Different Temperature Dependence of Magnetic Susceptibility of Different Molecular Complexes of Copper (II) with 7-Hydroxy-4-methyl-5-aza-hept-4-en-2-on

L. Merz and W. Haase

Physikalische Chemie I der TH Darmstadt

(Z. Naturforsch. **31 a**, 177–182 [1976]; received December 24, 1975)

Two principally different molecular structures in the crystalline state are known from the copper (II) complex with 7-hydroxy-4-methyl-5-aza-hept-4-en-2-on. The magnetic susceptibilities of three forms of this compound [α-$(CuEIA)_4$, β-$(CuEIA)_4$, and β-$(CuEIA)_4 \cdot 2\,C_6H_6$] have been measured in the temperature range 2.6–300 K. The results indicate that principally different molecular structures correspond to principally different magnetic properties. While the α-form shows antiferromagnetic spin coupling in the $S'=0$ ground state, the electrons in the β-form are coupled ferromagnetically in the $S'=2$ ground state. A fitting procedure of a theoretical equation based on the isotropic HDVV-model led to a satisfactory agreement between calculated and experimental data for α-$(CuEIA)_4$ and β-$(CuEIA)_4$, while this was not possible for β-$(CuEIA)_4 \cdot 2\,C_6H_6$. The exchange parameters obtained for α-$(CuEIA)_4$ ($g=2.13$, $J_{12}=-17\ cm^{-1}$, $J_{13}=+3.5\ cm^{-1}$, and $N_\alpha=60\cdot10^{-6}$ cgs-emu) are in good agreement with the values given by Ginsberg et al. For β-$(CuEIA)_4$ a weak antiferromagnetic intercluster interaction could be determined at low temperatures. The fitting procedure yielded the following values: $g=2.05$, $J_{12}=-6.4\ cm^{-1}$, $J_{13}=+24.2\ cm^{-1}$, $N_\alpha=10\cdot10^{-6}$ cgs-emu, $\Theta=-0.27°$.

1. Introduction

Of the copper(II) complex with 7-hydroxy-4-methyl-5-aza-hept-4-en-2-on, $(CuEIA)_4$, two principally different tetrameric molecular structures are known in the crystalline state [1, 2]. Figure 1 shows

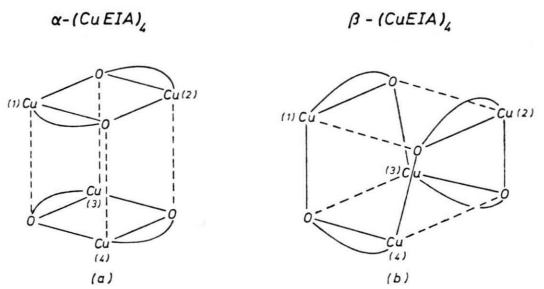

Fig. 1. Principal molecular structures of the Cu_4O_4-cores of α-$(CuEIA)_4$ (a) and β-$(CuEIA)_4$ (b). Cu–O: ~1.97 Å; Cu– –O: ~2.37 Å; CuO: chelate group.

the principal structures of the Cu_4O_4-cores. A similar behavior is found with the group of copper(II) complexes with N,N-disubstituted aminoalcohols [3–6]. For these it could be demonstrated that spin coupling of the magnetic centres inside the tetrameric molecules is different and that one of the principal structures goes with antiferromagnetic spin coupling, while the other one goes with ferromagnetic spin coupling. $(CuEIA)_4$ offers the opportunity to investigate the magnetism of tetrameric Cu(II) structures with different Cu_4O_4 cubane type cores within one chemical compound in order to get information about the magnitude of the magnetic interaction between the single copper(II) ions. The exchange integrals J_{ij} can be determined from the temperature dependence of magnetic susceptibility using the isotropic Heisenberg-Dirac-van Vleck-model (HDVV-model), in which the effective Hamiltonian describing the energy difference between states with different total spin S' has the form [7–9]

$$\hat{H} = -2 \sum_{i>j} J_{ij}\, \hat{S}_i \cdot \hat{S}_j .$$

The investigation includes α-$(CuEIA)_4$ [1], β-$(CuEIA)_4$, and β-$(CuEIA)_4 \cdot 2\,C_6H_6$ [2]. The crystal structure of β-$(CuEIA)_4$ resulting from β-$(CuEIA)_4 \cdot 2\,C_6H_6$ by loss of benzene is not known. β-$(CuEIA)_4$ is also the product resulting from direct preparation [2].

In his review [7] Ginsberg gave the values for the exchange integrals of α-$(CuEIA)_4$. We have not found the experimental data of the magnetic susceptibility as a function of temperature in the literature.

2. Experimental

The compound CuEIA was prepared as described by Jäger [10]. Proof of the existence of β-$(CuEIA)_4$ [as β-$(CuEIA)_4 \cdot 2\,C_6H_6$ and β-$(CuEIA)_4$], besides the known α-$(CuEIA)_4$ [1], was given in Ref. [2] including the preparation conditions.

Magnetic susceptibilities in the temperature range 2.6 – 300 K were determined by the Foner method as in Ref. [6]. In the case of β-(CuEIA)$_4$·2 C_6H_6 one must be aware that the compound does not decompose by loss of benzene during the performance of the suspectibility determination.

Susceptibility data were field independent above 10 K and measured at 10 kG. Below 10 K a small field dependence of susceptibility data was determined and susceptibility data were obtained at 1 kG. Corrections for the underlying diamagnetism were applied using published values [11].

In the fitting procedure of the theoretical susceptibility equation based on the HDVV-model (symmetry S_4) to the experimental data, the following terms were used as criterion

$$\sum_i \frac{|\chi_{M\,exp_i} - \chi_{M\,calc_i}|}{\chi_{M\,exp_i}} \quad [\alpha\text{-(CuEIA)}_4] \qquad (1)$$

and

$$\sum_i (\chi_{M\,exp_i} - \chi_{M\,calc_i})^2 T_i^2 \qquad (2)$$

$$[\beta\text{-(CuEIA)}_4,\quad \beta\text{-(CuEIA)}_4\cdot 2\,C_6H_6]\,.$$

3. Results and Discussion

α-(CuEIA)$_4$

α-(CuEIA)$_4$ has S_4-symmetry in the crystalline state [1] as indicated in Figure 1 a. Cu – Cu distances are 3.006(9) Å (2×) and 3.259(8) Å (4×) [1]. Because of the direct comparison with β-(CuEIA)$_4$ and β-(CuEIA)$_4$·2 C_6H_6 the temperature dependence of magnetic susceptibility (Table 1, Fig. 2) was determined, as it is neither given in Ref. [7] nor elsewhere.

The appropriate susceptibility Eq. (3) for this problem (4 centres-spin-1/2-system of symmetry S_4, the equation for symmetry D_{2d} is analogous)

$$\chi_M = \frac{N g^2 \beta^2}{4kT} \cdot \frac{10\,e^{2x} + 2\,e^{-2x} + 4\,e^{-2y}}{5\,e^{2x} + 3\,e^{-2x} + e^{-4x} + 6\,e^{-2y} + e^{-4y}} + N_\alpha, \qquad (3)$$

$[x = J_{13}/kT,\ y = J_{12}/kT,\ \chi_M$: per mol copper(II)] was fitted to the experimental susceptibility data in the temperature range >20 K. The data in the range <20 K were omitted because of the probable existence of a small paramagnetic impurity. The fitting process yielded the following values of the exchange integrals: $J_{12} = -17\ cm^{-1}$ [between the short bonded copper atoms 1 – 2 and 3 – 4 (Fig. 1a)] and $J_{13} = +3.5\ cm^{-1}$ [between the longer bonded copper atoms 1 – 3, 1 – 4, 2 – 3, and 2 – 4 (Fig. 1 a)] ($g = 2.13$, $N_\alpha = 60 \cdot 10^{-6}$ cgs-emu) in good agreement with the values given by Ginsberg et al. [7] ($J_{12} = -15\ cm^{-1}$, $J_{13} = +4\ cm^{-1}$). The mean percentual deviation per experimental point in the temperature range >20 K is 0.35%.

Table 1. Experimental and with Eq. (3) calculated magnetic susceptibilities $\chi_{M\,exp}$ and $\chi_{M\,calc}$ [cgs-emu] and magnetic moment μ_{eff} ($=2.828\ \sqrt{\chi_{M\,exp} \cdot T}$ of α-(CuEIA)$_4$.

T [K]	$\chi_{M\,exp} \cdot 10^6$	μ_{eff} [BM]	$\chi_{M\,calc} \cdot 10^6$
1.9	1034	0.12	60
2.1	962	0.13	60
2.6	820	0.13	60
3.0	772	0.14	60
3.5	797	0.15	60
5.1	699	0.17	84
6.0	715	0.19	145
6.5	743	0.20	207
7.1	837	0.22	314
7.5	907	0.23	407
8.0	1012	0.25	548
8.5	1178	0.28	718
9.0	1341	0.31	914
9.5	1514	0.34	1136
10.0	1743	0.37	1380
10.5	1978	0.41	1643
11	2236	0.44	1921
12	2780	0.52	2512
13	3312	0.59	3122
14	3854	0.66	3729
16	4886	0.79	4858
18	5869	0.92	5802
20	6529	1.02	6534
22	7077	1.12	7065
24	7409	1.19	7425
26	7627	1.26	7646
28	7725	1.32	7759
30	7775	1.37	7792
32	7732	1.41	7765
34	7660	1.44	7694
36	7599	1.48	7592
38	7448	1.50	7469
40	7327	1.53	7330
45	6948	1.58	6953
50	6541	1.62	6566
60	5860	1.68	5845
70	5233	1.71	5228
80	4704	1.73	4712
90	4273	1.75	4281
100	3949	1.78	3919
120	3361	1.80	3346
140	2945	1.82	2917
160	2605	1.83	2585
180	2331	1.83	2322
200	2106	1.84	2107
220	1931	1.84	1930
240	1774	1.85	1780
260	1648	1.85	1653
280	1531	1.85	1543
300	1438	1.86	1447

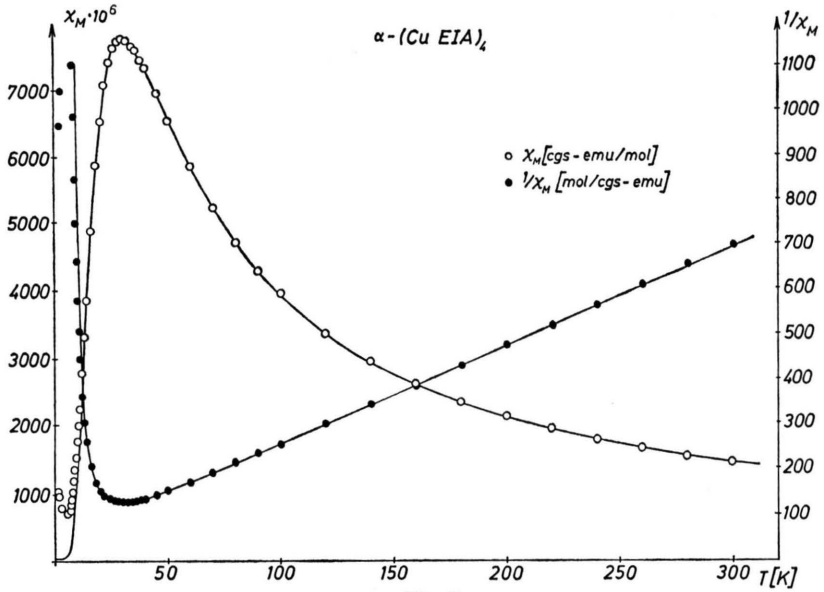

Fig. 2

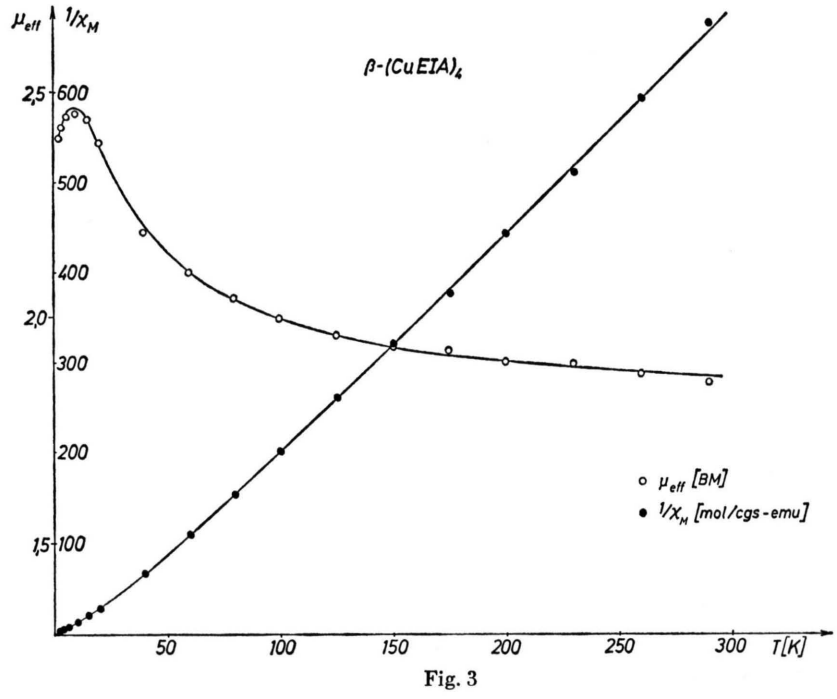

Fig. 3

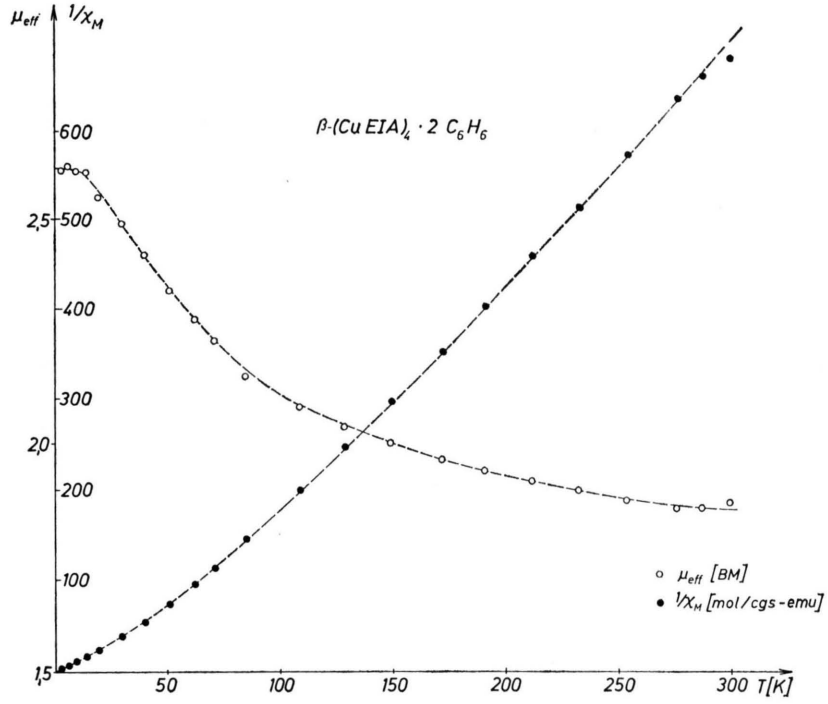

Fig. 4

Fig. 2. Susceptibility and reciprocal susceptibility of α-(CuEIA)$_4$ (open and full circles are experimental values, full lines are calculated).

Fig. 3. Magnetic moment and reciprocal susceptibility of β-(CuEIA)$_4$ (open and full circles are experimental values, full lines are calculated).

Fig. 4. Experimental magnetic moment and reciprocal susceptibility of β-(CuEIA)$_4$·2 C$_6$H$_6$.

The result indicates antiferromagnetic spin coupling in the ground state (Fig. 5, see later). Spin coupling via the different Cu – O bonds has different signs (antiferromagnetic interactions via two short Cu – O bonds and weaker ferromagnetic interactions via one short and one long Cu – O bond).

Ginsberg [7] has reported possible exchange pathways in accordance with the model of superexchange.

β-(CuEIA)$_4$ and β-(CuEIA)$_4$·2 C$_6$H$_6$

A crystal structure determination [2] proved that the molecule β-(CuEIA)$_4$ in crystalline β-(CuEIA)$_4$ ·2 C$_6$H$_6$ only has symmetry C_1. It can be approximated by S_4-symmetry as shown schematically for the Cu_4O_4-core in Figure 1 b. All molecular forms, of which the Cu_4O_4-core is principally identical with the one in Fig. 1b, are called β-form [2]. They possess ferromagnetic spin coupling in the ground state [β-(CuEIA)$_4$ and β-(CuEIA)$_4$·2 C$_6$H$_6$, Table 2, Figs. 3, 4] in contrast to the antiferromagnetism of the α-form (Table 1, Figure 2). As the magnetism of the structurally unknown powder β-(CuEIA)$_4$ is very similar to that of the structurally known β-(CuEIA)$_4$·2 C$_6$H$_6$, and as β-(CuEIA)$_4$ results from β-(CuEIA)$_4$·2 C$_6$H$_6$ by loss of benzene, we believe proved that the molecules in the powder β-(CuEIA)$_4$ are really of the β-form.

Assuming the highest possible symmetry S_4 for β-(CuEIA)$_4$ a fitting procedure of a slightly modified form of Eq. (3) to the experimental data was undertaken. To allow for weak intercluster interactions T in Eq. (3) was replaced by $(T-\Theta)$, where Θ means the Weiss constant. The exchange integral J_{12} corresponds to the longer Cu-Cu-distances (2×) [mean value 3.30 Å in the β-(CuEIA)$_4$ ·2 C$_6$H$_6$], while the exchange integral J_{13} corresponds to the shorter Cu-Cu-distances (4×) [mean value 3.12 Å in β-(CuEIA)$_4$·2 C$_6$H$_6$]. The fitting procedure in the temperature range 2.6 – 290 K yielded the following values: $J_{12} = -6.4\ cm^{-1}$, $J_{13} = +24.2\ cm^{-1}$, $g = 2.05$, $N_\alpha = 10 \cdot 10^{-6}$ cgs-emu, and $\Theta = -0.27°$ [deviation $2.91 \cdot 10^{-4}$, Gl. (2)]. The agreement between calculated and experimental data is good (Table 2 a, Figure 3).

This result indicates that ferromagnetic spin coupling between the four copper (II) pairs with shorter Cu-Cu-distances (1 – 3, 1 – 4, 2 – 3, and 2 – 4) is stronger than antiferromagnetic spin coupling between the two copper (II) pairs with longer Cu-Cu-distances (1 – 2 and 3 – 4) (Figure 1 b). This is in agreement with the estimated values of the exchange integrals in the structurally similar compounds (CuBuCl)$_4$ and γ-(CuBuBr)$_4$ [6].

It should be noted that a similar good agreement between calculated and experimental data for β-(CuEIA)$_4$ could be achieved with the parameters $g = 2.05$, $J_{12} = +25\ cm^{-1}$, $J_{13} = -5.8\ cm^{-1}$, $N_\alpha = 30 \cdot 10^{-6}$ cgs-emu, and $\Theta = -0.27°$ [deviation

Table 2. Experimental and with Eq. (3) calculated (β-(CuEIA)$_4$) susceptibilities $\chi_{M\,exp}$ and $\chi_{M\,calc}$ [cgs-emu] andand magnetic moment μ_{eff} $(=2.828\ \sqrt{\chi_{M\,exp} \cdot T})$ of β-(CuEIA)$_4$ (a) and β-(CuEIA)$_4$·2 C$_6$H$_6$ (b).

a) β-(CuEIA)$_4$

T [K]	$\chi_{M\,exp} \cdot 10^6$	μ_{eff} [BM]	$\chi_{M\,calc} \cdot 10^6$
2.6	276448	2.40	274650
3.5	209680	2.42	209083
6	124664	2.45	125597
10	75260	2.45	75830
15	49589	2.44	49257
20	35607	2.39	35428
40	14972	2.19	15186
60	9179	2.10	9209
80	6518	2.04	6500
100	4983	2.00	4986
125	3836	1.96	3843
150	3120	1.93	3119
175	2649	1.93	2620
200	2260	1.90	2257
230	1953	1.90	1935
260	1687	1.87	1692
290	1482	1.85	1503

b) β-(CuEIA)$_4$·2 C$_6$H$_6$

T [K]	$\chi_{M\,exp} \cdot 10^6$	μ_{eff} [BM]
2.6	328434	2.61
5.7	150892	2.62
9.4	90741	2.61
13.9	61169	2.61
19.1	42593	2.55
29.5	26294	2.49
39.5	18557	2.42
50.4	13591	2.34
61.8	10497	2.28
70.5	8832	2.23
84.4	6862	2.15
108.2	5015	2.08
128.2	4053	2.04
148.8	3365	2.00
171.4	2823	1.97
190.5	2477	1.94
211.1	2183	1.92
232.0	1947	1.90
253.1	1741	1.88
275.5	1572	1.86
286.8	1512	1.86
299.0	1467	1.87

$4.18 \cdot 10^{-4}$, Gl. (2)]. This means that the interaction between all copper atoms is ferromagnetic and is greater for the longer Cu-Cu-distances (1 – 2 and 3 – 4). This set of parameters was excluded due to the following reasons: a) In general, shorter Cu-Cu-distance means greater overlap of metal d-orbitals with orbitals of bridging oxygen leading to stronger interaction. b) Only weak spin coupling (antiferromagnetism or weak ferromagnetism) should be expected with a Cu-O . . . Cu bond angle of $\sim 97^\circ$ [12].

We interpret that ferromagnetic spin coupling (between atoms 1 – 3, 1 – 4, 2 – 3, and 2 – 4) results from orthogonality of the p_x- and p_y-orbitals at bridging oxygen with a Cu-O . . . Cu bond angle of 90° [mean value in β-(CuEIA)$_4 \cdot 2\,C_6H_6$]. This is consistent with the 90° superexchange model of Anderson, Goodenough and Kanamori [13]. In contrast to this the spin coupling via the Cu-O-Cu bridge with bond angle 105° [mean value in β-(CuEIA)$_4 \cdot 2\,C_6H_6$] should be antiferromagnetic. The antiferromagnetic spin coupling (between atoms 1 – 2 and 3 – 4) via Cu-O . . . Cu bridge with bond angle 97° [mean value in β-(CuEIA)$_4 \cdot 2\,C_6H_6$] results from the overlap of half occupied metal d-orbitals with s-orbital at bridging oxygen.

The negative value of the Weiss-constant $\Theta = -0.27^\circ$ indicates a weak antiferromagnetic interaction between the ferromagnetic coupled tetrameric clusters, resulting in a decrease of the magnetic moment below 10 K rather than showing a low-temperature plateau when μ_{eff} has reached the value expected for an $S' = 2$ ground state with parallel alignment of the spins.

The effect of antiferromagnetic intercluster interaction is confirmed by the magnetization values at 2.6 K (Table 3). Calculated values with Eq. (4)

$$\langle \mu \rangle = g S' \left\{ \frac{2S'+1}{2S'} \coth\left(\frac{2S'+1}{2S'} \frac{H}{T} \frac{g \beta S'}{k} \right) - \frac{1}{2S'} \coth\left(\frac{1}{2S'} \frac{H}{T} \frac{g \beta S'}{k} \right) \right\}, \qquad (4)$$

where S' is the effective spin of the cluster and H is taken as $H = H_{\text{ex}} + H_{\text{m}}$ [H_{ex} is the applied external field and H_{m} the molecular field related to the Weiss constant by Eq. (5)],

$$H_{\text{m}} = N \beta \langle \mu \rangle \frac{3 k \Theta}{N g^2 \beta^2 S'(S'+1)} \qquad (5)$$

are compared with the experimental values, taking $g = 2.05$, $H = H_{\text{ex}}$, and $H = H_{\text{ex}} + H_{\text{m}}$. H_{m} is calculated with Eq. (5), $\Theta = -0.27^\circ$.

Table 3. Magnetization data of β-(CuEIA)$_4$ [BM/tetramer] at 2.6 K [$\langle \mu \rangle_{\text{calc}}$ calculated with Eqs. (4) and (5) taking $g = 2.05$, $S' = 2$, and $\Theta = 0$ (*) and $\Theta = -0.27^\circ$ (**)].

H [kG]	$\langle \mu \rangle_{\text{exp}}$	$\langle \mu \rangle^{*}_{\text{calc}}$	$\langle \mu \rangle^{**}_{\text{calc}}$
1	0.20	0.22	0.20
2	0.39	0.43	0.39
4	0.77	0.86	0.78
5	0.96	1.06	0.97
6	1.14	1.25	1.15
8	1.48	1.62	1.50
10	1.79	1.95	1.82

Figure 5 shows the energy niveau diagram for α-(CuEIA)$_4$ and β-(CuEIA)$_4$ resulting from the interpretation of the magnetic susceptibility data with the isotropic Heisenberg-Dirac-van Vleck-model (HDVV-model), assuming symmetry S_4 of the tetrameric clusters. The most interesting feature is the $S' = 0$ ground state for α-(CuEIA)$_4$, while the ground state for β-(CuEIA)$_4$ is of total spin $S' = 2$.

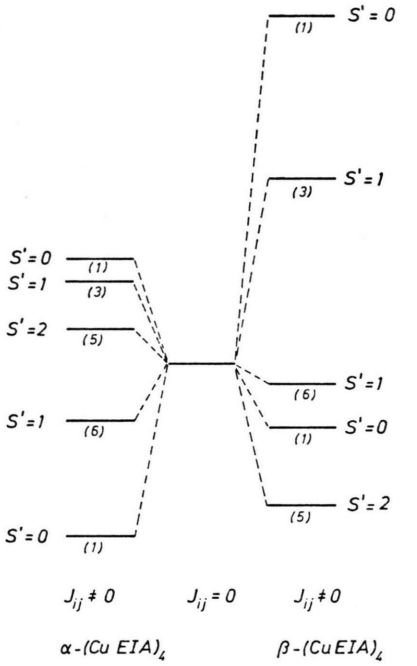

Fig. 5. Schematic energy splitting diagram of both forms of (CuEIA)$_4$.

The experimental susceptibility data for β-(CuEIA)$_4 \cdot 2\,C_6H_6$ (Table 2 b, Fig. 4) are very similar to that of β-(CuEIA)$_4$. The susceptibility increases steadily with decreasing temperature. The magnetic moment μ_{eff} increases with decreasing

temperature, indicating ferromagnetic spin coupling in the $S' = 2$ ground state fully populated below ~ 15 K. The existence of a low-temperature plateau in μ_{eff} is in contrast to β-$(CuEIA)_4$ and shows the absence of an intercluster interaction as do the magnetization data at 2.6 K. The distance between the tetrameric clusters in β-$(CuEIA)_4 \cdot 2\,C_6H_6$ should be greater than in β-$(CuEIA)_4$ because of the intervening benzene molecules.

A fitting procedure of Eq. (3) to the experimental susceptibility data did not lead to a satisfactory agreement between the experimental and calculated values. The reason for this may be that the assumption of S_4-symmetry of the cluster is not justified. The exact symmetry as shown by a crystal structure determination is only C_1 [2].

We would like to express our gratitude to Dr. G. Keller for carrying out the magnetic measurements.

[1] J. A. Bertrand and J. A. Kelley, Inorg. Chim. Acta **4**, 203 [1970].
[2] R. Mergehenn, L. Merz, W. Haase, and R. Allmann, Acta Cryst. **B** (in press).
[3] W. Haase, Habilitationsschrift, Universität Marburg 1970.
[4] W. Haase, Chem. Ber. **106**, 3132 [1973].
[5] R. Mergehenn, W. Haase, and R. Allmann, Acta Cryst. **B 31**, 1847 [1975].
[6] L. Merz, W. Haase, and G. Keller, Ber. Bunsenges. physik. Chem. (in press).
[7] A. P. Ginsberg, Inorg. Chim. Acta Rev. **5**, 45 [1971].
[8] R. L. Martin in "New Pathways in Inorganic Chemistry", edited by E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, Cambridge 1968, Chapter 9.
[9] E. Sinn, Coordin. Chem. Rev. **5**, 313 [1970].
[10] E. G. Jäger, Z. Chem. **6**, 111 [1966].
[11] P. W. Selwood, Magnetochemistry, Interscience, New York 1956, 2. Aufl., pp. 78, 92.
[12] D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, Inorg. Chem. **11**, 2216 [1972].
[13] J. B. Goodenough, Magnetism and the Chemical Bond, Interscience, New York 1963, p. 165 ff.