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.

Acknowledgment. The generous financial assistance of the Natural Sciences and Engineering Research Council of Canada's Strategic Energy Programme is greatly appreciated. In addition, J. G. McCaffrey expresses his gratitude for a University of Toronto Open Scholarship.

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 Recent unpublished research by R. Pearson and P. Barrett also appears to support the view that it is Fe atoms and not Fe_2 that react with CH_4 (private communication).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.

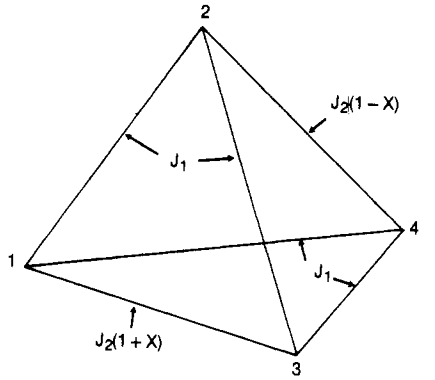

Figure 1. Coupling constants of the copper tetrahedron.

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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produce the experimental data remarkably well. In our opinion such a model provides at least as good an explanation of the behavior of the system as any other. The best fits to Wong's data are presented in Table I and plotted in Figure 3. Fits to the other data are discussed briefly below.

The Heisenberg Model

The Heisenberg exchange Hamiltonian for a regular tetrahedron of spin $^1/_2$ atoms can be written

$$H = -J[S(S + 1) - 3]$$

$$(\text{where } S = S_1 + S_2 + S_3 + S_4 = \text{total spin})$$

This yields a moment that is a monotonic function of temperature. To reproduce behavior involving a $\mu_{\max}$ with an isotropic Hamiltonian, more than one exchange parameter, J, must be introduced.

A distortion of the copper tetrahedron from T_d symmetry would be expected to produce more than one J. Consider distortions from J = constant as shown in Figure 1. These pairwise distortions occur along the "E" vibrational normal mode. Such a distortion does not conflict with available X-ray data,[7,14] which show the copper tetrahedron to be approximately T_d and to have thermal anisotropies that are not unusual, since: (a) a fluxionality of the distortion about the degenerate "E" mode, i.e., through the various possible pairwise distortions, might be expected to occur, leading to the mean copper positions being approximately T_d, and (b) even a very small distortion may be enough to produce the large differences in intramolecular J values invoked below. Melnik[15] showed that for binuclear copper complexes a change of 0.1 Å in the Cu–Cu distance was associated with a change of ~200 cm^{-1} in J. There is no reason to suppose the tetranuclear complexes discussed here are any less sensitive to distortion; indeed, they may be more sensitive as the two possible exchange pathways (Cu–O–Cu, Cu–X–Cu) could be affected differently by a distortion. A motion of, e.g., 0.1 Å lies well within the thermal ellipsoids of the Cu atoms.

A variety of exchange mechanisms might be postulated. One possibility is that the coupling constants may result from ferromagnetic interactions via orthogonal chlorine p orbitals and antiferromagnetic interactions through Cu–O–Cu bridges, as expected for a bond angle of 109°.[15]

In Figure 1, $X = 0$ corresponds to equal pairwise distortions from J = constant, D_{2d} symmetry; $X \neq 0$ corresponds to unequal pairwise distortions, C_{2v} symmetry, and splitting of the E vibrational mode. Such distortions might be expected to occur since the free energy of the system would be reduced by removing the degeneracy of the spin state associated with a regular tetrahedron.

The Hamiltonian for this system can be written

$$H = -J_1[S^2 - 3] - [J_2(1 + X) - J_1][(S_O{}^2 - 1.5)] - [J_2(1 - X) - J_1][(S_E{}^2 - 1.5)]$$

where $S = S_1 + S_2 + S_3 + S_4$, $S_O = S_1 + S_3$, and $S_E = S_2 + S_4$ are all good quantum numbers; i.e., S^2, $S_O{}^2$, and $S_E{}^2$ commute with H. Specifying S, S_O, and S_E uniquely defines an eigenstate of the Hamiltonian which will be represented by the notation $|S,S_O,S_E\rangle$ and which has the energy given by

$$E(|S,S_O,S_E\rangle) = -J_1[S(S + 1) - 3] - [J_2(1 + X) - J_1] \times [S_O(S_O + 1) - 1.5] - [J_2(1 - X) - J_1][S_E(S_E + 1) - 1.5]$$

The six spin states and energies for H are thus

$$|2,1,1\rangle = -2J_1 - J_2 \qquad |1,1,1\rangle = +2J_1 - J_2$$
$$|1,1,0\rangle = +J_2(1 - 2X) \qquad |1,0,1\rangle = +J_2(1 + 2X)$$
$$|0,1,1\rangle = +4J_1 - J_2 \qquad |0,0,0\rangle = +3J_2$$

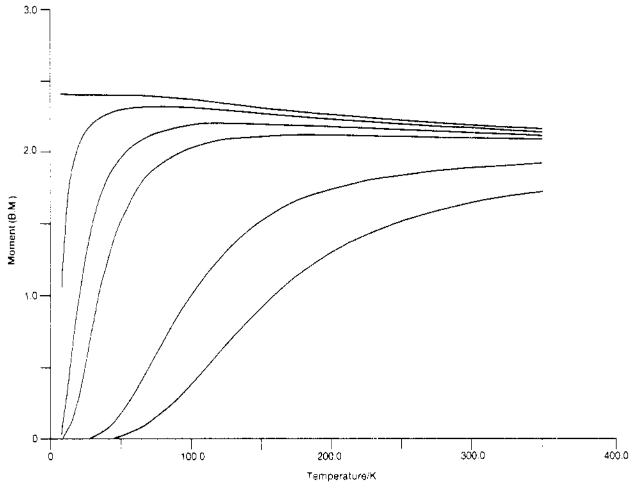

Figure 2. Effective magnetic moments plotted as a function of temperature calculated with use of the Heisenberg model with J_1 = 200 cm^{-1}, g = 2.15, X = 0, and, from top to bottom, J_2 = −100, −102, −106, −112, −160, and −200 cm^{-1}.

Note that the parameter X only affects the triplet states $|1,0,1\rangle$ and $|1,1,0\rangle$, which are degenerate for $X = 0$.

Magnetic behavior involving a $\mu_{\max}$ is predicted by this model if the ground state is a singlet with the other singlet state thermally accessible only at high temperatures. This situation arises if J_1 is positive and $J_2/J_1 < -0.5$. If in addition $X = 1$, a triplet state becomes degenerate with the ground state. Figure 2 shows the theoretical predictions for $\mu(T)$ as J_2 is changed from −100 to −200 cm^{-1} for J_1 = 200 cm^{-1}, g = 2.15, and X = 0.

Discussion of Results

A comparison of data published for $(NMe_4)Cu_4OCl_{10}$[10-12] and for $Cu_4OBr_6(py)_4$[10,12] indicates that experimental error in many of the data for these copper tetramers is quite large. In particular, both Wong's[12] and Lines'[10] data show discontinuities near T = 80 K, where the method used to measure μ was changed. Wong's data rise sharply as T is increased near 80 K while Lines' data fall sharply in the same temperature region. The large discrepancies between data for the same compound suggest that there is little point in trying to choose between theoretical models solely on the basis of fits to available experimental results. All that can be done, until more accurate results are obtained, is to show that the Heisenberg model fits the data as well as any other.

The experimental data were fitted with use of a least-squares program. The fits were found to be extremely insensitive to either J_1 or J_2 alone but very sensitive to the quantity $J_1 + 2J_2$. For example, Wong's data for $Cu_4OCl_6(pyo)_4$ are fitted comparably well by each of the following J_1, J_2 parameter sets: 150, −76; 210, −106; 270, −136 cm^{-1}. $J_1 + 2J_2$ = −2 cm^{-1} in every case. Because of this and the experimental difficulties mentioned above the magnitude of J_1 must be regarded as qualitative only. Similarly the fits are extremely insensitive to X except when $X \simeq 1$, in which case a triplet lies near the ground state. Despite these difficulties visual comparisons of the fits in Figure 3 with those in ref 10 and 12 show that the fits using the Heisenberg model are at least as good as those using the orbitally degenerate model.

The complexes apparently fall into two discrete groups, those with a triplet near the ground state ($X \simeq 1$) and those without such a low-lying triplet state. No explanation of this seems possible at this time; the existence of the two groups may be associated with details of the mechanism and rate of the fluxionality of the distortion. It is hoped to discuss this aspect in more detail in a later work.

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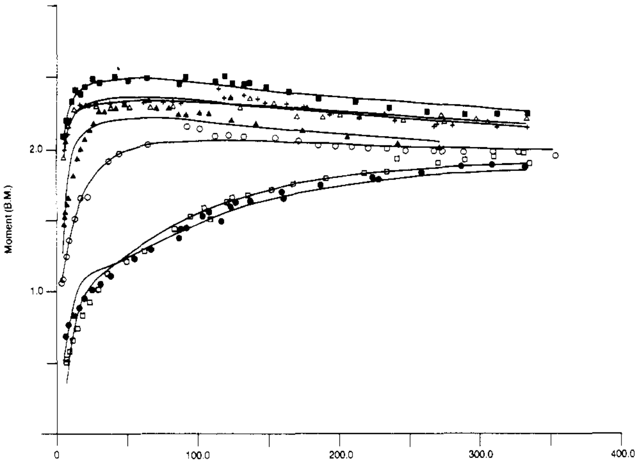

Figure 3. Effective magnetic moments plotted as a function of temperature for the $[Cu_4OX_6L_4]$ complexes of ref 12. The smooth curves are the best fits to the Heisenberg model with parameters listed in Table I. In order of increasing theoretical moment at 200 K, the following X, L pairs are shown: Cl, Br (●); Cl, Cl (□); Br, py (○); Cl, tmu (▲); Cl, pyo (+); Cl, Me_2SO (△); Br, Me_2SO (■).

A striking feature of all the fits is that $J_1 + 2J_2$ is always small and negative. This corresponds to a singlet ground state with a low-lying quintet. The ferromagnetic interactions invoked with use of the Heisenberg model are larger than those of the orbitally degenerate model. As a consequence Wong's unusually high *g* values are replaced by values lying in a more normal range.

The data for $Cu_4OCl_6(3\text{-quin})_4$[7] cannot be fitted to a strict Heisenberg model. This compound is exceptional in that it has $\mu_{max} > 2.6\ \mu_B$, significantly larger than is usual for these compounds, strongly suggesting a quintet ground state with no low-lying low-spin states. This and the fact that the intercluster model fits the experimental results extremely well for zJ' as small as 0.316 cm^{-1} (cf. 2–8 cm^{-1} typical for the model)[10] indicate that in this case intercluster exchange is probably the most important factor involved in the low-temperature magnetic behavior. All other data considered give acceptable fits to the simple Heisenberg model.

In view of the extreme sensitivity, with this model, of $\mu(T)$ to small changes in the ratio $J_2{:}J_1$, it is expected that, until an even larger range of results than is at present available is obtained, correlation between the chemical nature of the substituents on the Cu_4O tetrahedron and the magnetic behavior will be extremely difficult.

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Dehydration of Aldoximes at Ruthenium(II) Centers[1]

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Several examples of enhanced reactivity of N-bonded ligands on Ru(II) and Ru(III) centers are known.[2] In most of the previous cases the reactions involve a net change in the oxidation state of the ruthenium or the nitrogen *atom*, making it difficult to independently assess the contribution of dπ–π^* back-bonding to the overall driving force.

Table I. Spectral Properties of Reaction Products from $Ru(NH_3)_5H_2O^{2+}$ + HON=CHR

R	ν(C≡N),[a] cm^{-1}	$\lambda_{max}(\epsilon)$,[b] nm
CH_3	2250	229 (15 400)
C_6H_5	2185	376 (8100)
2-C_4H_4N	2180	408 (10 120) 505 (12 100)[c]
3-C_4H_4N	2175	398 (8425) 460 (7326)[d]
4-C_4H_4N[e]	2175	522 (...); 425 (...) 528 (...)[d]
4-C_4H_4N[f]	2180	425 (8965) 535 (13 100)[d]

[a] ClO_4^- salts. [b] In aqueous solution. [c] In 2 M HCl. [d] In 1 M HCl. [e] [oxime]/[Ru] ≈ 2.0. [f] [oxime]/[Ru] ≃ 10.

We report here a case in which ligand substitution is following by rapid dehydration with no redox change.

Experimental Section

$[Ru(NH_3)_5Cl]Cl_2$ was prepared[3] from $RuCl_3{\cdot}nH_2O$. Oximes were used as purchased or prepared by reacting the appropriate aldehyde with hydroxylamine. Aldoximes (HON=CHR) used in this study has R = CH_3, C_6H_5, and 2-, 3-, and 4-pyridyl. Reactions with pyridinecarboxaldoxime were carried out in 0.1 M $HC_2F_3O_2$, deionized water, and 0.2 M NaOH.

In a typical reaction, 100 mg (0.34 mmol) of $[Ru(NH_3)_5Cl]Cl_2$ was converted to $Ru(NH_3)_5OH_2^{3+}$(aq) by base hydrolysis or treatment with $AgCF_3COO$.[4] A twofold to tenfold molar excess of oxime was added and the final volume adjusted to 6 mL. The solution was degassed with argon for 15 min and amalgamated Zn added to initiate the reaction. The reaction proceeded for 45 min, during which time aliquots were removed to monitor reaction progress, after which the reaction mixture was filtered and treated with saturated aqueous $NaClO_4$. The products were isolated by filtration, washed successively with ethanol and ether, and air-dried. Solid-product yields were in the range of 60–70% of the theoretical values.

Products were characterized by electronic (Cary 15) and infrared (Pye-Unicam) spectral properties.

Results

Solution Spectra. The reduction of $Ru(NH_3)_5OH_2^{3+}$ in the presence of oxime leads to a gradual color change, which was complete within 45 min. The solution spectra of all the reaction mixtures except the CH_3C=NOH reaction showed strong absorptions in the visible region of the electronic spectra. With the 4-pyridinecarboxaldeoxime, the visible spectrum of the final solution was dependent on initial oxime concentration: at high oxime concentration a single peak (H^+ dependent) was observed, while at low oxime concentration an additional peak (H^+ independent) occurs. During the course of the reactions no intermediate species were detected.

Spectral Properties of Isolated Products. Infrared. The infrared spectral properties of the isolated solids all showed strong peaks in the 2100–2250-cm^{-1} region of the spectrum. These peaks are characteristic of nitrile ligands coordinated to ruthenium(II) centers. Other peaks characteristic of ruthenium(II) ammine compounds are present at ~1280 cm^{-1}.[2b,5] Spectral properties of the products obtained from the reaction of pyridinecarboxaldoximes were virtually independent of solvent medium.

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