binding energies bear this out (*cf.* Table I). If the M→P π bonding were more important in the complex formation than the P→M σ bonding, the increased M→P donation would increase the electron density of the phosphorus and thus decrease the electron binding energy, which is exactly the effect noted. The very slight drop in binding energy of the phosphorus 2p electrons between free triphenylphosphine and triphenylphosphine in the complexes indicates that back-donation from the occupied d orbitals of the metal atoms probably occurs to a greater extent than the sharing of the phosphorus lone pair with the cadmium. Here the assumption must be made that the σ-bonding electrons have at least equal if not greater effect on core-electron binding energies than π-bonding electrons.

Another aspect of the data is the considerable shift which occurs when the phosphorus is bound to an oxygen, an element of very high electronegativity. In this case a σ and a π bond are also formed between the atoms[8,9] with the σ bond involving P→O and the π bond involving O→P donation. The significant shift here indicates a depletion of electron density from around the phosphorus atom. The high electronegativity of the oxygen atom leads directly to a low polarizability. The combination of high electronegativity and low polarizability could cause the oxygen to dominate the σ-bonding electrons while π bonding less efficiently and thus effect the drift of electron density away from the phosphorus.

Little can be said regarding the spectra of the coordinated chloride. The low polarizability of the chloride ion would lead one to expect very little change in the binding energy of the chlorine core electrons among similar complexes, and indeed a very constant value is obtained.

Since we are here concerned only with the relative binding energies of atoms within similar compounds, we assume that any solid-state interactions that might affect the data will be small and/or essentially invariant.

Spectra of this sort seem to be capable of providing a kind of information on bonding in complexes which allows a direct assessment of the relative importance of donation *via* σ bonds *vs.* back-donation from appropriate metal orbitals.

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[8] H. K. Wang, *Acta Chem. Scand.*, **19**, 879 (1965).

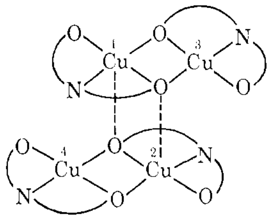
[9] C. I. Branden and I. Lindqvist, *ibid.*, **15**, 167 (1961).

Correspondence

Exchange Coupling in Tetranuclear Complexes. The Model and Some of Its Limitations

Sir:

Recently Hatfield and Inman[1] set up a four-center exchange-coupled model to describe the magnetic properties of acetylacetonemono(*o*-hydroxyanil)copper(II), **1**, and its analogs. **1** had previously been treated as a dimer,[2] whose magnetic properties therefore followed the Bleaney–Bowers equation[3]



1

$$\chi_{\mathrm{Cu}} = \frac{Ng^2\beta^2}{kT}(3 + e^{-2J/kT})^{-1} + N\alpha \tag{1}$$

where the symbols have their usual meaning, but **1** is in fact a weakly linked tetramer.[4] The general treatment of such multinuclears involves a calculation outlined elsewhere,[5,6] specific results for which have been given for tri-, tetra-, and multinuclear interacting complexes.[5-7] The general results, applicable to complex **1**, based on a spin-only Heisenberg exchange model with all integrals J_{ij} (between the ith and jth spins) independent, have been given.[6] The Hamiltonian is

$$\mathcal{H} = -2\sum_{j>i=1}^{n} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \tag{2}$$

and the magnetic susceptibility is given by

$$\chi_{\mathrm{M}} = \frac{Ng^2\beta^2}{4kT} \times \frac{10e^{-E_2/kT} + 2e^{-E_1{}^{\mathrm{a}}/kT} + 2e^{-E_1{}^{\mathrm{b}}/kT} + 2e^{-E_1{}^{\mathrm{c}}/kT}}{5e^{-E_2/kT} + 3e^{-E_1{}^{\mathrm{a}}/kT} + 3e^{-E_1{}^{\mathrm{b}}/kT} + 3e^{-E_1{}^{\mathrm{c}}/kT} + e^{-E_0{}^{\alpha}/kT} + e^{-E_0{}^{\beta}/kT}} + N\alpha \tag{3}$$

where the E_2, etc., are the energies of the total spin states $S_{\mathrm{T}} = 2, 1, 1, 1, 0, 0$. The validity of the treatment of the multinuclear spin model is demonstrated by its ability to predict the results of the extended Kambe method,[5,6,8,9] but like all spin–spin coupling models its applicability is limited by experimental error, by the possibility of paramagnetic impurities,

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[1] W. E. Hatfield and G. W. Inman, Jr., *Inorg. Chem.*, **8**, 1376 (1969).

[2] G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc., London*, 264 (1961).

[3] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc., Ser. A*, **214**, 451 (1952).

[4] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

[5] E. Sinn, Ph.D. Thesis, University of New South Wales, 1967.

[6] E. Sinn, *Coord. Chem. Rev.*, in press.

[7] E. Sinn, *Inorg. Nucl Chem. Lett.*, **5**, 193 (1969).

[8] K. Kambe, *J. Phys. Soc. Jap.*, **5**, 48 (1950).

[9] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Chem. Phys.*, **49**, 2183 (1968).

and by deviation from the theory not specifically considered in the model or Hamiltonian (eq 2). It is such limitations that must be considered in the interpretation of the magnetic properties of the tetranuclear complex **1**.

The tetranuclear spin–spin interaction model was applied to the magnetic properties[1] of acetylacetonemono(*o*-hydroxy-5-nitroanil)copper(II), **2**, the structure of which should be analogous to that of **1**. The limits of accuracy of the experimental results were not estimated, but the improvement in fit to the data, of the tetranuclear over the binuclear model, appears small in the context of the accuracy obtained with the usual methods of measuring magnetic susceptibilities. This accuracy of course depends on the particular sample size, density, and the concentration of unpaired spins, but the last two factors are unfavorable for compounds of type **1**. Although the purity of the sample was not discussed, a small concentration of paramagnetic impurities would bring the binuclear model to still closer agreement with the experimental points. The importance of paramagnetic impurities in such measurements is amply documented,[10–12] but the extent of this effect in the present complex can probably not be determined without measurements down to liquid helium temperatures. However, using the g and $N\alpha$ values obtained for **2** on the basis of the tetramer model,[1] assuming paramagnetic impurities obeying a Curie law, the data can be fitted to the binuclear model described by eq 1 (Figure 1).

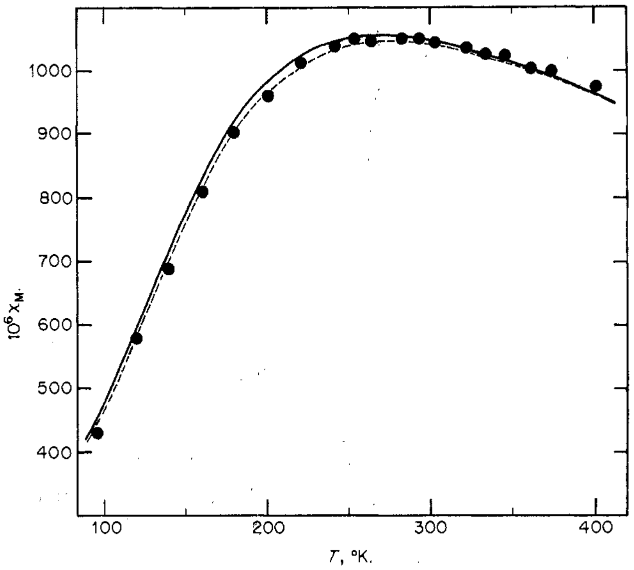

Figure 1.—Experimental data for complex **2**.[1] The full curve was calculated from eq 1 with $g = 2.33$, $N\alpha = 10^{-4}$ cgs emu, and $J = -156$ cm^{-1}, including 1.5% paramagnetic impurity of molecular weight 0.5 that of complex; the broken curve is as above but with $J = -159$ cm^{-1} and including 0.8% paramagnetic impurity of molecular weight 0.25 that of complex.

The impurities are here assumed to be cupric with the same g value, but if more strongly paramagnetic impurities are assumed, eq 1 gives a better fit for slightly lower g values. If g values significantly lower than 2.3 are used, neither the dimer nor the tetramer models fit the data as well unless non-Curie law impurities are assumed to be present.

Magnetic measurements down to liquid helium temperatures have been made on a series of complexes which are analogous to **1** and therefore also presumably weakly linked tetramers.[13] At these temperatures the magnetism should arise mainly from magnetic impurities, and the quantity of these can then be estimated. Assuming Curie law impurities, the results fit well to the dimer model, and the g values were close to 2.1 where the proportion of impurities was not too high (<0.5%). With large proportions of impurities poorer fits and a wider range of g values were obtained, which suggests that the treatment of the impurities as Curie law paramagnetics is an assumption. The largest g value obtained was 2.16 ± 0.1.

To test the high g value (2.33) obtained for complex **2** using the tetramer model,[1] esr measurements at 300 and 77°K have been carried out on the known tetrameric complex **1** and g was found to be 2.13. If complex **2** is structurally analogous to **1**, its g value should be similar. In that case neither the dimer nor the tetramer model can fit the magnetic susceptibility data well unless considerable experimental error or some kind of magnetic impurity has contributed to these data. If on the other hand, the g value of 2.33 obtained for complex **2** is real, it implies considerable orbital and hence also spin–orbit coupling contributions, which impose an additional temperature dependence upon the magnetic properties.

In considering the small differences between the tetrameric and dimeric models and their relation to complex **2**, it is unrealistic to use eq 1 and 3, in which spin–orbit coupling and all other deviations from the pure-spin model are represented by the deviation of the constant g from 2.00 and by the arbitrary constant $N\alpha$. Important factors that should be considered specifically include orbital contribution, spin–orbit coupling, the temperature dependence of exchange integrals, and long-range magnetic ordering. The effect of spin–orbit coupling may be approximated by adding $\Sigma_{i=1}{}^{n}\lambda_i\mathbf{L}_i\cdot\mathbf{S}_i$ to the Hamiltonian (2)[6] and the orbital contribution effect may be approximated by adding $\beta\Sigma_{i=1}{}^{n}(k_i\mathbf{L}_i + 2\mathbf{S}_i)\cdot\mathbf{H}$ in place of the term $g\beta\mathbf{H}\cdot\mathbf{S}_\mathrm{T}$, which would normally be added to account for the magnetic field interaction with S_T where the symbols have their usual meanings. The temperature dependence imposed by these terms is damped somewhat by the distortion term $\delta L_z{}^2$ that must also be added. Accurate calculations are being carried out, but the general effect is to increase the susceptibility at higher temperatures. This results in a better fit of the dimer model at high temperatures without improving it at lower temperatures. At the same time, the tetramer

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[10] C. M. Harris and E. Sinn, *Inorg. Chim. Acta*, **2**, 296 (1968).

[11] E. Sinn, *ibid.*, **3**, 11 (1969).

[12] K. E. Hyde, G. Gordon, and G. F. Kokoszka, *J. Inorg. Nucl. Chem.*, **30**, 2155 (1968).

[13] A. P. Ginsberg, R. C. Sherwood, and E. Koubek, *ibid.*, **29**, 353 (1967).

model no longer fits the data unless the various J values are adjusted. (If g were not 2.33, but nearer 2, the use of eq 1 or 3, without specific inclusion of orbital terms, would be a valid approximation.) Thus it appears that in the absence of magnetic impurities or experimental error, even orbital effects would not entirely account for the small deviations of the magnetic data from eq 1 (dimer model); yet the pure-spin tetramer model will account for the data, provided the high g value is overlooked. However, the tetramer model does have the advantage of multiple parameters, even when the symmetry restrictions $J_{13} = J_{24} = J_A$, $J_{23} = J_{14} = J_B$, $J_{12} = J_C$, and $J_{34} = J_D$ are applied. In addition, the effect of long-range magnetic ordering and a slight temperature dependence of the exchange integrals, which would normally be considered negligible, might be significant in the context of the small differences in χ *vs.* T curves under consideration.[3,6,14,15] Nevertheless, the parameter values that give this good fit with the tetrameric model need to be considered.

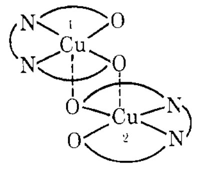
The J values obtained from a least-squares fit to the tetramer model are[1]

$$J_A = 140\ \text{cm}^{-1},\ J_B = 134\ \text{cm}^{-1},\ J_C = -48\ \text{cm}^{-1},\ J_D = 0 \qquad (4)$$

A fairly strong interaction (-48 cm^{-1}) is proposed between atoms 1 and 2, although it has previously been pointed out[16] that there is no precedent for significant interactions in this type of complex between copper atoms linked by weak Cu-O bonds (*i.e.*, significantly larger than 2.0 Å); the Cu–O bonds connecting the two dimeric units of the tetramer are very weak (2.64 Å).[4] The direct experimental evidence available to date in fact mitigates strongly against this interaction. N,N′-Ethylenebis(salicylaldimine)copper(II) (CuES), **3**, contains the same kind of Cu–O linkages connecting pairs of monomeric units to form a dimer, but the system is not complicated by any other interactions. There is evidence that coupling is similar in such structurally similar fragments whether these occur in bi- or multinuclear complexes[6,9,16–18] The linkages are stronger in **3** (2.41 Å)[19] than in **1** and acceptance of $J_C = -48$ cm^{-1} implies an even stronger interaction in **3**. Thus **3** should have magnetic susceptibility given by eq 1 with $-J \geq 48$ cm^{-1}, but experimental data shown in Figure 2 down to liquid nitrogen temperature[16,20] do not deviate very much from a Curie law equation (eq 5), so that if eq 1 is obeyed, we must have $-J$ considerably less than 10

$$\chi = \frac{Ng^2\beta^2}{4kT} \qquad (5)$$

cm^{-1} in complex **3**, which suggests an even smaller $-J_C$ value in complex **1**. The χ *vs.* T curves obtained for the tetramer with $J_C < 10$ cm^{-1} are little different from that for $J_C = 0$ so that in this case interaction between atoms 1 and 2 can be ignored in complex **1**. On the other hand there is ample evidence for strong interactions between copper atoms linked by strong Cu–O bonds of the type connecting atoms 1 and 3 in **1**.[4,9,13,16,18,21–23] Once J_C is taken as approximately zero, it is no longer necessary nor desirable to use $J_B = 134$ cm^{-1} to fit the data. Such a large ferromagnetic interaction seems improbable between atoms as remote from one another as 1 and 4, although there is no direct experimental evidence against it. The existence of pairwise ferromagnetic interactions has in fact been suggested in the binuclear copper(II) complexes $[(4\text{-NO}_2\text{-C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$[7] and $[(\text{C}_5\text{H}_5\text{NO})_2\text{Cu}(\text{NO}_3)_2]_2$,[1] although in the latter case, the magnetic moment values do not suggest ferromagnetism and the linking Cu–O bonds are rather weak (2.4 Å).[24]



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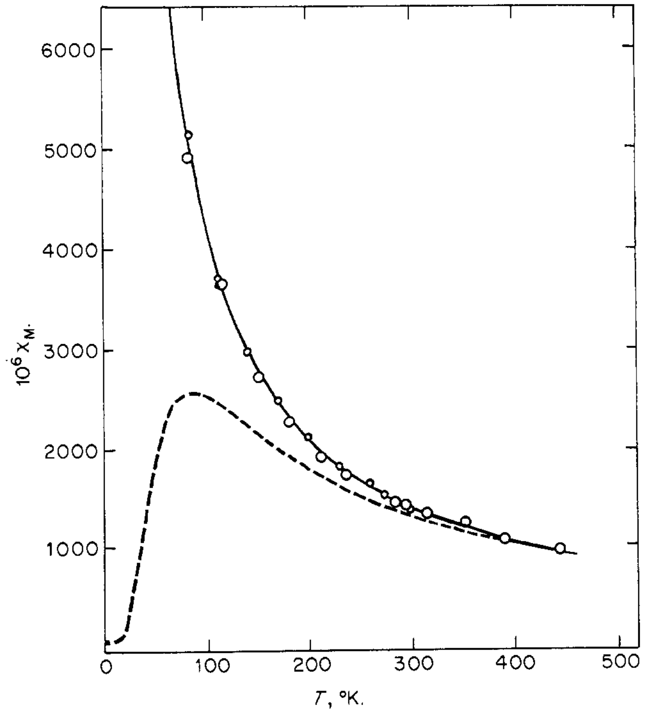

Figure 2.—Experimental data for CuES: O, ref 16; ₒ, ref 20. The full curve was calculated from eq 5 with $g = 2.13$; the broken curve, from eq 1, using $g = 2.13$, $J = -48$ cm^{-1}, and $N\alpha = 10^{-4}$ cgs emu (*cf.* ref 1).

It now seems probable that g is less than 2.33 and

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(14) A. Mookherji and S. C. Mathur, *J. Phys. Soc. Jap.*, **18**, 977 (1963).

(15) B. C. Guha, *Phil. Mag.*, **11**, 175 (1965); **13**, 619 (1966).

(16) S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Chem.*, **7**, 268 (1968).

(17) S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).

(18) E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969).

(19) D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).

(20) J. Lewis and R. A. Walton, *ibid.*, *A*, 1559 (1966).

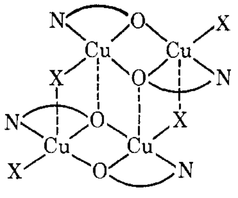
(21) J. C. Morrow, H. L. Schafer, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(22) S. J. Gruber, C. M. Harris, E. Kokot, S. L. Lenzer, T. N. Lockyer, and E. Sinn, *Aust. J. Chem.*, **20**, 2403 (1967), and references given.

(23) G. F. Kokoszka and H. C. Allen, Jr., *J. Chem. Phys.*, **46**, 3013 (1967).

(24) S. Scavinar and B. Matkovic, *Chem. Commun.*, 217 (1967).

that J_C and J_B are small so that eq 3 collapses to eq 1. Thus, on the evidence available, the dimer model seems better than the tetramer and should not be discarded. The validity of the binuclear model is also important in the treatment of the antiferromagnetism of salicylaldimine complexes of copper halides, **4**, for which a weakly linked tetrameric structure was suggested although a binuclear interaction model was generally considered to be adequate.[18,25]



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(25) C. M. Harris, J. M. James, P. J. Milham, and E. Sinn, *Inorg. Chim. Acta*, **3**, 81 (1969).

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RECEIVED DECEMBER 2, 1969

Exchange Coupling Constants for Tetrametallic[1] Complexes[2]

Sir:

Sinn[3] has presented an analysis of the four-center exchange-coupled model which we[4] have suggested is appropriate for the description of the magnetic properties of the tetrametallic Schiff base complexes related to acetylacetonemono(*o*-hydroxyanil)copper(II). The tetrameric structure of the molecule was carefully described by Barclay and Hoskins[5] although the substance was called a dimer in the text of their paper and in the preliminary communication[6] of the magnetism and structure. This description has persisted.[7,8] It is common practice to ignore the out-of-plane copper–ligand interactions in the commonly seen "4 + 1" and "4 + 2" coordination of square-planar copper,[9] and it appears that it is this oversight which has led Sinn to his conclusions. It is our contention based on a variety of spectral and magnetic data[10] that such out-of-plane interactions cannot be ignored and that their neglect leads to a model which may be able crudely to account for the temperature variation of magnetism but which is fully incapable of describing the true nature of the magnetic interactions.

There are, of course, difficulties with the tetramer model, and it is accepted[11] that coupling constants derived from a model which neglects other important effects such as the orbital contribution to the magnetism and spin–orbit coupling are only first approximations. As Sinn[3] has pointed out, inclusion of these effects results in a proliferation of parameters and fitting processes become meaningless. These limitations, as originally noted by Kambe[12] in his early work on trimetallic chromium and iron carboxylates, do not render the treatment invalid but rather stimulate efforts toward the solution of the concomitant problems.

The evidence offered by Sinn in his critique concerns the dimer N,N′-ethylenebis(salicylaldimine)copper(II).[13] He noted that the "direct experimental evidence available . . . mitigates strongly against the tetranuclear (*sic*) model." We believe this statement to be premature since there are distinct structural and electronic differences between the two, and there are no empirical bases to guide or assess the transferability of coupling constants between molecules. In N,N′-ethylenebis(salicylaldimine)copper(II), the oxygen atom bridging the two copper(II) ions is bonded to only one other atom and has an unused lone pair of electrons, while in the tetramer acetylacetonemono(*o*-hydroxyanil)copper(II), the bridging oxygen atom is bonded to two other atoms (a third copper(II) ion and a carbon atom of the phenol ring). In addition there are structural differences[13a] in the four-member copper–oxygen ring which may have an important bearing on the mechanism of the magnetic interactions.

Detailed studies of copper complexes with out-of-plane "4 + 1" or "4 + 2" interactions are rare. Investigations which are germane to this discussion include that by Blumberg and Peisach,[14] who have shown that pairs of copper(II) ions in 3-ethoxy-2-ketobutyraldehydebis(thiosemicarbazone)copper(II) are exchange coupled giving a singlet ground state with a singlet–triplet splitting energy of 16 cm^{-1}. In this example, the square-planar complexes are linked into pairs by "4 + 1" coordination of the copper(II) ion to a sulfur atom in the adjacent molecule, and the out-of-plane copper–sulfur distance is 3.1 Å. Also, it has been shown[15] using low-temperature magnetic susceptibility measurements and electron paramagnetic resonance that the dimer $Cu_2(C_5H_5NO)_4(NO_3)_4$, which has structural features[16] in common with N,N′-ethylenebis(salicylaldimine)copper(II) and an out-of-plane Cu–O sep-

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[1] Henceforth, metal complexes containing two or more metal ions will be referred to as dimetallic, trimetallic, etc., instead of the more commonly used terms of dinuclear, trinuclear, ... Each atom in the complex has a nucleus and, consequently, the latter terms lack definition. In the context of this work the metal ions are, in most cases, the focus of attention, and the terms dimetallic, trimetallic, . . . , are more appropriate.

[2] We are grateful for support of this research by the National Science Foundation under Grant GP-7400.

[3] E. Sinn, *Inorg. Chem.*, **9**, 2376 (1970).

[4] W. E. Hatfield and G. W. Inman, *ibid.*, **8**, 1376 (1969).

[5] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

[6] G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc., London*, 264 (1961).

[7] M. Kato, H. B. Jonassen, and J. O. Fanning, *Chem. Rev.*, **64**, 99 (1964).

[8] W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, **5**, 47 (1969).

[9] For example, see R. D. Willett, *J. Chem. Phys.*, **41**, 2243 (1964).

[10] See, for example, I. M. Procter, B. J. Hathaway, and P. Nicholes, *J. Chem. Soc. A*, 1678 (1968).

[11] R. L. Martin, "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968.

[12] K. Kambe, *J. Phys. Soc. Jap.*, **5**, 48 (1950).

[13] (a) D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960) (structure); (b) J. Lewis and R. A. Walton, *ibid., A*, 1559 (1966) (magnetism).

[14] W. E. Blumberg and J. Peisach, *J. Chem. Phys.*, **49**, 1793 (1968).

[15] W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and E. R. Jones, Jr., *J. Amer. Chem. Soc.*, **92**, 4982 (1970). .

[16] S. Scavinar and B. Matkovic, *Chem. Commun.*, 217 (1967).