

EPR Spectra of and Exchange Interactions in Trinuclear Complexes. 2. Metal(II) Adducts of Tetradentate Schiff Base Copper(II) Complexes¹

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The single-crystal EPR spectra of $(\text{CuSALen})_2\text{Cu}$, bis[(*N,N'*-ethylenebis(salicylaldiminato))copper(II)]copper(II) diperchlorate trihydrate, and $(\text{CuHAPen})_2\text{Cu}$, bis[(*N,N'*-ethylenebis(*o*-hydroxyacetophenone iminato))copper(II)]copper(II) diperchlorate dihydrate, have been recorded at 4.2 K with the aim of relating the *g* tensor of the triad of copper(II) ions to the *g* tensors of the individual ions. For this purpose, formulas have been obtained for the general cases of three different J_{ij} values. Reasonable agreement with experiment was found for $(\text{CuHAPen})_2\text{Cu}$, while much less satisfactory results were obtained for $(\text{CuSALen})_2\text{Cu}$. The role of intermolecular exchange in complicating the interpretation of the experimental data is discussed. The EPR spectra of the corresponding zinc(II) adducts are also reported and discussed.

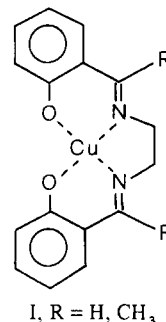
Introduction

We have recently started a project of characterizing the exchange interactions in trinuclear complexes that on the whole are much less understood than the interactions in dinuclear complexes. For instance, the magnetic susceptibility data of trinuclear species in which the metal ions are to a good approximation equivalent, e.g. lying on the vertices of an equilateral triangle,^{3,4} could be interpreted by using an asymmetric arrangement of the metal ions.^{3,5-9} Recent suggestions attribute this behavior to the necessity to include either higher order spin-spin interactions^{10,11} or antisymmetric exchange terms into the effective spin Hamiltonian,¹² but the problem does not yet appear to be well-defined.

Another field where the debate is still open is that of relating the spin Hamiltonian parameters (*g*, *A*, *D*, ...) observed for the triad of metal ions to the corresponding parameters of the individual metal ions. For instance both positive and negative iron hyperfine splitting was found in magnetically perturbed Mössbauer spectra of 3Fe-3S proteins, which were accounted for by allowing for different J_{ij} coupling constants.¹³ In another case we found that the *g* values of octachlorodideneumtriacopper(II) tetrahydrate ($\text{Cu}_3(\text{ade})_2\text{Cl}_8$) are temperature dependent and attributed this behavior to a Boltzmann population of the spin multiplets of the triad.¹

Although these interpretations appear to be rational, it would be desirable to have more information on the spin Hamiltonian parameters of the individual ions to fully support the proposed relations.

In order to collect more experimental data on simple compounds the series of trinuclear copper(II) complexes of general formula¹⁴ $\text{M}(\text{CuL})_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$, obtained as adducts of copper(II) ions with some tetradentate Schiff base metal(II) complexes (I), was considered (*M* = Zn, Cu). For the copper



compounds, crystal structure determinations and variable-temperature magnetic susceptibility data are available.¹⁴⁻¹⁶ Furthermore, the spin Hamiltonian parameters of the moieties (I) are reasonably well-known.¹⁷ The central copper ions in the triad achieve either five- or six-coordination by interacting with two CuL moieties (I) and one or two water molecules, respectively.

Experimental Section

The $(\text{CuSALen})_2\text{Cu}$ (bis[(*N,N'*-ethylenebis(salicylaldiminato))copper(II)]copper(II) diperchlorate trihydrate), $(\text{CuHAPen})_2\text{Cu}$ (bis[(*N,N'*-ethylenebis(*o*-hydroxyacetophenone iminato))copper(II)]copper(II) diperchlorate dihydrate), $(\text{CuSALen})_2\text{Zn}$ (bis[(*N,N'*-ethylenebis(salicylaldiminato))copper(II)]zinc(II) diperchlorate hydrate), and $(\text{CuHAPen})_2\text{Zn}$ (bis[(*N,N'*-ethylenebis(*o*-hydroxyacetophenone iminato))copper(II)]zinc(II) diperchlorate) were prepared according to the general procedure previously reported.¹⁸

Single crystals were grown by slow evaporation of nitromethane/chloroform solutions of the complexes.

The crystals have been found to conform to the reported X-ray crystal structure with a Philips PW1100 automatic diffractometer. The $(\text{CuSALen})_2\text{Cu}$ crystals have a monoclinic cell,¹⁶ of space group $P2_1/n$, with $a = 15.49 \text{ \AA}$, $b = 21.88 \text{ \AA}$, $c = 10.88 \text{ \AA}$, $\beta = 94.28^\circ$, and $Z = 4$, and the well-developed faces are (010), (0 $\bar{1}$ 0) and (001), (00 $\bar{1}$).

The $(\text{CuHAPen})_2\text{Cu}$ crystals have an orthorhombic cell,¹⁶ space group $Pbca$, $a = 26.88 \text{ \AA}$, $b = 19.09 \text{ \AA}$, $c = 15.74 \text{ \AA}$, and $Z = 8$, and the well-developed faces are (100), ($\bar{1}$ 00) and (010), (0 $\bar{1}$ 0).

ESR spectra at X- (9 GHz) and Q-band (35 GHz) frequencies in the range 77-300 K were recorded with a Varian E-9 spectrometer equipped with a standard variable-temperature accessory. X-Band spectra at 4.2 K were obtained with an Oxford Instrument ESR9 continuous-flow cryostat.

Results

$(\text{CuSALen})_2\text{Zn}$. The polycrystalline powder ESR spectra of $(\text{CuSALen})_2\text{Zn}$ at Q-band frequency at 77 K are shown in Figure 1. They are very similar at both X- and Q-band

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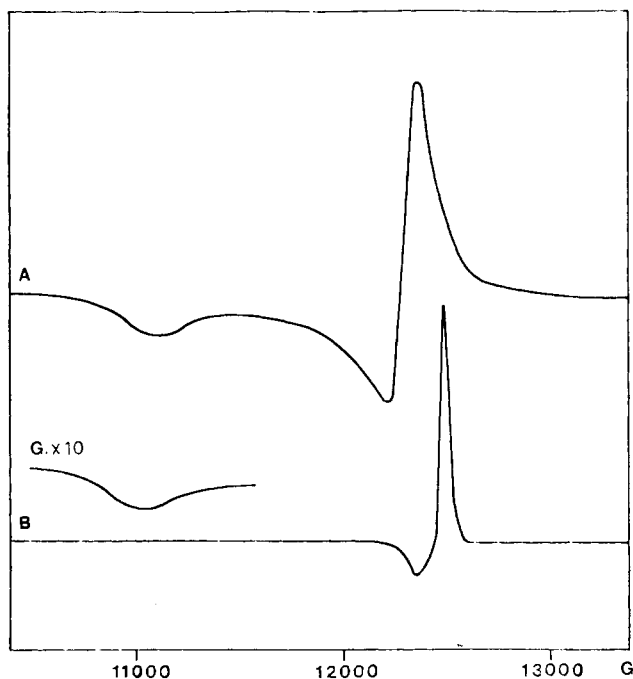


Figure 1. Polycrystalline powder EPR spectra at Q-band frequency (34.84 GHz) and 77 K: (A) $(\text{CuHAPen})_2\text{Zn}$; (B) $(\text{CuSALen})_2\text{Zn}$.

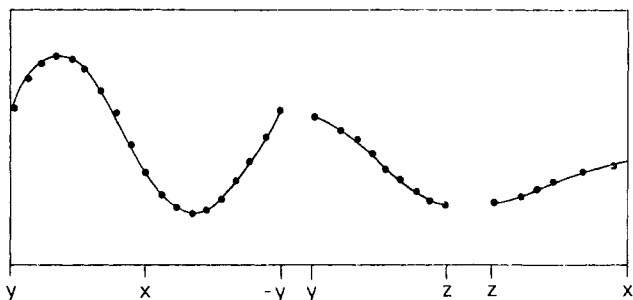


Figure 2. Angular dependence of g^2 values for $(\text{CuSALen})_2\text{Zn}$.

frequencies and do not show any dramatic dependence on temperature. They can be interpreted with an $S = 1/2$ spin Hamiltonian with $g_{\parallel} = 2.17$ and $g_{\perp} = 2.05$. The fact that no hyperfine is resolved at liquid-helium temperature is indicative that the compound remains paramagnetic down to 4.2 K. Single-crystal ESR spectra were recorded at room temperature. The crystals are monoclinic, but only one signal was detected for each orientation, indicating substantial intermolecular exchange interactions. The angular dependence of the g^2 values is given in Figure 2. The principal values are $g_1 = 2.167$, $g_2 = 2.050$, and $g_3 = 2.043$. Since the crystal structure is not known, it is not possible to orient the g tensor in the molecular frame. The linewidth is very anisotropic, having a maximum parallel to the highest g value. Since the latter corresponds to g_{\parallel} , it is expected to have the largest copper hyperfine, so that the anisotropic line width is probably due to unresolved hyperfine.

$(\text{CuHAPen})_2\text{Zn}$. The polycrystalline powder ESR spectra of $(\text{CuHAPen})_2\text{Zn}$ at Q-band frequency at 77 K are shown in Figure 1. They can be interpreted with an $S = 1/2$ spin Hamiltonian with $g_{\parallel} = 2.16$ and $g_{\perp} = 2.05$. The liquid-helium temperature X-band spectra show a copper hyperfine pattern with seven lines yielding $A_{\parallel} \approx 90$ G. The fact that a hyperfine is resolved may be indicative of magnetic dilution occurring at low temperature.

$(\text{CuSALen})_2\text{Cu}$. The polycrystalline powder ESR spectra of $(\text{CuSALen})_2\text{Cu}$ are very temperature dependent as shown in Figure 3. At room temperature and at 77 K a single very broad feature is observed centered at $g \approx 2.1$ that gradually

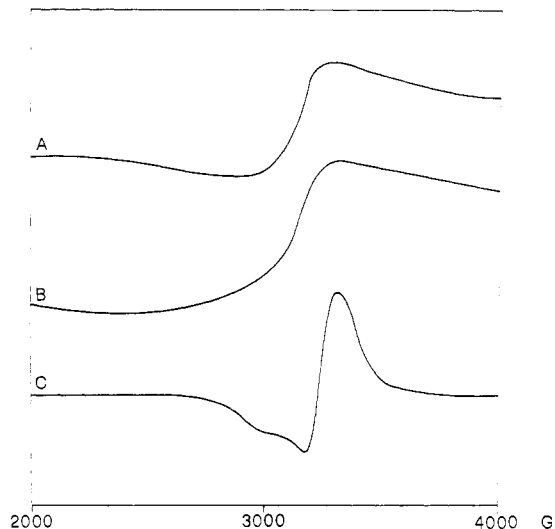


Figure 3. Polycrystalline powder EPR spectra at X-band frequency (9.1 GHz) of $(\text{CuSALen})_2\text{Cu}$ at (A) 300 K, (B) 77 K, and (C) 4.2 K.

narrows, until at liquid-helium temperature an axial $S = 1/2$ spectrum with $g_{\parallel} = 2.18$ and $g_{\perp} = 2.02$ is resolved. Similar behavior is observed at Q-band frequency.

Single-crystal spectra were recorded at 4.2 K and X-band frequency. Only one signal was recorded for each crystal orientation showing that intermolecular exchange is operative. The principal g values are $g_1 = 2.18$, $g_2 = 2.01$, and $g_3 = 2.00$. g_1 is parallel to $c^* = a \times b$, g_2 is parallel to b , and g_3 is parallel to a . Also in this case the line width is very anisotropic, showing a maximum parallel to g_1 .

$(\text{CuHAPen})_2\text{Cu}$. The polycrystalline powder ESR spectra of $(\text{CuHAPen})_2\text{Cu}$ show a much less intense dependence on the temperature as compared to those of $(\text{CuSALen})_2\text{Cu}$. The spectra are axial with $g_{\parallel} = 2.13$ and $g_{\perp} = 2.04$.

Single-crystal spectra were recorded at both liquid-nitrogen and liquid-helium temperature, by rotating in the (100), (010), and (001) planes. Only one signal was recorded for each crystal orientation showing that intermolecular exchange is operative. The principal g values are found parallel to the crystal axes, as required for exchange narrowed signals. The values at 4.2 K are $g_a = 2.139$, $g_b = 2.042$, and $g_c = 2.044$. The values at 77 K are identical within error.

Discussion

Cu-Zn-Cu Complexes. The temperature dependence of the magnetic susceptibility of $(\text{CuSALen})_2\text{Zn}$ ¹⁸ shows that a weak antiferromagnetic coupling between the copper atoms is operative. The EPR data are in agreement with these results since signals are observed down to 4.2 K. For the $(\text{CuHAPen})_2\text{Zn}$ complex copper hyperfine is resolved at 4.2 K showing that also in this complex the copper atoms are antiferromagnetically coupled and that the energy difference between the singlet and triplet states is presumably larger than in $(\text{CuSALen})_2\text{Zn}$.

The ESR spectra of both complexes can be interpreted by using a $S = 1/2$ spin Hamiltonian showing that the zero-field splitting of the $S = 1$ spin state originating by either the exchange or dipolar interactions¹⁹ between the copper ions must be small. Since the crystal structure of these complexes is not known, it is not possible to calculate the dipolar contributions to the zero-field splitting. In any case, with use of the geometrical coordinates found in the structure of the

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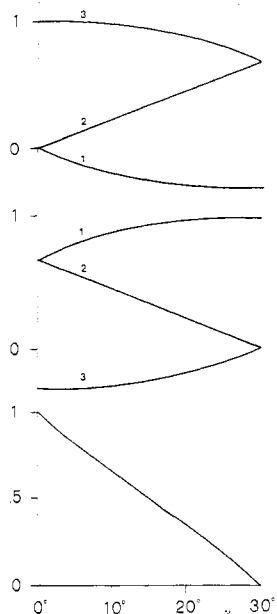


Figure 4. Dependence on γ of (bottom) R , (middle) the coefficients of g_1 , g_2 , and g_3 for g_- , and (top) the coefficients of g_1 , g_2 , and g_3 for g_+ . γ , R , g_+ , and g_- are defined in eq 2-4.

corresponding Cu-Cu-Cu complexes, D_{dip} , which is expected to be parallel to the copper-copper direction,^{17,20} is evaluated as 19 and 38 G for the SALen and HAPen derivatives, respectively.

With these small values it is conceivable that the spectra, which show rather broad lines, are very similar to those of doublet spectra and do not give evidence of a triplet state.

The g values compare well with those reported for monomeric CuSALen²⁹ ($g_{\parallel} = 2.192$, $g_{\perp} = 2.042$) as is expected for two weakly coupled equivalent copper ions.^{22,23}

The small deviations from the single ion value are presumably due to the misalignment of the two CuSALen moieties in the trinuclear units. Similar considerations hold also for $(\text{CuHAPen})_2\text{Zn}$. It is interesting to note that the average g values are very similar in the mononuclear (2.092) and in the trinuclear species (2.087) supporting this interpretation.

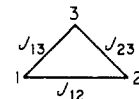
Cu-Cu-Cu Complexes. The spectra of $(\text{CuSALen})_2\text{Cu}$ at high temperature are very broad. In principle the broadening might be due to either inter- or intramolecular exchange phenomena. The fact that nitromethane solutions of the complex show reasonably narrow NMR signals at room temperature²⁴ seems to indicate that the high-temperature broadening is of intramolecular nature, due to the thermal population of the two doublet and the quartet spin states.

A confirmation of this interpretation comes from the fact that the EPR spectra at liquid-helium temperature, where only the lowest doublet is populated, are exchange narrowed by intermolecular interactions and not broadened. Further, in the analogous $(\text{CuHAPen})_2\text{Cu}$ complex, where magnetic susceptibility data showed a much larger exchange interaction ($J = 380$ against $J = 86 \text{ cm}^{-1}$),^{14,15} the lines are much narrower at high temperature.

The broad lines observed at high temperature do not allow us to recognize whether a temperature dependence of the g values, as found in $\text{Cu}_3(\text{ade})_2\text{Cl}_8$ is operative also in this case.

No temperature dependence of the g values was observed for $(\text{CuHAPen})_2\text{Cu}$ in the range 77–4.2 K.

The observed g values and directions must be referred to the individual g tensors of the three copper moieties. For this purpose the expressions were previously reported for a linear symmetric complex.¹ Since in this case there is no symmetry in the triads, it is useful to derive expressions for the g values in the general case, i.e. when the three exchange coupling constants J_{12} , J_{23} , and J_{13} are all different from each other.



The three $S = 1/2$ spins are coupled to give one quartet and two doublets, which are admixed. The energies of the doublets can be expressed^{25,26} as

$$E_{\pm} = -\frac{1}{4}(J_{23} + J_{13} + J_{12}) \pm \frac{1}{2}(J_{23}^2 + J_{13}^2 + J_{12}^2 - J_{12}J_{23} - J_{12}J_{13} - J_{13}J_{23})^{1/2} \quad (1)$$

and the corresponding g values are given by

$$g_{+} = 2 \left(\frac{\sin^2 \gamma}{3} - \frac{\sin \gamma \cos \gamma}{3^{1/2}} \right) g_1 + 2 \left(\frac{\sin^2 \gamma}{3} + \frac{\sin \gamma \cos \gamma}{3^{1/2}} \right) g_2 - \left(\frac{\sin^2 \gamma}{3} - \cos^2 \gamma \right) g_3 \quad (2)$$

$$g_{-} = 2 \left(\frac{\cos^2 \gamma}{3} + \frac{\sin \gamma \cos \gamma}{3^{1/2}} \right) g_1 + 2 \left(\frac{\cos^2 \gamma}{3} - \frac{\sin \gamma \cos \gamma}{3^{1/2}} \right) g_2 - \left(\frac{\cos^2 \gamma}{3} - \sin^2 \gamma \right) g_3 \quad (3)$$

where

$$\gamma = \frac{1}{2} \tan^{-1} \frac{3^{1/2}(J_{23} - J_{13})}{J_{23} + J_{13} - J_{12}}$$

and + and - refer to the states that are described as $|1/2, (1)\rangle$ and $|1/2, (0)\rangle$, respectively, in the limit of symmetric trinuclear complexes.

In the present case, if the external copper atoms are labeled 1 and 2, it may be assumed that J_{12} is small, as shown by the magnetic and ESR data of $(\text{CuSALen})_2\text{Zn}$ and $(\text{CuHAPen})_2\text{Zn}$; therefore, γ can be expressed as a function of the ratio of the J_{23} and J_{13} constants:

$$\gamma = \frac{1}{2} \tan^{-1} \left(\frac{3^{1/2} \frac{1 - R}{1 + R}}{R} \right) \quad R = J_{13}/J_{23} \quad (4)$$

Since the expressions (2) and (3) have ternary symmetry, it will be only necessary to consider values ranging from 0 to 30° , higher values corresponding merely to a renaming of the atoms. In Figure 4 are shown the coefficients for g_{\pm} and the value of R as a function of γ . For $\gamma = 0^\circ$, $J_{13} = J_{23}$, while for $\gamma = 30^\circ$ J_{13} goes to zero. If the assumption $J_{12} = 0$ is relaxed, $\gamma = 30^\circ$ requires $J_{12} = J_{13}$, which means that the triangle must be isosceles, but the two equivalent atoms are now atoms 2 and 3, while at $\gamma = 0^\circ$ the 1 and 2 atoms are equivalent.

Since the g_{\pm} values depend on R , measuring the g values of the triad may in principle yield information on the J_{ij} values to complement that obtained from the magnetic susceptibility measurements.

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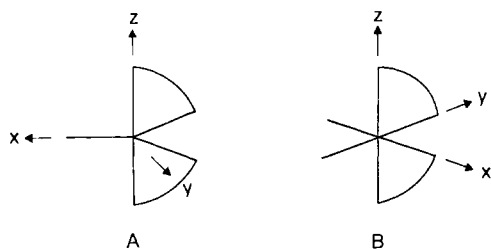


Figure 5. Sketch of the coordination environments of the central copper ions in (A) $(\text{CuHAPen})_2\text{Cu}$ and (B) $(\text{CuSALen})_2\text{Cu}$.

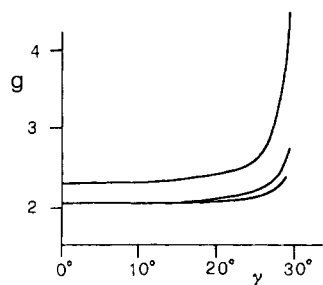


Figure 6. Dependence on γ of the g_x , g_y , and g_z values of the central copper ion in the $(\text{CuHAPen})_2\text{Cu}$ triad.

In order to use expressions 2 and 3 for calculating the g values of the triad, it is necessary to make some assumptions on the g values and directions of the three individual copper ions. It seems to be a reasonable assumption to use the g values of the monomeric complex CuSALen (and of CuHAPen) for the g values of the two external copper ions. A confirmation of the validity of this assumption comes also from the g values of the Cu-Zn-Cu complexes. We further assume that g_z is orthogonal to the CuSALen plane and g_x and g_y are roughly parallel to the copper-nitrogen bond directions.²¹

For the central copper ion we feel it is difficult to assume the g values, but it seems to be possible to fix the principal directions. As a matter of fact, the coordination environment of the central atom is distorted octahedral in $(\text{CuSALen})_2\text{Cu}$ and distorted trigonal bipyramidal in $(\text{CuHAPen})_2\text{Cu}$, as shown in Figure 5. Comparison with the reported spectra for these classes of copper complexes suggests that the choice of axes depicted in Figure 5 is reasonable.^{27,28}

With these assumptions, using expression 2, relative to the ground doublet, we are in the position of calculating the g values of the central ions using the experimental g values.

The g tensors of the three copper(II) ions are expressed in the reference system that is parallel to the principal axes of the experimental g tensor. The three tensors are summed by using the coefficients of (2), and finally the equations are solved to obtain g_x , g_y , and g_z of the central ion as a function of γ .

The g values calculated for $(\text{CuHAPen})_2\text{Cu}$ in the range $\gamma = 0-30^\circ$ are shown in Figure 6. The g values computed with $0^\circ < \gamma < 11^\circ$ can be considered satisfactory for a distorted five-coordinated copper(II) ion.^{27,28} As a matter of fact, the largest g value is calculated parallel to the copper-water bond direction, which is the largest metal-ligand distance observed in the structure¹⁶ and corresponds to the unique axis of a tetragonal pyramid. The value calculated parallel to z , which is the trigonal axis of the bipyramid, is slightly higher than would be anticipated.^{27,28} Therefore, we may interpret

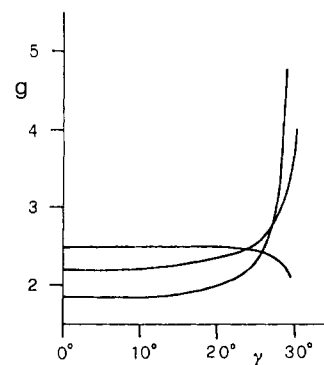


Figure 7. Dependence on γ of the g_x , g_y , and g_z values of the central copper ion in the $(\text{CuSALen})_2\text{Cu}$ triad.

the g values of $(\text{CuHAPen})_2\text{Cu}$ to indicate that the J_{13} and J_{23} constants must be fairly close to each other. This result is in agreement with the structural data¹⁶ that show that the bond distances and bond angles of the central copper(II) ion with the two complex CuSALen ligands are rather similar to each other.

Much less satisfactory are the calculated g values for $(\text{CuSALen})_2\text{Cu}$, as shown in Figure 7. Reasonable g values, i.e. $g \geq 2.0$ but not too different from 2, are calculated only in the range $20^\circ < \gamma < 24^\circ$, but the highest g values are calculated parallel to either x or y and not parallel to z as expected for a tetragonal copper complex.²⁷

We tried also an alternative approach, assuming reasonable g values for the central ion and calculating the experimental g values. We let g_x , g_y , and g_z vary and looked for the best fit. It was found for g_x , g_y , = 2.09, g_z = 2.30, and γ = 18° . The calculated g values are 2.20, 2.04, and 2.00, which can be considered only rough estimates of the experimental g values.

Further, it must be noted that the γ value that is required is fairly large, demanding a large difference between J_{13} and J_{23} . Although the structure of $(\text{CuSALen})_2\text{Cu}$ does show some difference in the bridging environments of Cu_3 with Cu_1 and Cu_2 , in particular in the angles between CuSALen planes and the CuO_2 planes,¹⁶ it seems unreasonable to justify such large deviation of the J values from those expected for an isosceles triangle.

It must be recalled here that the analysis of the temperature dependence of the magnetic susceptibility of $(\text{CuSALen})_2\text{Cu}$ from 4.2 to 300 K yielded $g = 2.091$ and $J = 86 \text{ cm}^{-1}$, although the fit of the experimental data was satisfactory only above 100 K, at lower temperatures the observed susceptibilities being higher than the calculated ones.¹⁵

The fact that we cannot reproduce satisfactorily the g values might be indicative of some distortion of the complex in the low-temperature range that makes the room-temperature X-ray data inadequate to describe the low-temperature structure.

In conclusion, we want to stress that although in principle the analysis of the g values of trinuclear systems may yield useful information on the J_{ij} coupling constants, the analysis is rather difficult and sensitive to small variations in the structural parameters and in the g values of the individual ions. Perhaps better results might be obtained by finding systems for which intermolecular exchange interactions are not strong enough to exchange narrow the signals. We are still looking for such a system.

Registry No. $\text{Cu}(\text{CuSALen})_2(\text{ClO}_4)_2$, 49729-57-9; $\text{Cu}(\text{CuHAPen})_2(\text{ClO}_4)_2$, 49729-88-6; $\text{Zn}(\text{CuSALen})_2(\text{ClO}_4)_2$, 49729-66-0; $\text{Zn}(\text{CuHAPen})_2(\text{ClO}_4)_2$, 87615-73-4.

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