

# Crystal and Molecular Structure of and Magnetic Coupling in Two Complexes Containing Gadolinium(III) and Copper(II) Ions

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**Abstract:** The tetradentate copper(II) Schiff base complexes CuHAPen and CuSALen react with  $\text{Gd}(\text{ClO}_4)_3$  to yield crystalline materials of formula  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3](\text{ClO}_4)_3 \cdot 2\text{CuHAPen}$  (I) and  $[(\text{CuSALen})_2\text{Gd}(\text{H}_2\text{O})_3](\text{ClO}_4)_3 \cdot 2\text{CuSALen} \cdot 0.5\text{C}_2\text{H}_5\text{NO}_2$  (II), respectively. Their crystal structures were determined through X-ray diffraction at room temperature: I crystallizes in the monoclinic system, space group  $C2/c$  with lattice constants  $a = 16.092$  (4) Å,  $b = 31.262$  (6) Å,  $c = 15.249$  (4) Å,  $\beta = 95.44$  (5)°, with  $Z = 4$ ; and II crystallizes in the monoclinic system, space group  $P2_1/a$  with lattice constants  $a = 18.333$  (5) Å,  $b = 33.233$  (7) Å,  $c = 11.864$  (3) Å,  $\beta = 95.94$  (5)°, with  $Z = 4$ . Least-squares refinement of the structure led to a conventional  $R$  factor of 0.059 (I) and 0.061 (II). In both structures a tripositive ion, three perchlorate, and two copper Schiff base molecules are present. In the tripositive ion a central gadolinium(III) is bound in a distorted pentagonal-bipyramidal fashion to three water molecules and to four oxygen atoms of two copper(II) Schiff base complexes. The temperature dependence of the magnetic susceptibility of both I and II was investigated in the range 1.2–300 K. The effective magnetic moments of both compounds have been found to increase steadily on decreasing temperature. These data have been interpreted with use of a Heisenberg spin Hamiltonian in the following form:  $\mathcal{H} = J(S_1 \cdot S_2 + S_2 \cdot S_3) + J'S_1 \cdot S_3$ , where 1 and 3 refer to copper(II) ions and 2 refers to gadolinium. The least-squares fit of the experimental susceptibilities yielded  $g = 1.992$  (4),  $J = -5.32$  (5)  $\text{cm}^{-1}$ ,  $J' = 4.2$  (3)  $\text{cm}^{-1}$  for I and  $g = 1.97$  (1),  $J = -7.38$  (7)  $\text{cm}^{-1}$ ,  $J' = 12.23$  (3)  $\text{cm}^{-1}$  for II. The observed Gd–Cu coupling is ferromagnetic and fairly substantial, a result which opens new perspectives in the field of magnetic interactions between rare-earth and transition-metal ions.

The nature of the magnetic interaction between rare-earth and transition-metal ions has been long debated in the physical literature,<sup>2-14</sup> not only for the relevant theoretical interest to recognize the relative roles of isotropic, anisotropic, and antisymmetric exchange contributions but also for the possible use of rare-earth orthoferrites, orthochromites, and garnets as materials for constructing magnetic bubble devices.<sup>15,16</sup> The interactions have been found to be weak, as one can expect given the relatively low covalency of the lanthanide-to-ligand bonds, but their effects are by no means negligible, producing profound modifications on the nature of the magnetic materials, depending on the nature of the rare-earth and transition-metal ions involved.

Although the papers we are referring to contain accurate investigations on the nature of the magnetic interactions, generally they do not attempt to correlate the type of magnetic exchange with the electronic structure of the metal ions. One difficulty in

doing this is that ionic lattices, such as those studied, are inherently slightly flexible, in the sense that it is not possible in general to vary systematically the coordination environments and the relative geometries of the coupled metal ions.

In principle simple discrete (oligonuclear) complexes should be much more flexible under this respect, offering the possibility of dramatically influencing the electronic structures of the metal ions by carefully choosing the ligands, but very few complexes containing transition-metal and rare-earth ions have been reported in the literature.<sup>17-20</sup> Indeed only one crystal structure analysis has appeared, where europium(III) ions are bound to diamagnetic nickel(III) dithiooxalate complexes.<sup>21</sup>

We decided to pursue these objectives and started a project of synthesizing oligonuclear complexes containing transition-metal and rare-earth ions. A convenient starting point appeared to be that of the use of copper(II) complexes of tetradentate salicylaldimines, which are known to act as ligands toward other transition-metal and also rare-earth ions.<sup>22,23</sup> Being interested in the study of magnetic properties we chose gadolinium(III) as the rare earth, since its ground state is orbitally nondegenerate and well-separated from the excited states, giving simple single ion magnetic properties.

We report here the synthesis, X-ray, and magnetic characterization of two complexes in which gadolinium(III) is bound to tetradentate copper salicylaldimines. The formulas of these compounds are the following:  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3] \cdot 2\text{CuHAPen}$  (I), where CuHAPen is  $[N,N'$ -ethylenebis(o-

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(2) Moskvin, A. S.; Bostrem, I. G. *Sov. Phys. Solid State (Engl. Transl.)* **1977**, *19*, 1532.

(3) Cooke, A. H.; Martin, D. M.; Wells, M. R. *J. Phys. C* **1974**, *7*, 3133.

(4) Veltrusky, I.; Nekversie, V. *J. Phys. C* **1980**, *13*, 1685.

(5) Cashion, J. D.; Cooke, A. H.; Martin, D. M.; Wells, M. R. *J. Phys. C* **1970**, *3*, 1612.

(6) Foglio, M. E.; Van Vleck, J. H. *Proc. R. Soc. London, A* **1974**, *A336*, 115.

(7) Wickersheim, K. *Phys. Rev.* **1962**, *122*, 1376.

(8) Levy, P. M. *Phys. Rev. Sect. A* **1964**, *135*, A 155.

(9) Kadomtseva, A. M.; Bostrem, I. G.; Vasilieva, L. M.; Krynetskii, I. B.; Lukina, M. M.; Moskvin, A. S. *Sov. Phys. Solid State (Engl. Transl.)* **1980**, *22*, 1146.

(10) Golovenchits, E. I.; Sanina, V. A. *Sov. Phys. Solid State (Engl. Transl.)* **1981**, *23*, 977.

(11) Yamaguchi, T.; Tushima, K. *Phys. Rev. B: Solid State* **1973**, *B8*, 5187.

(12) Yamaguchi, T. *J. Phys. Chem. Solids* **1974**, *55*, 479.

(13) Kadomtseva, A. M.; Lukina, M. M.; Moskvin, A. S.; Khafizova, N. A. *Sov. Phys. Solid State (Engl. Transl.)* **1978**, *20*, 1235.

(14) Washimiya, S.; Satoko, C. *J. Phys. Soc. Jpn.* **1978**, *20*, 1235.

(15) Blunt, R. *Chem. Br.* **1983**, *19*, 740.

(16) Nielsen, J. W. *IEEE Trans. Magn.* **1976**, *12*, 327.

(17) Condorelli, G.; Fragalà, I.; Giuffrida, S.; Cassol, A. *Z. Anorg. Allg. Chem.* **1975**, *251*, 412.

(18) Musumeci, A.; Bonomo, R. P.; Cucinotta, V.; Seminara, A. *Inorg. Chim. Acta* **1982**, *59*, 133.

(19) Chisari, A.; Musumeci, A.; Vidali, M.; Seminara, A. *Inorg. Chim. Acta* **1984**, *81*, L19.

(20) Seminara, A.; Guiffrida, S.; Musumeci, A.; Fragalà, I. *Inorg. Chim. Acta* **1984**, *95*, 201.

(21) Trombe, J. C.; Glaizes, A.; Galy, J. C. R. *Acad. Sci. Paris* **1982**, *294*, 1369.

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

(23) Leslie, K. A.; Drago, R. S.; Stucky, G. D.; Kitko, D. J.; Breese, J. A. *Inorg. Chem.* **1979**, *18*, 1885.

**Table I.** Summary of Crystal Data, Intensity Collection, and Structure Refinement

	I	II
formula	C <sub>78</sub> H <sub>78</sub> N <sub>8</sub> O <sub>23</sub> GdCu <sub>4</sub> Cl <sub>3</sub>	C <sub>64</sub> H <sub>62</sub> N <sub>8</sub> O <sub>23</sub> Cu <sub>4</sub> Cl <sub>3</sub> · C <sub>1</sub> H <sub>2.5</sub> N <sub>0.5</sub> O <sub>1</sub>
fw	1941.2	1866.6
space group	C2/c	P2 <sub>1</sub> /a
a, Å	16.092 (4)	18.333 (5)
b, Å	31.262 (6)	33.233 (7)
c, Å	15.249 (4)	11.864 (3)
β, deg	95.44 (5)	95.94 (5)
V, Å <sup>3</sup>	7636.7	7189.5
Z	4	4
density, gcm <sup>-3</sup>	1.69	1.73
crystal size, mm	0.12 × 0.30 × 0.08	0.25 × 0.68 × 0.08
μ(Mo, K), cm <sup>-1</sup>	20.3	21.7
transm. factors, max-min	0.86-0.78	0.82-0.55
scan type	-2	-2
scan width (O(20)), deg	1.00 ± 0.3	1.00 ± 0.3
scan speed, deg min <sup>-1</sup>	3.6	3.6
bkdg/scan time ratio	0.5	0.5
2θ limits, deg	5-50	5-50
data collection range	+h, k, l; h + k = 2n	+h, k, l
no. of data F <sub>o</sub> <sup>2</sup> ≤ 3(F <sub>o</sub> <sup>2</sup> )	3262	5782
no. of variables	286	549
R	0.059	0.061
R <sub>w</sub>	0.057	0.059

hydroxyacetophenoneiminato]copper(II), and [(CuSALen)<sub>2</sub>Gd(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuSALen·0.5C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> (II), where Cu(SALen) is [N,N'-ethylenebis(salicylaldiminato)]copper(II). The main result of this investigation is that the copper(II) and gadolinium(III) ions are coupled in a ferromagnetic fashion with isotropic coupling constants of the order of five to seven wavenumbers, thus showing that moderate coupling can be established between transition-metal and rare-earth ions.

### Experimental Section

**Synthesis of the Complexes.** The copper Schiff base complexes, [N,N'-ethylenebis(salicylaldiminato)]copper(II) (CuSALen) and [N,N'-ethylenebis(o-hydroxyacetophenoneiminato)]copper(II) (CuHAPen), were prepared as previously described.<sup>24</sup> Hydrated gadolinium(III) perchlorate was prepared from Gd<sub>2</sub>O<sub>3</sub> with perchloric acid. One millimole of the gadolinium(III) salt was dissolved in ca. 20 mL of absolute ethanol. The copper complexes (3.5 mmol) were dissolved in ca. 200 mL of chloroform; the two solutions were warmed under stirring and then mixed. A precipitate was immediately formed, and the suspension was stirred at room temperature for 3-4 h. The precipitate was filtered, washed with chloroform-petroleum ether, and dried in vacuo. These compounds analyze satisfactorily for (1) Gd(CuHAPen)<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub>·2EtOH and (2) Gd(CuSALen)<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub>·2EtOH, respectively. Anal. Calcd for C<sub>38</sub>H<sub>66</sub>N<sub>6</sub>O<sub>20</sub>Gd<sub>1</sub>Cu<sub>3</sub>Cl<sub>3</sub>: C, 42.96; H, 4.10; N, 5.18; Cu, 11.76. Found: C, 42.84; H, 4.0; N, 5.40; Cu, 11.80. Calcd for C<sub>52</sub>H<sub>54</sub>N<sub>6</sub>O<sub>20</sub>Gd<sub>1</sub>Cu<sub>3</sub>Cl<sub>3</sub>: C, 40.63; H, 3.54; N, 5.47; Cu, 12.40. Found: C, 39.78; H, 3.47; N, 5.41; Cu, 12.03.

In the attempt to obtain crystals suitable for X-ray analysis the compounds were dissolved in hot nitroethane, and the solutions were allowed to evaporate at room temperature. Wine-red crystals were formed in a few days. The compounds analyzed satisfactorily for [Gd(CuHAPen)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuHAPen and [Gd(CuSALen)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuSALen·0.5EtNO<sub>2</sub>. Anal. Calcd for C<sub>72</sub>H<sub>78</sub>N<sub>8</sub>O<sub>23</sub>Gd<sub>1</sub>Cu<sub>4</sub>Cl<sub>3</sub>: C, 44.55; H, 4.05; N, 5.77. Found: C, 44.34; H, 4.05; N, 5.70. Calcd for C<sub>65</sub>H<sub>64.5</sub>N<sub>8.5</sub>O<sub>24</sub>Gd<sub>1</sub>Cu<sub>4</sub>Cl<sub>3</sub>: C, 41.83; H, 3.48; N, 6.38. Found: C, 41.48; H, 3.45; N, 6.42.

**X-ray Structure Determination.** [(CuHAPen)<sub>2</sub>Gd(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuHAPen. A crystal of [(CuHAPen)<sub>2</sub>Gd(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuHAPen (I), shaped as an irregular prism, of approximate dimensions 0.12 × 0.30 × 0.08 mm, was used for crystal data and intensity data collection. Diffraction data were collected on a Philips PW1100 automated diffractometer equipped with a Mo X-ray tube and a graphite monochromator. Details on crystal data and intensity data collection are given in

Table I. The orientation matrix and unit cell parameters were obtained from 21 machine centered reflections with 9 ≤ θ ≤ 12. Intensities of three check reflections measured every 120 min revealed no decay over the duration of data collection. Data were corrected for Lorentz and polarization effects, as well as for absorption.

The systematic absences *hkl* (*h* + *k* = 2*n*), *h0l* (*h*, *l* = 2*n*), and *0k0* (*k* = 2*n*) indicated two possible space groups: *Cc* and *C2/c*. The structure was solved in the *Cc* space group by locating the Gd and Cu atoms with direct methods. All the remaining non-hydrogen atoms, except one ClO<sub>4</sub><sup>-</sup> anion, were located by Fourier and difference Fourier maps and least-squares refinement.

Programs used in the crystallographic calculations are given in ref 25. Atomic scattering factors were taken from a standard source.<sup>26</sup>

After a few least-squares cycles it was apparent that the procedure failed to converge. The *C2/c* space group was then used, locating the Gd and one bound water molecule on the *C*<sub>2</sub> axis. The refinement converged in this space group to *R* = 0.08. At this stage of the refinement some extra peaks were left in the difference Fourier maps as high as 1.5-2.0 eÅ<sup>-3</sup> which were assigned to a disordered ClO<sub>4</sub><sup>-</sup> anion. This anion actually does not lie on the *C*<sub>2</sub> axis, as the stoichiometry and the space group symmetry require, and it was refined with 1/2 site occupation factor. Anisotropic thermal parameters, were assigned to all the non-hydrogen atoms except carbons and oxygens of the ClO<sub>4</sub><sup>-</sup> anions. Hydrogen atoms were located in calculated positions (C-H = 1.08 Å) and introduced in structure factor calculations with an isotropic thermal parameter 20% larger than that of the corresponding carbon atom.

The refinement converged to *R* = ||F<sub>o</sub>|| - ||F<sub>c</sub>||/||F<sub>o</sub>|| = 0.059 and *R*<sub>w</sub> = [w(|F<sub>o</sub>|| - ||F<sub>c</sub>||)<sup>2</sup>/w|F<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup> = 0.057 with *w* = 1.24/σ<sup>2</sup>(F<sub>o</sub>). Two residual peaks in the last difference Fourier map were ~0.9 eÅ<sup>-3</sup> and were located around an oxygen of one ClO<sub>4</sub><sup>-</sup> ion (O(10)). All the other peaks were less than 0.6 eÅ<sup>-3</sup>. Final atomic positional parameters for non-hydrogen atoms are collected in Table II. Atomic positional parameters for hydrogen atoms and thermal parameters for non-hydrogen atoms are available as supplementary material (Tables SI and SII). A listing of observed and calculated structure factors is also available.

[(CuSALen)<sub>2</sub>Gd(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuSALen·0.5C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>. A crystal of [(CuSALen)<sub>2</sub>Gd(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuSALen·0.5C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> (II), of approximate dimensions 0.25 × 0.08 × 0.68 mm, was used for crystal data and intensity data collection. Diffraction data were collected at 25 °C on a Phillips PW1100 automated diffractometer using graphite monochromated Mo radiation. Details on crystal data and intensity data collection are given in Table I. The orientation matrix and unit cell parameters were obtained from 23 reflections in the range 7 ≤ θ ≤ 13. Intensities of three check reflections measured every 120 min revealed no decay over the duration of data collection. Data were corrected for Lorentz and polarization effects, as well as for absorption.

The systematic absences *h0l* (*h* = 2*n*) and *0k0* (*k* = 2*n*) unambiguously indicated *P2*<sub>1</sub>/*a* as the space group, an alternative setting of the conventional *P2*<sub>1</sub>/*c*.

The structure was solved by locating Gd and Cu atoms with direct methods. All the remaining non-hydrogen atoms were located by Fourier and difference Fourier maps and least-squares refinement. The structure was refined by using the blocked full matrix least-squares method. Programs used in the crystallographic calculations are listed in ref 25. Atomic scattering factors were taken from a standard source.<sup>26</sup>

Anisotropic thermal parameters were assigned to all the non-hydrogen atoms except carbons and the oxygens of the ClO<sub>4</sub><sup>-</sup> anions. Hydrogen atoms were located in calculated positions (C-H = 1.08 Å) and introduced in structure factor calculations with isotropic thermal parameters 20% larger than those of the corresponding carbon atoms. One of the ClO<sub>4</sub><sup>-</sup> anions was found to be disordered over two positions around the Cl atom. To the oxygen atoms of these two perchlorate units were assigned 0.8 and 0.2 site occupation factors, respectively. A residual electron density was also found which was assigned to 0.5 molecule of solvent C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, according to the elemental analysis. The atoms in the solvent molecule were refined isotropically.

The refinement converged to *R* = ||F<sub>o</sub>|| - ||F<sub>c</sub>||/||F<sub>o</sub>|| = 0.061 and *R*<sub>w</sub> = [w(|F<sub>o</sub>|| - ||F<sub>c</sub>||)<sup>2</sup>/w|F<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup> = 0.059 with *w* = 2.29/σ<sup>2</sup>(F<sub>o</sub>). Some residual peaks of 1-0.9 eÅ<sup>-3</sup> were found in the last difference Fourier map located around the solvent molecule, indicating that some disorder exists which was not possible to solve, since the fitting procedure is quite insensitive to the location of the solvent molecule.

(25) (a) Stewart, J. M.; Kundall, F. A.; Baldwin, J. C. Technical Report TR192, University of Maryland, College Park, Md., 1972. (b) Sheldrick, G. "SHELX 76 System of Computing Programs", University of Cambridge, England, 1976. (c) Johnson, C. K. "ORTEP", Report ORNL 3.794, Oak Ridge, Tenn. 1965.

(26) "International Tables of X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 71.

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

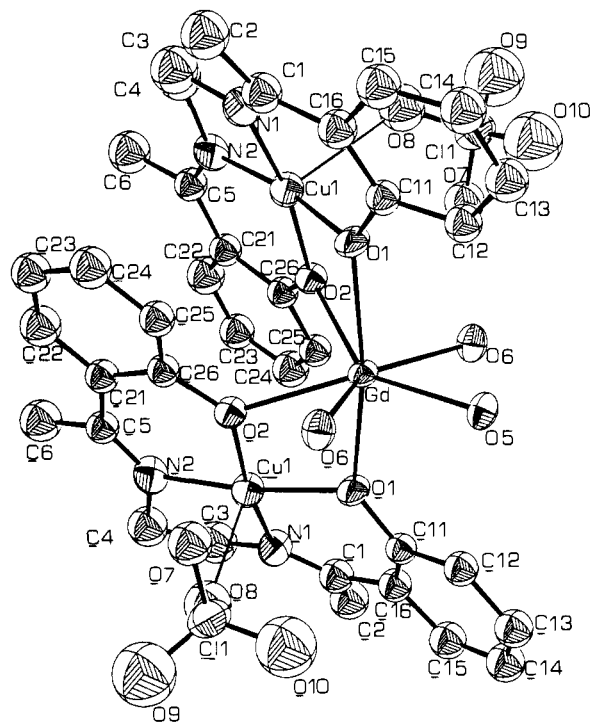
**Table II.** Positional Parameters for  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3](\text{ClO}_4)_3 \cdot 2\text{CuHAPen}^a$ 

atom	x	y	z
Gd	5000	1478	2500
Cu1	3553 (1)	835 (1)	1446 (1)
O1	3597 (4)	1412 (3)	1913 (6)
O2	4737 (4)	864 (2)	1582 (6)
O5	5000	2236 (3)	2500
O6	5503 (5)	1708 (2)	1169 (6)
N1	2351 (7)	784 (3)	1577 (8)
N2	3551 (6)	224 (3)	1179 (8)
C1	1869 (9)	1075 (5)	1811 (10)
C2	1024 (10)	960 (5)	2078 (12)
C3	2131 (11)	340 (5)	1485 (13)
C4	2687 (9)	95 (5)	1008 (12)
C5	5854 (8)	-28 (4)	3805 (9)
C6	6015 (10)	-495 (5)	3908 (12)
C1 1	2916 (8)	1669 (4)	1820 (9)
C1 2	3065 (8)	2107 (4)	1737 (9)
C1 3	2411 (9)	2403 (5)	1643 (10)
C1 4	1608 (10)	2256 (5)	1670 (10)
C1 5	1465 (9)	1824 (5)	1763 (10)
C1 6	2092 (8)	1513 (4)	1840 (9)
C2 1	5006 (8)	109 (4)	1290 (9)
C2 2	5648 (10)	-178 (5)	1220 (11)
C2 3	6484 (9)	-70 (5)	1252 (10)
C2 4	6719 (10)	347 (5)	1387 (11)
C2 5	6113 (8)	649 (4)	1472 (9)
C2 6	4731 (8)	539 (4)	3547 (9)
C11	3943 (2)	1370 (1)	-615 (3)
O7	4800 (2)	1289 (1)	-320 (3)
O8	3414 (2)	1095 (1)	-147 (3)
O9	3844 (2)	1245 (1)	-1506 (3)
O10	3767 (2)	1797 (1)	-482 (3)
C12	591 (7)	56 (3)	4214 (10)
O13	-10 (7)	82 (3)	3475 (10)
O14	268 (7)	-153 (3)	4903 (10)
O15	1283 (7)	-143 (3)	3889 (10)
O16	884 (7)	460 (3)	4474 (10)
Cu2	6713 (1)	2783 (1)	1297 (1)
O3	3218 (5)	2201 (3)	4042 (6)
O4	4468 (5)	2722 (3)	3749 (7)
N3	2060 (7)	2869 (4)	3631 (8)
N4	3384 (7)	3381 (4)	3325 (8)
C7	1545 (10)	2606 (5)	3877 (11)
C8	642 (10)	2771 (5)	3927 (13)
C9	1887 (10)	3319 (5)	3372 (12)
C10	2549 (9)	3520 (5)	2895 (11)
C11	3998 (10)	3634 (5)	3396 (11)
C12	3922 (11)	4080 (5)	3106 (12)
C3 1	2538 (9)	1972 (4)	4136 (10)
C3 2	1715 (9)	2163 (5)	4064 (10)
C3 3	1068 (10)	1864 (5)	4173 (11)
C3 4	1159 (10)	1454 (5)	4316 (11)
C3 5	1949 (11)	1271 (6)	4404 (11)
C3 6	2617 (10)	1539 (5)	4307 (10)
C4 1	5000 (9)	3046 (4)	3946 (10)
C4 2	4822 (8)	3486 (4)	3775 (9)
C4 3	5456 (10)	3775 (5)	4013 (11)
C4 4	6228 (11)	3658 (5)	4394 (11)
C4 5	6413 (10)	3238 (5)	4513 (10)
C4 6	5803 (8)	2922 (5)	4330 (10)

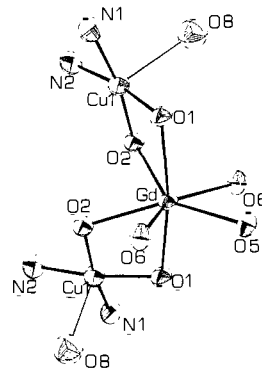
<sup>a</sup>Coordinates multiplied by  $10^4$ . Standard deviations in the last significant digits are in parentheses.

Final atomic positional parameters for non-hydrogen atoms are collected in Table III. Atomic positional parameters for hydrogen atoms and thermal parameters for non-hydrogen atoms are available as supplementary material (Tables SIII and SIV). A listing of observed and calculated structure factors is also available.

**Magnetic and EPR Measurements.** The EPR spectra were recorded with a Bruker ER200 spectrometer. The magnetic susceptibilities were measured in the 4.2–20 K range by an ac mutual inductance technique at near zero field.<sup>27</sup> The magnetic susceptibilities in the 4.2–300 K range were determined with a Faraday balance equipped with a Cahn R-100



**Figure 1.** ORTEP view of the cation  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3]^{3+}$  showing also the perchlorate ions nearest to CuHAPen.



**Figure 2.** Schematic view of the cation  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3]^{3+}$ . Only the metals and the coordinated atoms are shown. Oxygens of the perchlorate ions are shown with a finer bond.

microbalance, a Bruker electromagnet operating at 2 T, and an Oxford Instruments continuous flow CF200 cryostat. The internal helium pressure was adjusted at  $10^{-1}$  mmHg. The system was calibrated with  $[\text{Ni}(\text{en})_3](\text{S}_2\text{O}_3)$ .

## Results

**Structural Description of  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3](\text{ClO}_4)_3 \cdot 2\text{CuHAPen}$ .** The crystal structure of I consists of the trinuclear species  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3]^{3+}$  of overall  $C_2$  symmetry, where the gadolinium and the oxygen atom of a water molecule, O(5), lie on the binary axis, three  $\text{ClO}_4^-$  anions, and two CuHAPen symmetry related molecules. Selected bond distances and angles are collected in Tables IV and V.

The coordination polyhedron of gadolinium is formed by four phenolic oxygen atoms of two CuHAPen molecules and three water molecules O(5), O(6), and O(6'). An ORTEP view of the trinuclear cation is shown in Figure 1. A simplified view of the molecule showing only the metals and the coordinated atoms is given in Figure 2. The O(2), O(2'), O(5), O(6), and O(6') atoms roughly form a plane. The deviations from the least-squares plane are 0.68, 0.38, and 0.00 Å for O(2), O(5), and O(6), respectively. Gd lies on this plane and O(1) is 2.34 Å away. The coordination around the gadolinium ion can thus be described as a distorted pentagonal bipyramid with O(1) and O(1)' in the axial positions.

Table III. Positional Parameters for  $[(\text{CuSALen})_2\text{Gd}(\text{H}_2\text{O})_3](\text{ClO}_4)_3 \cdot 2\text{CuSALen} \cdot 0.5\text{C}_2\text{H}_5\text{NO}_2^{a,b}$ 

atom	x	y	z	atom	x	y	z
Gd	2519	3470	9120 (1)	O16	4603 (2)	3493 (1)	7417 (3)
Cu1	2070 (1)	2539 (1)	9740 (2)	O17	3678 (2)	3482 (1)	5944 (3)
Cu2	2538 (1)	3164 (1)	6469 (1)	O18	4853 (2)	3640 (1)	5614 (3)
O1	2577 (4)	2980 (3)	10540 (7)	O19	4195 (2)	4080 (1)	6598 (3)
O2	1592 (4)	2944 (2)	8775 (7)	Cu3	6501 (1)	73 (1)	347 (2)
O3	3007 (4)	2988 (3)	7907 (7)	Cu4	9698 (1)	673 (1)	1628 (2)
O4	2305 (4)	3653 (3)	7247 (7)	O5	1982 (5)	4515 (3)	11259 (7)
O9	2808 (4)	4081 (2)	10072 (7)	O6	935 (5)	4523 (3)	9485 (8)
O10	3795 (4)	3590 (2)	9255 (7)	O7	9033 (4)	503 (3)	367 (8)
O11	1409 (4)	3750 (3)	9689 (8)	O8	4736 (4)	3805 (3)	1003 (7)
N1	2566 (7)	2139 (3)	10703 (11)	N5	2126 (6)	5337 (3)	11101 (11)
N2	1636 (6)	2098 (4)	8876 (11)	N6	992 (7)	5369 (4)	9490 (11)
N3	2567 (6)	2636 (3)	5803 (9)	N7	4796 (6)	4872 (4)	12248 (10)
N4	2014 (6)	3313 (4)	5056 (9)	N8	185 (6)	844 (4)	3078 (9)
C1	3037 (9)	2191 (5)	11521 (14)	C13	1954 (2)	1219 (1)	6155 (4)
C2	2337 (10)	1732 (6)	10312 (17)	O20	1871 (2)	953 (1)	5212 (4)
C3	1932 (10)	1702 (6)	9279 (17)	O21	1740 (2)	1605 (1)	5748 (4)
C4	1174 (8)	2130 (5)	7962 (14)	O22	1469 (2)	1093 (1)	6924 (4)
C5	2892 (8)	2340 (5)	6182 (12)	O23	2669 (2)	1218 (1)	6627 (4)
C6	2098 (8)	2606 (5)	4730 (14)	C9	2571 (8)	5302 (5)	12041 (14)
C7	2037 (9)	3002 (5)	4187 (15)	C10	2015 (9)	5732 (5)	10535 (15)
C8	1637 (8)	3625 (5)	4872 (13)	C11	1303 (10)	5762 (6)	9944 (16)
C1 1	3281 (7)	2577 (4)	11951 (11)	C12	403 (9)	5331 (6)	8776 (14)
C1 2	3052 (7)	2951 (4)	11480 (12)	C13	9573 (8)	-199 (5)	1730 (14)
C1 3	3309 (7)	3295 (4)	12017 (12)	C14	5254 (8)	4863 (5)	13367 (14)
C1 4	3800 (8)	3291 (5)	12996 (13)	C15	5194 (9)	4469 (5)	13945 (14)
C1 5	4032 (8)	2925 (5)	13448 (14)	C16	528 (8)	1173 (5)	3329 (14)
C1 6	3781 (8)	2580 (5)	12945 (13)	C5 1	2658 (7)	4940 (5)	12634 (12)
C2 1	906 (7)	2491 (4)	7489 (12)	C5 2	2372 (7)	4565 (4)	12250 (12)
C2 2	1104 (7)	2879 (4)	7843 (11)	C5 3	2530 (7)	4234 (5)	12946 (12)
C2 3	798 (7)	3198 (4)	7256 (11)	C5 4	2933 (8)	4267 (5)	13987 (13)
C2 4	309 (8)	3158 (5)	6312 (13)	C5 5	3193 (8)	4635 (5)	14384 (14)
C2 5	111 (8)	2778 (5)	5951 (14)	C5 6	3073 (8)	4964 (5)	1371 (13)
C2 6	394 (8)	2448 (5)	6502 (14)	C6 1	112 (7)	4982 (5)	8354 (12)
C3 1	3326 (7)	2323 (4)	7296 (12)	C6 2	388 (8)	4590 (5)	8678 (12)
C3 2	3375 (7)	2640 (4)	8108 (11)	C6 3	47 (8)	4264 (5)	8142 (13)
C3 3	3806 (7)	2587 (4)	9127 (12)	C6 4	-526 (9)	4315 (5)	7327 (14)
C3 4	4177 (8)	2227 (5)	9389 (13)	C6 5	-784 (9)	4693 (5)	7046 (15)
C3 5	4109 (8)	1922 (5)	8614 (14)	C6 6	-483 (8)	5017 (5)	7525 (13)
C3 6	3697 (8)	1965 (5)	7589 (14)	C7 1	4183 (7)	5219 (4)	10647 (12)
C4 1	1616 (7)	3967 (4)	5621 (12)	C7 2	3922 (7)	4878 (5)	10013 (12)
C4 2	1975 (7)	3985 (4)	6727 (12)	C7 3	3515 (7)	4927 (5)	8947 (13)
C4 3	1961 (7)	4341 (4)	7342 (12)	C7 4	3401 (8)	5316 (5)	8512 (14)
C4 4	1604 (8)	4676 (5)	6865 (13)	C7 5	3687 (8)	5647 (5)	9177 (14)
C4 5	1242 (8)	4653 (5)	5791 (13)	C7 6	4048 (8)	5595 (5)	1019 (14)
C4 6	1247 (8)	4317 (5)	5193 (14)	C8 1	5538 (7)	3496 (5)	1253 (12)
C11	232 (2)	3451 (1)	1948 (4)	C8 2	5141 (7)	3494 (5)	11409 (12)
O12	293 (2)	3188 (1)	2879 (4)	C8 3	5197 (7)	3150 (5)	10766 (13)
O13	551 (2)	3821 (1)	2277 (4)	C8 4	5579 (8)	2813 (5)	1119 (14)
O14	-510 (2)	3508 (1)	1566 (4)	C8 5	5926 (9)	2824 (5)	12276 (15)
O15	574 (2)	3286 (1)	1059 (4)	C8 6	5907 (8)	3147 (5)	12923 (14)
O12 #	123 (17)	3591 (10)	729 (21)	N9*	2890 (9)	1190 (7)	3920 (17)
O13 #	860 (18)	3225 (11)	1925 (36)	O24*	3072 (9)	1577 (7)	3683 (17)
O14 #	327 (20)	3820 (9)	2602 (27)	O25*	2832 (9)	1194 (7)	2782 (17)
O15 #	-428 (20)	3272 (17)	2093 (44)	C17*	3658 (9)	1106 (7)	4025 (17)
Cl2	4319 (2)	3672 (1)	6369 (3)	C18*	4250 (9)	781 (7)	4310 (17)

<sup>a</sup> Coordinates multiplied by  $10^4$ . Standard deviations in the last significant digits are in parentheses. <sup>b</sup> Atoms belonging to the solvent molecule are marked with an asterisk. Oxygen atoms of the disordered perchlorate marked with a # and have 0.2 site occupation factor.

Table IV. Bond Distances (Å) for  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3](\text{ClO}_4)_3 \cdot 2\text{CuHAPen}^a$ 

bond	length, Å	bond	length, Å
Gd-O1	2.35 (4)	Gd-O2	2.39 (1)
Gd-O5	2.37 (1)	Gd-O6	2.37 (3)
Gd-Cu1	3.36 (5)	Cu1-O8	2.55 (1)
Cu1-O1	1.93 (1)	Cu1-O2	1.90 (1)
Cu1-N1	1.97 (1)	Cu1-N2	1.96 (1)
Cu2-O3	1.90 (1)	Cu2-O4	1.90 (1)
Cu2-N3	1.99 (1)	Cu2-N4	1.97 (1)

<sup>a</sup> Standard deviations in the last significant digits are in parentheses.

The average in-plane Gd-O bond length is 2.375 (2) Å, and the bond angles O-Gd-O average to 74.6 (3)° which has to be compared with 72° in a regular pentagon. The Gd-O bond distances are in the normal range. The pentagonal-bipyramidal

Table V. Bond Angles (deg) for  $[(\text{CuHAPen})_2\text{Gd}(\text{H}_2\text{O})_3](\text{ClO}_4)_3 \cdot 2\text{CuHAPen}^a$ 

bond	angle, deg	bond	angle, deg
O1-Gd-O2	66.2 (3)	O1-Gd-O5	95.0 (2)
O1-Gd-O6	95.4 (3)	O2-Gd-O6	78.4 (2)
O5-Gd-O6	72.3 (2)	O1-Cu1-O2	85.1 (3)
O1-Cu1-O8	92.9 (3)	O1-Cu1-N1	92.4 (4)
O2-Cu2-N2	92.9 (4)	O8-Cu1-N1	97.1 (3)
O8-Cu1-N2	96.6 (4)	N1-Cu1-N2	87.6 (4)
Gd-O1-Cu1	102.8 (3)	Gd-O2-Cu2	102.9 (3)
O3-Cu2-O4	88.7 (4)	O3-Cu2-N3	93.5 (4)
O4-Cu2-N4	90.0 (4)	N3-Cu2-N4	87.8 (5)

<sup>a</sup> Standard deviations in the last significant digits are in parentheses.

coordination around Gd is not very common and only a few examples of X-ray crystal structures of hepta-coordinated ga-

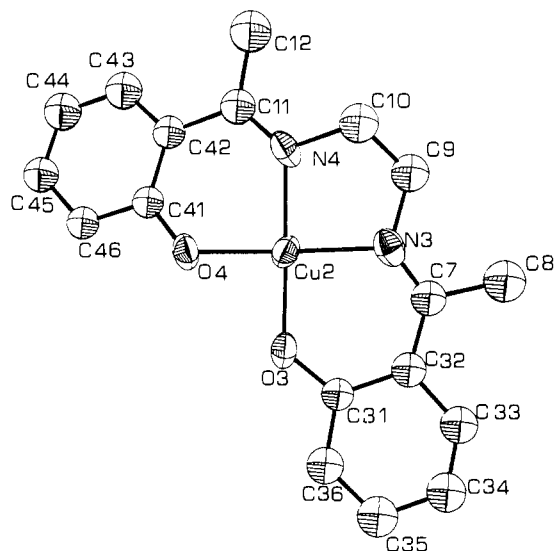


Figure 3. ORTEP view of the noncoordinated (CuHAPen) molecule.

dolinium(III) complexes have been reported so far.<sup>28</sup>

Two copper ions are bridged to the gadolinium(III) ion by the O(1) and O(2) phenolic oxygen of the HAPen ligand. The copper ion is five-coordinated by the four donor atoms of the HAPen ligand, O(1), O(2), N(1), and N(2), and an oxygen, O(8), of a perchlorate anion at a longer distance (2.551 (5) Å). The in-plane Cu–O and Cu–N bond distances average to 1.97 (8) and 1.96 (1) Å, respectively, which are the normal values for copper(II) coordinated to Schiff bases.<sup>29–32</sup> The copper ion is 0.18 Å displaced from the least-squares plane through N(1), N(2), O(1), and O(2) toward the O(8) atom.

The copper–gadolinium distance is 3.367 (2) Å. the Cu–O<sub>2</sub>–Gd bridge is asymmetric, the Cu–O bond distances being 0.45 Å shorter than the Gd–O ones. The two Cu–O–Gd angles are equal to each other within error (102.8 (3)° and 102.9 (3)°). The dihedral angle between the CuN<sub>2</sub>O<sub>2</sub> plane and the equatorial GdO<sub>5</sub> plane is 73.4°. The Cu–Cu distance is 4.561 (3) Å.

The copper atom of the CuHAPen molecule present in the asymmetric unit, Cu(2), is four-coordinate and lies only 0.01 Å away from the least-squares plane through the O(3), O(4), N(3), and N(4) atoms of the HAPen ligand. The average Cu–O and Cu–N bond distances are 1.90 (1) and 1.97 (1) Å, respectively. An ORTEP view of the molecule is shown in Figure 3. The Cu(2) atom has contacts with Gd, 5.34 Å, O(5), 3.85 (2) Å, and O(6), 3.88 (2)) Å. Contacts exist also between the phenolic oxygen of the CuHAPen molecules and the water molecules bound to Gd, indicating the existence of hydrogen bonds (O(3) – O(6) = 2.61 (2) Å, O(4) – O(5) = 2.64 (3) Å). The copper atom of another HAPen molecule, related to Cu(2) by the symmetry operation (1/2 – x, 1/2 – y, 1 – z), is at 5.2 (1) Å from Cu(2) and another one is at 6.9 (1) Å from Cu(2), related through the symmetry operation (1 – x, y, 1/2 – z). Therefore a sort of alternating chain of CuHAPen molecules is formed, with the chain axis roughly parallel to a.

A sketch of the unit cell is shown in Figure 4. Only atoms bound to the metals and perchlorate ions near to CuHAPen are shown.

**Structural Description of [(CuSALen)<sub>2</sub>Gd(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuSALen·0.5C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>.** The crystal structure of II is analogous to that of I. It consists of a trinuclear species [(CuSALen)<sub>2</sub>Gd(H<sub>2</sub>O)<sub>3</sub>]<sup>3+</sup>, three perchlorate anions, two CuSALen complexes,

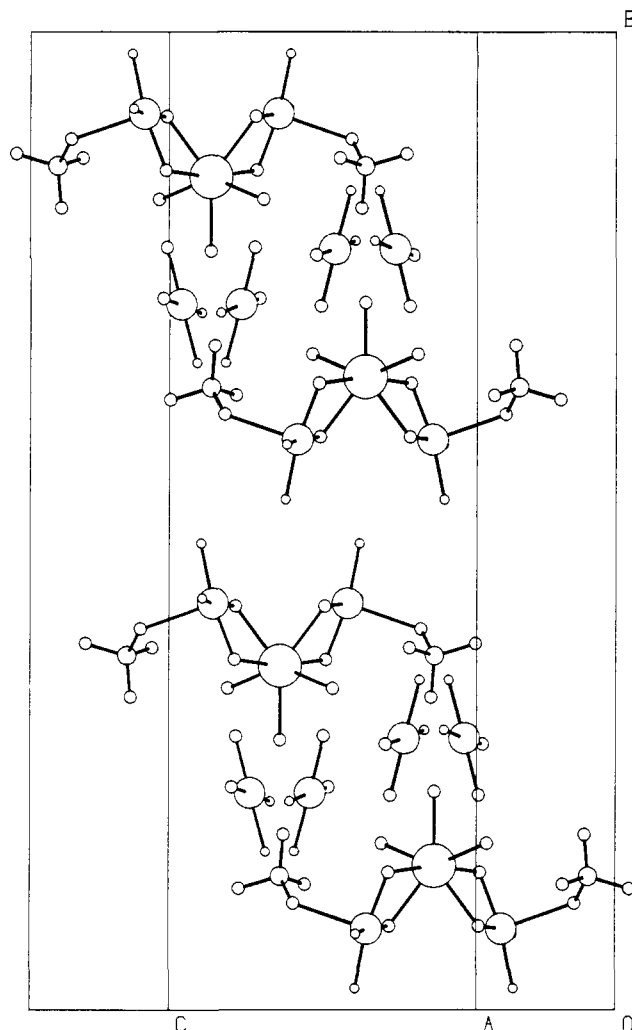


Figure 4. Schematic view of the unit cell of I.

Table VI. Bond Distances (Å) for [(CuSALen)<sub>2</sub>Gd(H<sub>2</sub>O)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2CuSALen·0.5C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub><sup>a</sup>

bond	length, Å	bond	length, Å
Gd–Cu1	3.30 (1)	Gd–Cu2	3.31 (1)
Gd–O1	2.34 (1)	Gd–O2	2.44 (2)
Gd–O3	2.39 (3)	Gd–O4	2.30 (2)
Gd–O9	2.36 (2)	Gd–O10	2.36 (1)
Gd–O11	2.40 (3)		
Cu1–O1	1.93 (2)	Cu1–O2	1.92 (3)
Cu1–N1	1.92 (3)	Cu1–N2	1.92 (2)
Cu2–O3	1.92 (4)	Cu2–O4	1.94 (1)
Cu2–N3	1.93 (1)	Cu2–N4	1.91 (4)
Cu2–O17	2.48 (3)	Cu3–O5	1.90 (3)
Cu3–O6	1.92 (3)	Cu3–N5	1.94 (3)
Cu3–N6	1.97 (3)	Cu4–O7	1.91 (5)
Cu4–O8	1.89 (1)	Cu4–N7	1.96 (1)
Cu4–N8	1.94 (4)		

<sup>a</sup>Standard deviations in the last significant digits are in parentheses.

and half of a nitroethane molecule, which is disordered. Selected bond distances and angles are shown in Table VI and VII.

The trinuclear Cu<sub>2</sub>Gd moiety in II has no crystallographic symmetry. The coordination around gadolinium is, however, very similar to that described for I. An ORTEP view of the trinuclear cation is shown in Figure 5. A simplified view of the molecule showing only the metals and the coordinated atoms is given in Figure 6. The O(2), O(3), O(9), O(10), and O(11) atoms define a least-squares plane (deviations: –0.29, 0.31, –0.02, –0.21, and 0.17 Å, respectively). The gadolinium ion lies on this plane and O(1) and O(4) are –2.22 and 2.24 Å away occupying the axial positions of the pentagonal bipyramid. The angle O(1)–Gd–O(4)

(28) Koppikar, D. K.; Sivapullaiah, P. V.; Ramakrishnan, L.; Soundararajan, S. *Struct. Bonding (Berlin)* **1978**, *34*, 135.

(29) Baker, E. N.; Hall, D.; Waters, T. N. *J. Chem. Soc. A* **1966**, 680.

(30) Bencini, A.; Benelli, C.; Dei, A.; Gatteschi, D. *Inorg. Chem.*, in press.

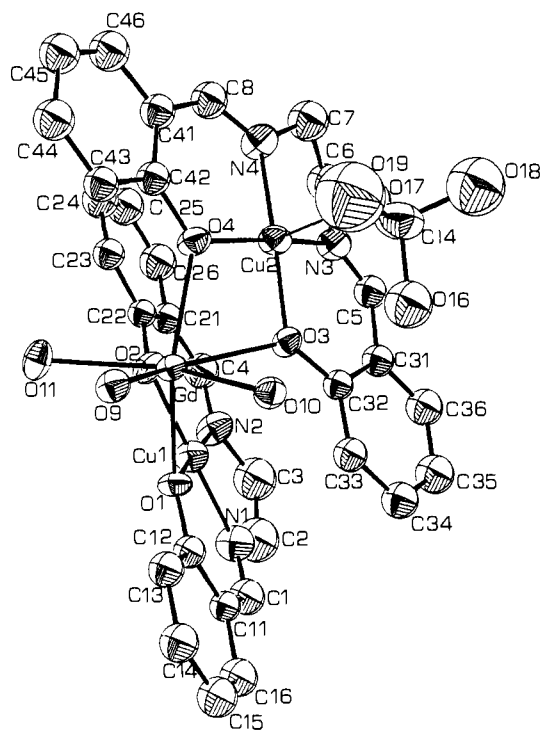
(31) O'Connor, C. J.; Freyberg, D. P.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1077.

(32) Bresciani Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L.; Fenton, D. E. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 180.

**Table VII.** Bond Angles (deg) for  $[(\text{CuSALen})_2\text{Gd}(\text{H}_2\text{O})_3](\text{ClO}_4)_3 \cdot 2\text{CuSALen} \cdot 0.5\text{C}_2\text{H}_5\text{NO}_2^a$ 

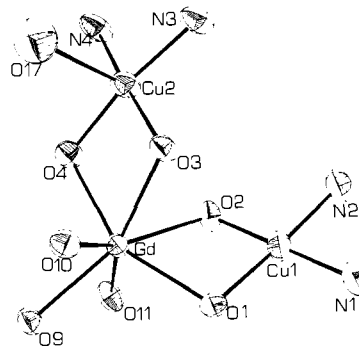
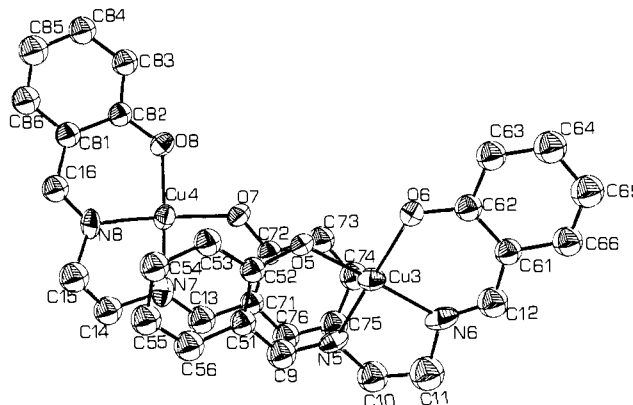
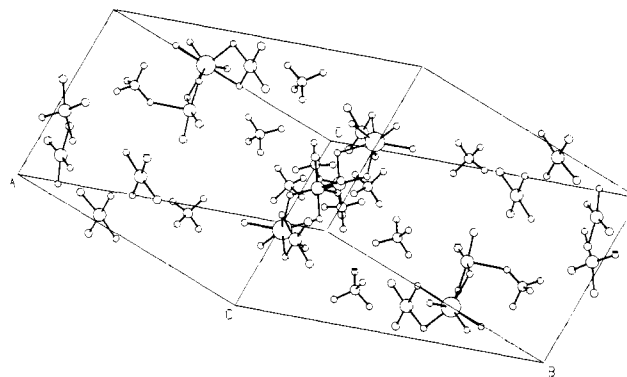
bond	angle, deg	bond	angle, deg
O1-Gd-O2	66.5 (3)	O1-Gd-O3	88.5 (3)
O1-Gd-O9	105.3 (3)	O1-Gd-O10	95.6 (3)
O1-Gd-O11	92.5 (3)	O2-Gd-O3	73.5 (3)
O2-Gd-O4	88.9 (3)	O2-Gd-O3	73.5 (3)
O2-Gd-O11	74.2 (3)	O3-Gd-O4	68.4 (3)
O3-Gd-O10	74.0 (3)	O4-Gd-O9	104.1 (3)
O4-Gd-O10	95.1 (3)	O4-Gd-O11	96.0 (3)
O9-Gd-O10	69.5 (3)	O9-Gd-O11	71.8 (3)
Gd-O1-Cu1	101.0 (3)	Gd-O2-Cu1	97.8 (3)
Gd-O3-Cu2	99.8 (4)	Gd-O4-Cu2	102.4 (4)
O1-Cu1-O2	85.8 (4)	O1-Cu1-N1	93.4 (4)
O2-Cu1-N2	94.5 (4)	N1-Cu1-N2	86.2 (5)
O3-Cu2-O4	86.2 (4)	O3-Cu2-N3	93.3 (4)
O3-Cu2-O17	92.4 (3)	O4-Cu2-O17	89.8 (3)
O4-Cu2-N4	94.9 (4)	N3-Cu2-N4	84.7 (5)
N3-Cu2-O17	103.0 (4)	N4-Cu2-O17	91.7 (4)
O5-Cu3-O6	89.6 (4)	O5-Cu3-N5	91.5 (4)
O6-Cu3-N6	92.6 (5)	N5-Cu3-N6	86.5 (5)
O7-Cu4-O8	90.6 (4)	O7-Cu4-N7	92.7 (4)
O8-Cu4-N8	92.7 (5)	N7-Cu4-N8	85.5 (5)

<sup>a</sup>Standard deviations in the last significant digits are in parentheses.

**Figure 5.** ORTEP view of the cation  $[(\text{CuSALen})_2\text{Gd}(\text{H}_2\text{O})_3]^{3+}$  showing also the perchlorate ion nearest to CuSALen.

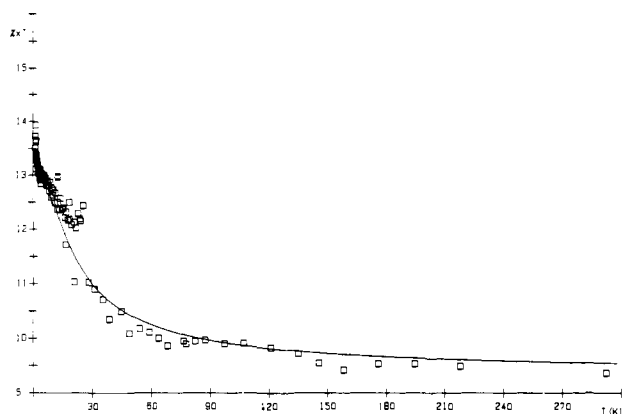
is  $150.6 (3)^\circ$  and indicates a large deviation from the idealized geometry, even larger than that observed in I, where the angle is  $169.8 (3)^\circ$ . The average in-plane bond length is  $2.39 (2) \text{ \AA}$ , and the bond angles to gadolinium average  $72.6 (3)^\circ$ .

The two copper atoms in the trinuclear cation are not equivalent. Cu(1) is four-coordinated by the N(1), N(2), O(1), and O(2) atoms of a SALen molecule and lies  $0.05 \text{ \AA}$  from the least-squares plane through the ligands. Cu(2) is five-coordinated by the four atoms N(3), N(4), O(3), and O(4) of a SALen molecule and by an oxygen of a perchlorate anion (O(17) at  $2.48 (3) \text{ \AA}$ ). The deviation of Cu(2) from the least-squares plane  $\text{N}_2\text{O}_2$  is  $0.14 \text{ \AA}$ . The average Cu-O and Cu-N distances are  $1.93 (2)$  and  $1.92 (3) \text{ \AA}$ , comparable to those found in I. The dihedral angles between the O(2)O(3)O(10)O(9)O(11) plane and the N(1)N(2)O(1)O(2) and N(3)N(4)O(3)O(4) planes are  $67.4^\circ$  and  $72.8^\circ$ , respectively. The bridging Cu-O-Gd angles are slightly smaller than those found in I, the average angles being  $99.4 (3)^\circ$  and  $101.1 (4)^\circ$ , respectively. The Cu(1)-Cu(2) distance is  $5.402 (3) \text{ \AA}$ .

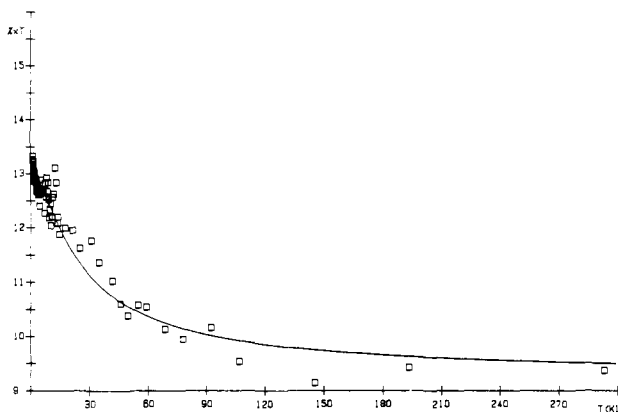
**Figure 6.** Schematic view of the cation  $[(\text{CuSALen})_2\text{Gd}(\text{H}_2\text{O})_3]^{3+}$ . Only the metals and the coordinated atoms are shown. The oxygen atom of the perchlorate ion is shown with a finer bond.**Figure 7.** ORTEP view of the two noncoordinated (CuSALen) molecules.**Figure 8.** Schematic view of the unit cell of II.

Two other CuSALen complexes are present in the unit cell. The ORTEP view of these two complexes is shown in Figure 7. The copper atoms, Cu(3) and Cu(4), are in a planar environment, the distances from the least-squares plane through the ligand donor atoms being  $0.02$  and  $0.04 \text{ \AA}$ , respectively. The bond distances and angles in the complexes are in the normal range.<sup>28-32</sup> The Gd-Cu distances are  $5.439 (4)$  and  $5.519 (5) \text{ \AA}$  for Cu(3) and Cu(4), respectively. The closest contacts of Cu(3) are  $3.84 (2)$  and  $3.96 (3) \text{ \AA}$  with O(9) and O(10), respectively. The closest contact of Cu(3) with another copper atom is with Cu(3') related by the symmetry operation  $(-x, 1-y, -z)$  ( $5.50 (4) \text{ \AA}$ ). The Cu(3)-Cu(4) distance is  $6.23 (7) \text{ \AA}$ , while Cu(4) and Cu(4'), related by  $(1-x, 1-y, -z)$ , are  $6.08 (4) \text{ \AA}$  apart. These contacts create a chain of CuSALen molecules along the  $a$  axis analogous to that seen in I. A sketch of the unit cell is shown in Figure 8. Hydrogen bonds are present between the phenolic oxygens and water molecules bound to gadolinium as indicated by the following contact distances: O(5)-O(9),  $2.61 (4) \text{ \AA}$ ; O(6)-O(11),  $2.71 (1) \text{ \AA}$ ; O(7)-O(9),  $2.63 (2) \text{ \AA}$ ; and O(8)-O(10),  $2.65 (7) \text{ \AA}$ .

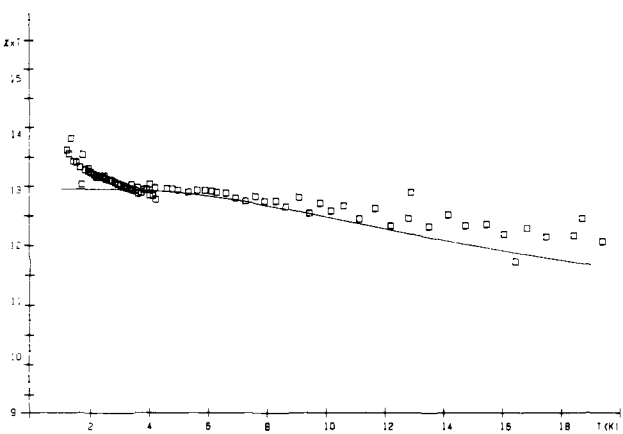
The packing of the CuSALen and CuHAPen molecules seen in the structures of I and II probably reflects the tendency of these



**Figure 9.** Temperature dependence of the magnetic susceptibility of I in the range 1.2–300 K. Experimental points are shown as squares. The curve was calculated as discussed in the text.



**Figure 10.** Temperature dependence of the magnetic susceptibility of II in the range 1.2–300 K. Experimental points are shown as squares. The curve was calculated as discussed in the text.

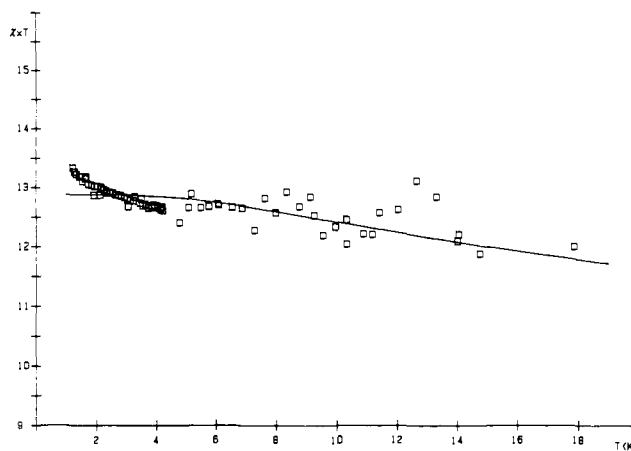


**Figure 11.** Temperature dependence of the magnetic susceptibility of I in the range 1.2–20 K. Experimental points are shown as squares. The curve was calculated as discussed in the text.

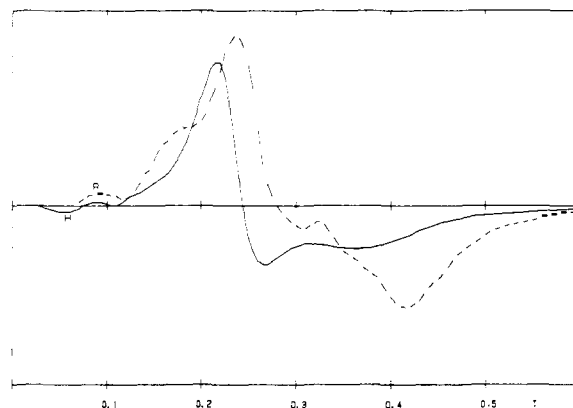
molecules to polymerize. This tendency is well-shown in the structures of several adducts of CuSALen.<sup>29,33,34</sup> In the pure CuSALen complex, two molecules stack one over the other to form a dimeric unit. Inclusion of solvent molecules, such as chloroform, in the unit cell tends to separate the two molecules which, however, interact with the solvent through hydrogen bonds.<sup>33,34</sup>

Bond distances and angles within the perchlorate anions are in the normal range.

**Magnetic and EPR Data.** The temperature dependence of the magnetic susceptibility of I and II in the range 1.2–300 K is shown



**Figure 12.** Temperature dependence of the magnetic susceptibility of II in the range 1.2–20 K. Experimental points are shown as squares. The curve was calculated as discussed in the text.



**Figure 13.** Polycrystalline powder EPR spectra of I at room (R) and liquid helium (H) temperature.

in Figures 9 and 10, in the  $\chi T$  vs.  $T$  form, while Figures 11 and 12 show the same data in the range 1.2–20 K. It is apparent that in both cases the effective magnetic moment increases on decreasing temperature, passing from  $8.66 \mu_B$  at 292 K to  $10.3 \mu_B$  at 1.2 K for I and from  $8.66 \mu_B$  at 292 K to  $10.1 \mu_B$  at 1.2 K for II. The room-temperature data correspond to the expected magnetic moment for one gadolinium and four copper ions which are essentially not interacting. If the data are fit to a Curie–Weiss law, in the form  $\chi = C/(T - \theta)$ , in both cases a fairly good agreement is found with  $C = 9.425$ ,  $\theta = 0.56$  K and  $r^2 = 0.9982$  for I and  $C = 9.488$ ,  $\theta = 0.59$  K, and  $r^2 = 0.9992$  for II ( $r$  is defined as  $(\sum_i (\chi_i^{\text{calcd}} - \chi_i^{\text{obsd}}) \times T_i^{\text{obsd}})^2 / \sum_i (\chi_i^{\text{obsd}} \times T_i^{\text{obsd}})^2$ ). These data, and the higher moments observed at low temperature, are indicative that some weak magnetic interaction is operative in these complexes.

Polycrystalline powder EPR spectra of I at room and liquid helium temperatures are shown in Figure 13. It is apparent that both the spectra are fairly complex, showing a strong feature at  $g = 2.5$ , but no clear feature in the  $g = 2$  region. The spectra of II are rather similar to those of I.

## Discussion

The increase in the effective magnetic moment of I and II as the temperature decreases clearly indicates that higher spin multiplicity states are occupied at low temperature and consequently that some form of magnetic interaction is operative among the various metal ions present in the cell.

The X-ray structure analysis has shown that trinuclear  $\text{GdCu}_2$  units are present in the asymmetric units, in which the gadolinium and copper ions are bridged by oxygen atoms of the Schiff base ligand. The other two copper ions appear to be essentially isolated, no contact being shorter than 3.80 Å. Therefore we tried to fit the magnetic data to a model which takes into account exchange

(33) Baker, E. N.; Hall, D.; Waters, T. N. *J. Chem. Soc. A* 1970, 400.

(34) Baker, E. N.; Hall, D.; Waters, T. N. *J. Chem. Soc. A* 1970, 406.

interaction within the GdCu<sub>2</sub> units and neglects interactions involving the remaining copper ions.

Gadolinium(III) is an f<sup>7</sup> ion, with a ground <sup>8</sup>S state. Since excited states are relatively high in energy, the zero-field splitting of the ground state is fairly small<sup>35</sup> (usually 1 cm<sup>-1</sup>) so that S = 7/2 is a good quantum number. The coupling of the spin momentum of gadolinium and of the two neighboring copper ions can be described by the spin Hamiltonian:

$$\mathcal{H} = J_{12}S_1 \cdot S_2 + J_{13}S_1 \cdot S_3 + J_{23}S_2 \cdot S_3$$

We have retained only bilinear spin terms, and 1 and 3 refer to copper ions and 2 to gadolinium. In I the two copper ions are symmetry related, and also in II, where no crystal symmetry is present, the coordination environments of the two copper ions are rather similar to each other, so that for both complexes it is possible to assume  $J_{12} = J_{23} = J$ ;  $J_{13} = J'$ . Within this assumption the energies of the total spin levels can be expressed<sup>36,37</sup> as

$$E(9/2) = 7/2J + J'/4$$

$$E(7/2,1) = -J + J'/4$$

$$E(5/2) = -9/2J + J'/4$$

$$E(7/2,0) = -3/4J'$$

where 7/2,1 and 7/2,0 refer to the states obtained by coupling S<sub>2</sub> = 7/2 with S\* = 1 and 0, respectively (S\* is the intermediate spin obtained by coupling the two copper ions).

In principle all these levels have different g values. Indeed by projecting out the individual g' of the copper and gadolinium ions on the total spins the following relations hold:<sup>36,38</sup>

$$g(9/2) = 0.78g_{\text{Gd}} + 0.22g_{\text{Cu}}$$

$$g(7/2,1) = 0.94g_{\text{Gd}} + 0.06g_{\text{Cu}}$$

$$g(5/2) = 1.29g_{\text{Gd}} - 0.29g_{\text{Cu}}$$

$$g(7/2,0) = g_{\text{Gd}}$$

$g_{\text{Gd}}$  is expected to be very close to 2, while  $g_{\text{Cu}}$  can be taken with reasonable accuracy to be 2.12, since such is the value observed in several copper(II) complexes with tetradentate Schiff bases.<sup>39</sup> The calculated g values for the total spin states are then in any case fairly close to 2 ( $g(9/2) = 2.03$ ,  $g(7/2, 1) = 2.01$ ,  $g(5/2) = 1.97$ , and  $g(7/2, 0) = 2.00$ ) so that it seems useless to employ four parameters instead of one. Therefore we tried to fit the temperature dependence of the magnetic susceptibility using the function

$$\chi T = N\mu_B^2 g^2 [210 + 252 \exp(9x/2 + x') + 252 \times \exp(-7x/2) + 990 \exp(-8x)] / (6kZ) + N\mu_B^2 (2.12)^2 / (2k)$$

with  $Z = 6 + 8 \exp(-9x/2 + x') + 8 \exp(-7x/2) + 10 \exp(-8x)$ . The second term describes the contribution of the two copper ions not directly bound to gadolinium.  $x$  and  $x'$  are  $J/kT$  and  $J'/kT$ , respectively.

The least-squares fit of the experimental data is obtained for the following sets of parameters: for I  $g = 1.992$  (4),  $J = -5.32$  (5) cm<sup>-1</sup>,  $J' = 4.2$  (3) cm<sup>-1</sup>, with  $r = 4.16 \times 10^{-2}$ ; for II  $g = 1.97$  (1),  $J = -7.38$  (7) cm<sup>-1</sup>,  $J' = 12.23$  (3) cm<sup>-1</sup>, with  $r = 7.63 \times 10^{-2}$ . The fit is fairly satisfactory for both I and II at higher temperatures but shows marked differences between calculated and observed points at low temperatures, as shown in Figures 9–12, where the curves are calculated with the above expressions and parameters. Indeed the calculated curves show a plateau below 5 K, as a consequence of the depopulation of the excited states leaving only the ground S = 9/2 state populated.

Several refinements might be made to the calculated values. Using different g's for different spin states is not expected to help in obtaining a better agreement between experimental and calculated points, since this choice cannot modify the calculated plateau. Zero-field splitting effects might, and perhaps should, be included. Indeed they are expected to be determined by both the intrinsic zero-field splitting of the gadolinium(III) ion and dipolar exchange effects.<sup>36,38</sup> We do not exclude at all that they are present, also because antisymmetric exchange effects have been claimed to be responsible for much of the observed magnetic interaction in some lanthanide orthoferrites and orthochromites,<sup>3,9,10,14</sup> but our feeling is that in the present case they should not be responsible for much of the deviation of the calculated values from the experimental ones. In fact, including zero-field splitting effects determines a lower degeneracy of all the spin levels, tending to give smaller values of the magnetic moment, while we observe that the experimental values are higher than calculated.

Another correction to the above simple model might be to include interactions involving the copper ions not directly bound to gadolinium. This possibility cannot be ruled out, since with a spin angular momentum as high as 9/2 even small exchange interactions can yield large effects. In fact if we introduce a J'' constant to describe the interaction of each GdCu<sub>2</sub> cluster with the other two copper ions, the ground S = 9/2 manifold is split into four states, with S = 11/2, 9/2, 7/2, and 9/2, respectively, separated by as much as 10 J''. Possible confirmation of the presence of magnetic coupling between the GdCu<sub>2</sub> cluster and the other two copper ions is the fact that we do not observe in the polycrystalline powder EPR spectra any feature which can be attributed to the copper ions which we have treated as free. Although spin relaxation might be responsible for broad bands we find it unusual not to observe any signal even at liquid helium temperature. This part of the data deserves further investigation and we are at present trying to obtain single crystals suitable for an EPR study which might possibly give a closer view of the magnetic interactions.

### Concluding Remarks

The analysis of the magnetic data offers conclusive evidence that magnetic exchange interactions are operative among the paramagnetic ions present in the unit cell of both I and II. The extent of the deviation of the magnetic susceptibility from a simple Curie law indicates that the coupling involves the gadolinium ions. By using the simplest possible approach, including only isotropic exchange, the coupling between gadolinium(III) and copper(II) ions is described as ferromagnetic and that between the two copper ions bound to the rare earth as antiferromagnetic. Although the calculated values for the latter interactions are slightly larger than usually found in trinuclear copper salicylaldiminate complexes which have a central transition-metal ion,<sup>30,40,44</sup> it must be remembered that J' in symmetric trinuclear species is usually obtained with rather poor accuracy from magnetic data,<sup>44,45</sup> due to the large covariance relating it to J.

The extent and the sign of the coupling of gadolinium(III) to copper(II) are somewhat surprising, since much smaller |J| values (and of opposite sign) had previously been reported from the analysis of the magnetic properties of rare-earth orthoferrites and orthochromites.<sup>3,10,13,14</sup> At the moment we prefer to stay at the experimental evidence and avoid as far as possible speculations, but we must observe that these data seem to confirm that covalency effects must be relevant also for lanthanides.<sup>46–48</sup>

(35) Newman, D. J.; Urban, W. *Adv. Phys.* **1975**, *24*, 793.

(36) Bencini, A.; Gatteschi, D. In "Magneto-Structural Correlations in Exchange Coupled Systems"; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, Netherlands, 1985; 241.

(37) Griffith, J. S. *Struct. Bonding (Berlin)* **1972**, *10*, 87.

(38) Scaringe, J.; Hodgson, D. J.; Hatfield, W. E. *Mol. Phys.* **1978**, *35*, 701.

(39) Goodman, B. A.; Raynor, J. B. In "Advances in Inorganic Chemistry and Radiochemistry"; Emelius, H. J., Sharpe, A. G., Eds.; Academic Press: New York, 1970; Vol. 13, p 85.

(40) Figgis, B. N.; Martin, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2174.

(41) Epstein, J. M.; Figgis, B. N.; White, A.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1974**, 1954.

(42) Gruber, S. J.; Harris, C. M.; Sinn, E. *J. Chem. Phys.* **1968**, *49*, 2183.

(43) Banci, L.; Bencini, A.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1983**, *22*, 401.

(44) Banci, L.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1983**, *22*, 2681.

(45) Brown, D. B.; Wasson, J. R.; Hall, J. W.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 2526.

(46) Yatsimirskii, K. B.; Davidenko, N. K. *Coord. Chem. Rev.* **1979**, *27*, 233.



Indeed ferromagnetic coupling between gadolinium(III) and copper(II) is possible only through a superexchange interaction mediated by the bridging oxygen ligands. In other words the magnetic orbitals centered on Gd and Cu must have a fairly large overlap density on the oxygen atom,<sup>49</sup> which can be obtained only through a fairly substantial covalency of the Gd-O bond.

Finally we would like to observe that ferromagnetic exchange, which up to now has been regarded as quite uncommon,<sup>50</sup> is indeed now rather frequently observed,<sup>30,51-53</sup> presumably because many

compounds containing different metal ions are being studied, or even in compounds containing one type of metal ion the interactions involving the ground and excited states are actively investigated.<sup>37,54,55</sup>

Further studies are in progress involving other lanthanides and different stoichiometries in order to get a deeper insight into this exciting field of magnetic interactions.

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**Registry No.** I, 98818-22-5; II, 98818-24-7; CuSALen, 14167-15-8; CuHAPen, 21350-69-6.

**Supplementary Material Available:** Tables of positional parameters for hydrogen atoms and thermal parameters for both compounds and observed and calculated structure factors (62 pages). Ordering information is given on any current masthead page.

(54) Banci, L.; Bencini, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1983**, *105*, 761.

(55) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, D. *J. Am. Chem. Soc.* **1984**, *106*, 5813.

(47) Linares, C.; Lonat, A.; Blanchard, M. *Struct. Bonding (Berlin)* **1977**, *33*, 174.

(48) Sinha, S. P. *Struct. Bonding (Berlin)* **1976**, *25*, 69.

(49) Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567.

(50) Stevens, K. W. H. In "Magneto-Structural Correlation in Exchange Coupled Systems", Willet, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, Netherlands, 1985; p 57.

(51) Kahn, O. In "Magneto-Structural Correlation in Exchange Coupled System"; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, Netherlands, 1985; p 57.

(52) Journaux, Y.; Kahn, O.; Zarembovitch, J.; Jand, J. *J. Am. Chem. Soc.* **1983**, *105*, 7585.

(53) Kahn, O.; Galj, J.; Journaux, Y.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 2165. See also the discussion in Chapter 9 of the following: Carlin, R. L. "Magnetochemistry"; Springer-Verlag: Berlin, Heidelberg, New York, Tokyo, 1985.

## Systematics of the Formation of $\Pi$ -CO Ligands in Four-Iron Clusters. Synthesis and Structures of $[\text{K}(18\text{-crown-6})][\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{13}]\cdot\text{CH}_2\text{Cl}_2$ , $\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{12}(\text{COCH}_3)$ , $[\text{PPN}][\text{Fe}_4(\text{CuPPh}_3)(\text{CO})_{13}]$ , and $[\text{PPN}][\text{Fe}_4(\text{HgCH}_3)(\text{CO})_{13}]$

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**Abstract:** The Lewis acid ligands  $[\text{R}_3\text{PAu}]^+$ ,  $[\text{LCu}]^+$ , and  $[\text{CH}_3\text{Hg}]^+$  interact with the metal framework of the tetrahedral iron cluster  $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ . In all cases, two products result, one of which consists of the  $\text{Fe}_4$  tetrahedron with the Lewis acid capping one face. The other more novel product is a  $\text{Fe}_4$  butterfly array with the Lewis acid ligand on the hinge and a  $\Pi$ -CO between the wingtips. By proper choice of counterion and conditions, either the butterfly or tetrahedral form can be crystallized. X-ray structures were determined for representative compounds of both products in this series. Tetrahedral iron frameworks were observed for  $[\text{PPN}][\text{Fe}_4(\text{CuPPh}_3)(\text{CO})_{13}]$  (**5a**) and  $[\text{PPN}][\text{Fe}_4(\text{HgCH}_3)(\text{CO})_{13}]$  (**6**(tetrahedron)). Both  $[\text{K}(18\text{-crown-6})][\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{13}]\cdot\text{CH}_2\text{Cl}_2$  (**3a**) and  $\text{Fe}_4(\text{AuPEt}_3)(\text{CO})_{12}(\text{COCH}_3)$  (**7**) have butterfly iron cores. Butterfly complexes such as **3a** display a characteristic and unique low-frequency  $\Pi$ -CO stretch in the  $1380\text{--}1430\text{-cm}^{-1}$  region of the IR spectrum. Additionally, NMR spectra of the individual isomers were obtained by dissolving the pure crystalline material at  $-80^\circ\text{C}$  and obtaining the spectrum at this temperature. The NMR spectra obtained in this manner were consistent with both IR spectra of the solid and the structure determined by X-ray crystallography.

The cleavage of CO on a metal such as Fe, Ru, or Ni is strongly implicated as a key step in Fischer-Tropsch and methanation catalysts.<sup>2</sup> It is thought that this reaction proceeds through a C- and O-bonded carbonyl,<sup>3</sup>  $\text{-CO I}$ , a point which is logical but

speculative.<sup>4</sup> In keeping with this interpretation, experiments on alloy catalysts suggest that for the methanation reaction a minimum ensemble of several metal atoms is necessary for CO cleavage.<sup>5</sup> The  $\Pi$ -CO ligand also is strongly implicated in the

(1) (a) Northwestern University. (b) Oklahoma State University. (c) On leave from University of Kentucky, Lexington, Kentucky, 40506.

(2) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165.

(3) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

(4) Sachtler, W. M. H.; Shriver, D. F.; Hollenberg, W. B.; Lang, A. F. *J. Catal.* **1985**, *92*, 429.

(5) (a) Araki, M.; Ponec, V. *J. Catal.* **1976**, *44*, 439. (b) Bond, G. C.; Turnham, B. D. *Ibid.* **1976**, *45*, 128.