several sets of J values, with $g_{\parallel} = 1.95$ and $g_{\perp} = 2.05$, and with D varying for each set from -0.5 to $+0.5$ cm^{-1}. As can be seen in Figures 3 and 4, most of the pairs of χT vs T curves obtained for $D = +0.5$ cm^{-1} are completely superimposed over the whole temperature range, indicating that a variation of D within these limits does not result in significant changes in the magnetic susceptibility. At the most, a minute variation is observed at low temperature when the mean value of the J parameters is close to zero or slightly positive.

Therefore, we can conclude at this point that the effect of the D term is a second-order effect compared to the effect of the superexchange interactions. It is not excluded, however, that in another hypothetical case (for example, with ions different from

manganese(II)) the D parameter may take much higher values and that its effect may be of greater importance.

Effect of the g Parameters. Figures 5 and 6 show a number of χT vs T curves obtained with $D = 0$ for several sets of J values. For each set, the isotropic case ($g_{\perp} = g_{\parallel} = 2$) and the limiting axial symmetry anisotropic case ($g_{\perp} = 2.1$; $g_{\parallel} = 1.9$) have been plotted. At low temperature, the resulting pairs of curves almost superimpose, but in the high-temperature range the effect of the g anisotropy on the magnetic susceptibility is not negligible. It should be kept in mind that the g dependence of the magnetic susceptibility is magnified by the T factor in the χT product at high temperature. Nevertheless, the g effect should probably be taken into account in anisotropic cases when comparing experimental and theoretical data in fitting processes.

Effect of the J Parameters. We have shown that the D factor can be reasonably set to zero. In the following investigation the studied hypothetical system has been assumed isotropic, with $g_{\perp}$
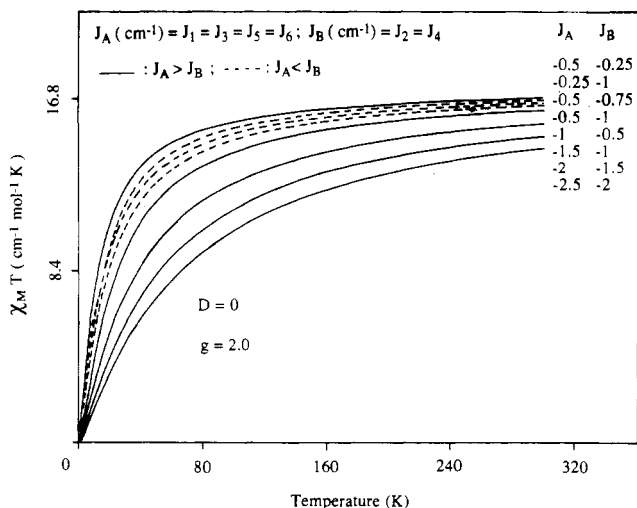
Figure 8. χT vs T plots obtained with the assumption of S_4 symmetry for J_A and J_B having the same sign and independently varying from −2.5 to +0.25 cm⁻¹, $D = 0$ cm⁻¹, and $g = 2.0$.
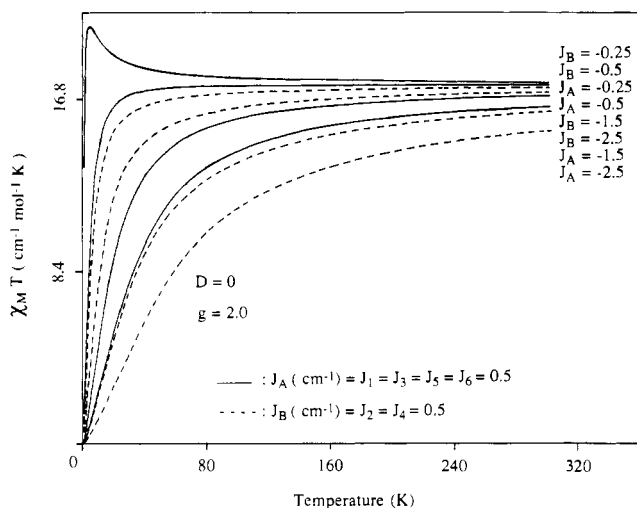
Figure 9. χT vs T plots obtained with the assumption of S_4 symmetry for J_A and J_B having opposite signs and independently varying from −2.5 to +0.25 cm⁻¹, $D = 0$ cm⁻¹, and $g = 2.0$.

$= g_\parallel = 2$. This simplified approach is likely to be valid for tetranuclear manganese(II) systems but may not apply to other tetranuclear complexes.

Among the six J parameters, the actual number of independent J's is governed by the symmetry of the metal ion–bridging ligand cubane core of the complex. On the basis of the numbering of the J parameters in the manganese(II)–ligand cubane core in Figure 1, the possible symmetries and the corresponding sets of exchange integrals are summarized as shown in Table I.

The χT vs T curves corresponding to the T_d, S_4, and C_{2v} cases with J_i varying from −2.5 to 0.25 cm⁻¹ are shown in Figures 7–10. For the sake of clarity within the S_4 case, two situations have been distinguished, depending on whether J_A and J_B have the same sign (Figure 8) or opposite signs (Figure 9).

As expected, the effect of the J parameters is the most important compared to those of the D and g parameters, especially at low temperature and for whatever the symmetry resulting from the geometry fo the manganese(II) complex may be, i.e. whatever the number of distinct J's. Figure 10, showing the C_{2v} case, evidences the overparametrization phenomenon that could be found when comparing theoretical and experimental data: in several instances, two superimposable curves are obtained for two different sets of J's. This overparametrization situation should be even worse in the C_2 case with four distinct J values, and therefore, the C_2 case was not investigated.

Comparison with the Experimental Magnetic Susceptibility of $(C_{12}H_{14}N_3OMn^{II})_4(ClO_4)_4\cdot 2H_2O$ **(1).** The temperature-dependent
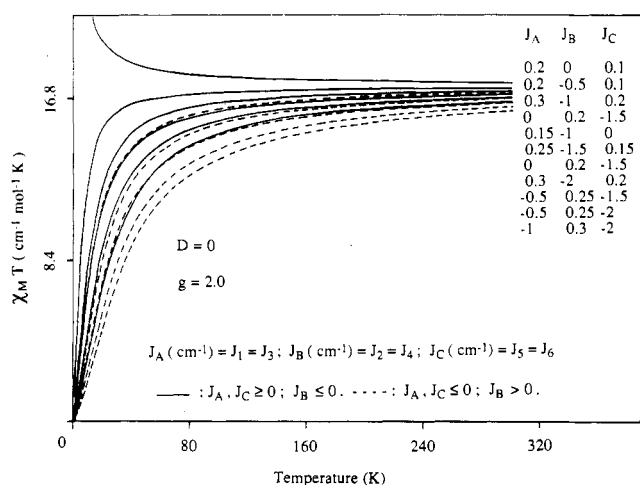
Figure 10. χT vs T plots obtained with the assumption of C_{2v} symmetry for J_A, J_B, and J_C independently varying from −2.5 to +0.25 cm⁻¹, $D = 0$ cm⁻¹, and $g = 2.0$.

Table II. Bond Lengths (Å) and Bond Angles (deg) in the Manganese–Oxygen Cubane Core of $[C_{12}H_{14}N_3OMn^{II}]_4(ClO_4)_4$[13]

| atoms	Mm(i)–Mn(j) bond length	Mn(i)–O(k)–Mn(j) bond angle	J
Mn(1)–Mn(2)	3.313	95.7, 100.9	J_1
Mn(3)–Mn(4)	3.313	95.7, 100.9	J_3
Mn(1)–Mn(3)	3.325	96.6, 100.5	J_5
Mn(2)–Mn(4)	3.326	96.6, 100.5	J_6
Mn(2)–Mn(3)	3.432	101.9, 101.9	J_2
Mn(1)–Mn(4)	3.450	102.0, 102.0	J_4

magnetic susceptibility of the tetranuclear manganese(II) complex **1**, previously described by McKee et al.,[13] has been determined. The resulting experimental χT vs T curve may now be compared with the calculated curves shown in Figures 3–10. It is clear that, given the number of varying parameters, one could not expect an accurate determination of these parameters by such a simple visual comparison. On the basis of the symmetry of the manganese–oxygen cubane core of complex **1**, which is reflected in the bond lengths and angles listed in Table II,[13] one may be tempted to consider two sets of J values, i.e. $J_1 \approx J_3 \approx J_5 \approx J_6 = J_A \neq J_2 \approx J_4 = J_B$. However, among the many theoretical curves calculated with this assumption (S_4 symmetry), only those obtained for $−0.5 < J_A \approx J_B < −1$ cm⁻¹ compare roughly with the experimental curve. Likewise, the comparison between the theoretical curves obtained with a set of identical J values (T_d symmetry) and the experimental curve indicated a similar range, $−0.5 < J < −1$ cm⁻¹.

This observation prompted us to tentatively fit the experimental magnetic susceptibility data by using a refinement program based on the simplex methods.[36] On the basis of the symmetry of the manganese–oxygen cubane core of complex **1**, the least-squares fitting of the data was carried out in the S_4 symmetry case with $J_1 = J_3 = J_5 = J_6$ ($=J_A$) varying independently from $J_2 = J_4$ ($=J_B$)), and with $D = 0$ and an isotropic g. Considering that the effect of the g parameter is more perceptible at high temperature, in the first step we set the J_A and J_B values at −0.5 cm⁻¹ and least-squares fit the experimental data only for the 100–300 K temperature range, allowing g to vary between 1.9 and 2.1. The best fit was obtained with $g = 1.957$. Then, g being set at this 1.957 value, we fitted the experimental data for the whole 4.2–300 K temperature range, allowing J_A and J_B only to vary. The best fit was obtained for $J_A = J_B = −0.53$ cm⁻¹. These results suggest that the slight distortion from the T_d to the S_4 symmetry experimentally observed for the cubane core of complex **1** and reflected in the observation of two sets of Mn---Mn separations

(36) James, F.; Roos, M. MINUIT Program, a System for Function Minimization and Analysis of the Parameters Errors and Correlations. *Comput. Phys. Commun.* **1975**, *10*, 345.
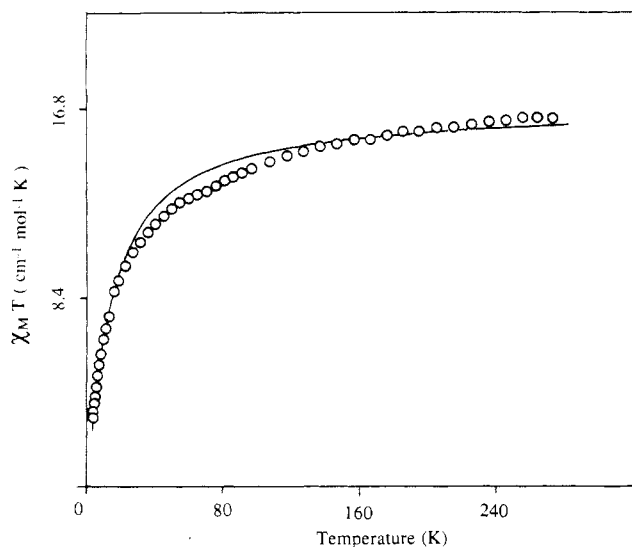
Figure 11. Experimental χT vs T data (O) obtained for [$C_{12}H_{14}N_3O$-$Mn^{II}]_4(ClO_4)_4 \cdot 2H_2O$ and a theoretical curve calculated on the assumption of T_d symmetry with $J = -0.51$ cm^{-1}, $D = 0$ cm^{-1}, and $g = 1.954$.
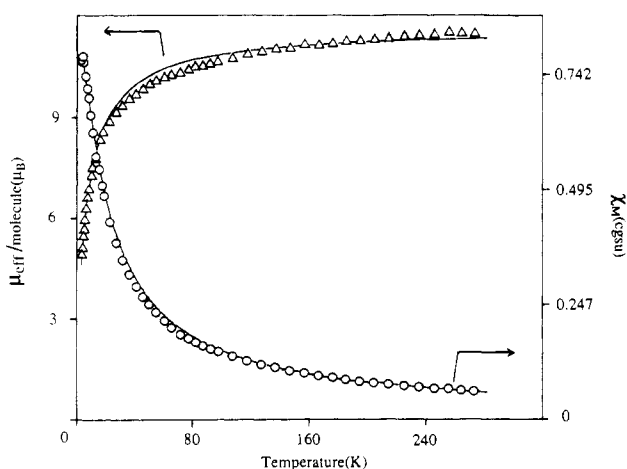
Figure 12. Experimental χ vs T (O) and μ vs T ($\triangle$) data obtained for [$C_{12}H_{14}N_3OMn^{II}]_4(ClO_4)_4 \cdot 2H_2O$ and theoretical curves calculated on the assumption of T_d symmetry with $J = -0.51$ cm^{-1}, $D = 0$ cm^{-1}, and $g = 1.954$.

(Mn(1)---Mn(2) $\cong$ Mn(1)---Mn(1') $\cong$ 3.32 Å and Mn(1)---Mn(2') $\cong$ 3.45 Å) is not large enough to induce measurable differences between the two sets of exchange integrals, J_A and J_B. Consequently, the least-squares fitting of the data was also carried out in the T_d symmetry case, with both J and g allowed to vary, but this last fitting gave values, $J = -0.51$ cm^{-1} and $g = 1.954$, almost identical with those previously obtained.

The experimental data and the least-squares fit are shown as χT vs T plots in Figure 11 and χ and μ vs T plots in Figure 12. As already noted, the χT vs T representation is the most severe, for it magnifies the discrepancies between the experimental and calculated data. The χ and μ vs T representations are the most commonly used and allow a better evaluation of the goodness of this fit compared to other fits reported in the literature. Moreover,

the χ vs T representation is in turn much more severe and accurate in the low-temperature range.

Conclusion

The calculation of the theoretical magnetic susceptibility of the four $S = {}^5/_2$ spin systems is no longer an out-of-sight, or useless, research objective. By use of a rigorous method based on the exact diagonalization of the effective spin Hamiltonian in the 1296 uncoupled spin state basis set, the magnetic susceptibility of hypothetical tetranuclear $S = {}^5/_2$ metal complexes as a function of temperature can be calculated for any set of values of the relevant J, D, and g parameters. This analysis, and its extension to other tetranuclear model manganese complexes, is strongly needed for a better understanding of the nature of the manganese site of photosystem 2. This method is general and can be applied to other four-spin systems such as the tetranuclear iron complexes.

In this paper, the temperature-dependent theoretical magnetic susceptibility data of more than 60 hypothetical tetranuclear manganese(II) complexes, presented as χT vs T plots, have been calculated for the first time by varying the J, D, and g parameters within reasonable limits: -2.5 cm$^{-1} \le J_i \le 0.25$ cm^{-1}; -0.5 cm$^{-1} < D < 0.5$ cm^{-1}; $1.9 < g_i < 2.1$. Systematic variations of these parameters have shown that, within these limits, the effect of the variation of D is negligible except at low temperature, when the J values are very small. The effect of the variation of the g parameters is observable down to 10–20 K, although more pronounced in the high-temperature range. As expected, the variation of the magnetic susceptibility is strongly affected by the variation of the J parameters, whatever the number of distinct J's may be, as determined by the symmetry resulting from the geometry of the complex.

This result has justified the tentative fitting of the experimental magnetic susceptibility data of the ($C_{12}H_{14}N_3OMn^{II})_4(ClO_4)_4 \cdot 2H_2O$ tetranuclear complex. Equally satisfactory fits of the magnetic susceptibility data of this complex have been obtained with assumed S_4 or T_d symmetry, indicating that a small distortion from the T_d to the S_4 symmetry does no induce a measurable difference between the two sets of exchange integrals, J_A and J_B; in the present case, this small distortion corresponds to a maximum difference of 0.13 Å in the Mn---Mn distances. This result indicates that exact matrix diagonalization was not required in the specific case of this example, but this could not be anticipated a priori. Moreover, this result brings up the interesting question of how large the differences in the distances between the coupled metal centers need be in order to result in differences between the exchange integrals. In order to address this question, we have initiated the study of the magnetic properties of several new manganese tetranuclear complexes[13b,37] with different types of lower symmetries, within the framework of this exact matrix diagonalization method.

(37) (a) Brooker, S.; McKee, V. *J. Chem. Soc., Chem. Commun.*, in press.
(b) McKee, V. Private Communication.