On the Magnetic behaviour of Tetrakis[2-Diethylamino-Ethanolato-μ_3-O-Copper(II)-Isocyanate]·Trichloromethane, $C_{28}H_{56}Cu_4N_8O_8 \cdot CHCl_3$, a Tetrameric Copper(II) Complex with Antiferromagnetic Ground State

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Dedicated to Professor Dr. A. Weiss on the Occasion of his 60th Birthday

The magnetic susceptibility of the title compound $C_{28}H_{56}Cu_4N_8O_8 \cdot CHCl_3$ in the temperature range of 5.1 to 280.6 K will be reported. The magnetic exchange integrals were evaluated on the basis of the isotropic Heisenberg-Dirac-van Vleck-model. The magnetic behaviour is similar to the solvent free modification of the title compound, obtained by recrystallization from benzene.

Introduction

Tetrameric copper(II) complexes of cubane type show the effect of plasticity: The geometry of the magnetically active Cu_4O_4-core varies in a wide range caused by different ligands. Mergehenn and Haase [1] classified these complexes geometrically: Type I complexes can be described as two slightly coupled dimers while type II complexes are chair-like. Between these types there is a continuous transition in the molecular arrangement of the Cu_4O_4-core. Such complexes will be considered as "transition type complexes".

An interpretation of the magnetic behaviour of tetrameric copper(II) complexes can be given by the isotropic Heisenberg-Dirac-van Vleck (HDvV) model, which allows one to calculate the magnetic exchange integrals. Type I complexes indicate dominating antiferromagnetic spin coupling, whereas type II complexes show dominating ferromagnetic interaction. In the transition type complexes antiferromagnetic and ferromagnetic interactions are in the same order of magnitude. Till now only transition type complexes with antiferromagnetic ground state are known. Recently we have reported the crystal and molecular structure of the title compound [2]. Figure 1 presents a picture of the tetrameric complex as an example of this class of complexes [2]. The magnetic behaviour of the title compound reported here is investigated as part of our studies on magnetostructural correlations in transition type complexes.

Magnetostructural correlations will be reported in a following paper, in which structures and magnetic behaviour reported previously (a solvent free modification, obtained by recrystallization from methanol (A) [3] and a solvent free modification, obtained by recrystallization from benzene (B) [4]) and further new modifications containing solvent will be considered [5].

Experimental

The magnetic susceptibility of powdered samples of the title compound was recorded by the Faraday method at about 1 T in the temperature range of 5.1 to 280.6 K. Experimental susceptibility data were corrected for the underlying diamagnetism ($107 \cdot 10^{-6}$ cm^3/mole Cu), estimated by the increment method given by Pascal. Magnetic moments were calculated using the formula

$$\mu = 2.828\,(\chi\, T)^{1/2}.$$

To convert into S. I. units χ should be multiplied by $4\pi \cdot 10^{-6}$ and the magnetic moment is then given by the expression

$$\mu = 797.74\,(\chi\, T)^{1/2}.$$

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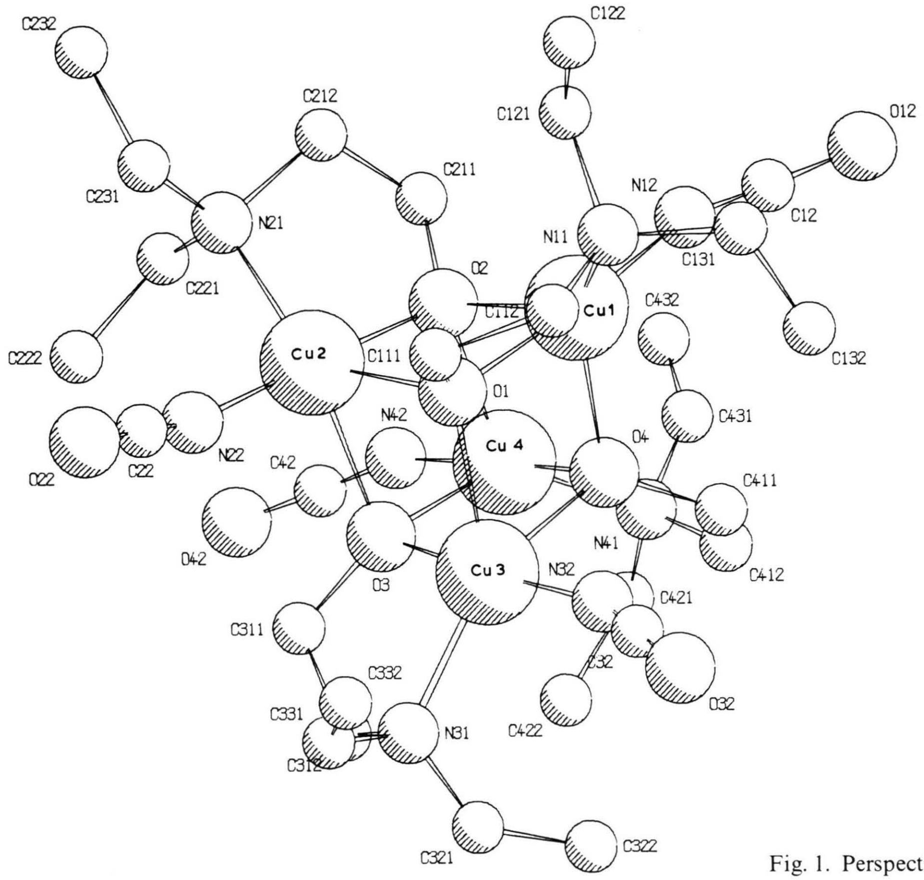

Fig. 1. Perspective view of $C_{28}H_{56}Cu_4N_8O_8$.

Results and Discussion

Magnetic Properties

The temperature dependence of the title compound in the range of 5.1 to 280.6 K is shown in Fig. 2 and Table 1.

The susceptibility data show a maximum at 84 K; from this temperature down to 12 K the susceptibility decreases; at lower temperatures it increases again, caused by paramagnetic impurities. The magnetic moment, starting with 0.18 B.M. at 5.1 K, rises to 1.82 B.M at 280.6 K; the latter can be interpreted as normal paramagnetic behaviour. The maximum susceptibility (2715×10^{-6} cm^3/mole) is a little bit higher than that of (B) (2678×10^{-6} cm^3/mole) [4] but clearly smaller than the maximum susceptibility of (A) (8075×10^{-6} cm^3/mole) [3].

The maximum susceptibility on the temperature scale indicates stronger antiferromagnetic coupling with increasing temperatures (34 for (A), 84 for this complex and 94 K for (B)).

Calculations

The magnetic properties of the spin coupled copper (II) complexes can be explained in terms of the isotropic HDvV-model:

$$\hat{H} = -2 J_{ij} \sum_{i,j} S_i \cdot S_j \,. \tag{1}$$

Figure 3 shows the principal arrangement of the copper atoms in the molecule. In case of the title complex the molecules possess no symmetry element. So (1) leads to six different exchange integrals. Taking into account the problem of symmetry

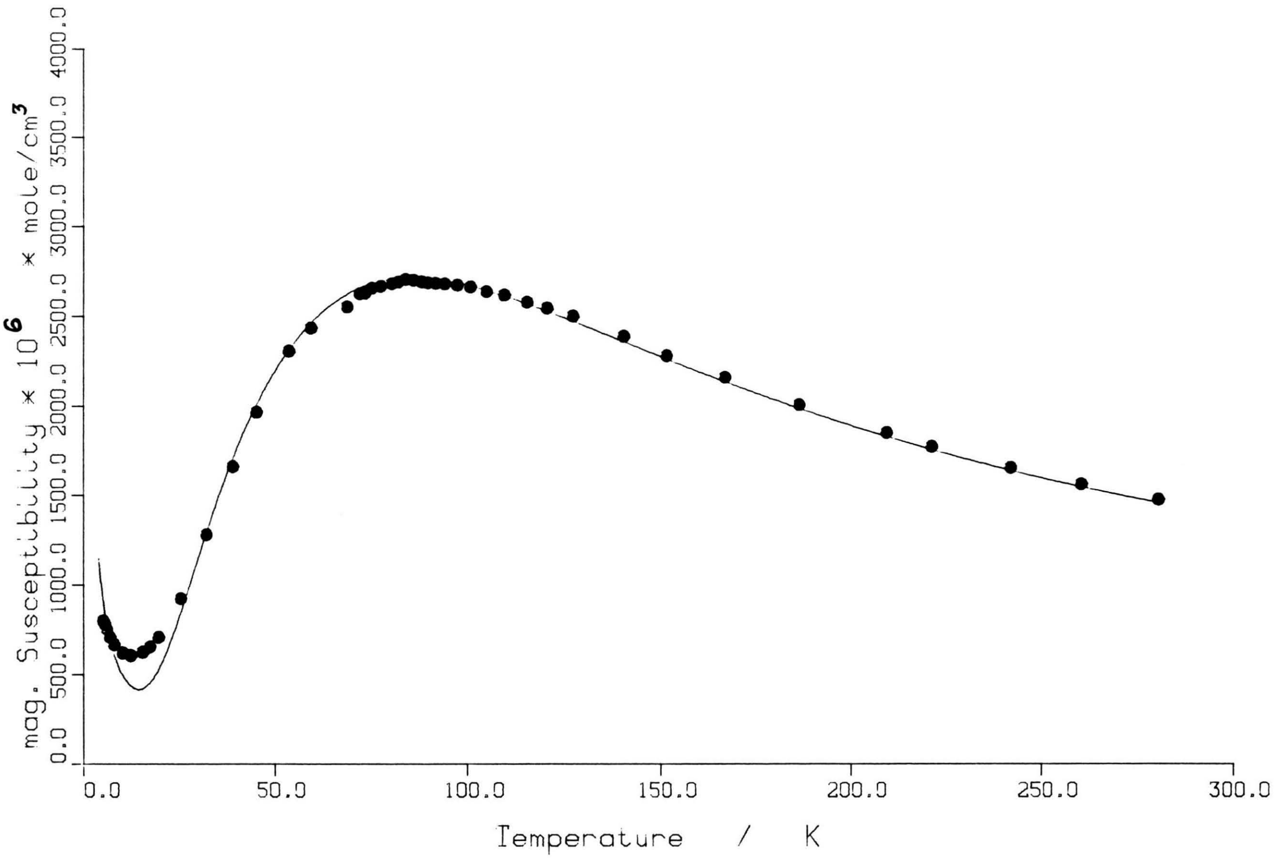

Fig. 2. Temperature dependence of the magnetic susceptibility of the title complex $C_{28}H_{56}Cu_4N_8O_8 \cdot CHCl_3$. Experimental points are compared with the calculated values (full line).

discussed in detail in [4], pseudo-C_2 symmetry will be considered in the calculations of the magnetic parameters (4 exchange integrals result):

$$\begin{aligned}\hat{H} = &-2J_{12}\,S_1 \cdot S_2 - 2J_{34}\,S_3 \cdot S_4 \\ &-2J_{13}(S_1 \cdot S_3 + S_2 \cdot S_4) \\ &-2J_{14}(S_1 \cdot S_4 + S_2 \cdot S_3)\,. \qquad (2)\end{aligned}$$

The formula of the magnetic susceptibility in terms of the exchange integrals and the temperature is wellknown [6] and will not be reported here.

The total paramagnetic susceptibility consists of three terms:

$$\chi_{\text{calc}} = (1-x)\,\chi_{\text{Tetramer}} + x\,\chi_{\text{para}} + N_\alpha\,, \qquad (3)$$

where χ_{para} is the paramagnetic susceptibility caused by impurities and x is their molar fraction.

The temperature independent paramagnetism N_α (TIP) was fixed at $60 \cdot 10^{-6}$ cm^3/mole Cu. The exchange integrals were evaluated by fitting (3) to the experimental susceptibility data.

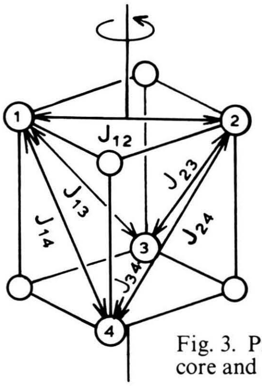

Fig. 3. Principle structure of the Cu_4O_4-core and the related exchange integrals.

Table 1. Experimental and calculated magnetic susceptibilities $\chi * 10^{+6}$ in cm^3/mole of $C_{28}H_{56}Cu_4N_8O_8 \cdot CHCl_3$.

T (K)	χ (experim.)	χ (calc.)
5.1	800	913.9
5.5	780	851.8
5.9	754	798.1
6.7	710	710.0
7.8	667	618.6
10.1	620	495.3
12.1	605	437.6
15.2	624	422.7
17.1	654	455.3
19.4	708	531.4
25.3	925	850.6
32.2	1281	1297.9
39.2	1662	1711.1
45.3	1966	2006.6
53.6	2309	2309.4
59.3	2437	2457.8
68.7	2555	2614.6
72.0	2629	2648.2
73.4	2631	2659.5
75.2	2659	2671.8
77.5	2670	2684.0
80.5	2686	2694.5
82.1	2694	2697.7
84.0	2715	2699.7
86.1	2705	2699.8
88.1	2696	2697.8
89.8	2690	2694.8
91.8	2687	2689.7
94.2	2684	2681.7
97.4	2677	2668.2
100.8	2667	2650.7
105.0	2641	2625.4
109.6	2621	2594.0
115.5	2581	2549.5
120.6	2548	2508.4
127.3	2504	2451.9
140.4	2391	2338.4
151.6	2283	2241.9
167.0	2162	2114.5
186.5	2007	1965.6
209.5	1851	1809.3
221.3	1773	1736.9
242.0	1656	1621.6
260.5	1564	1530.7
280.6	1477	1440.6

Table 2. Magnetic parameters of the title compound $C_{28}H_{56}Cu_4N_8O_8 \cdot CHCl_3$.

g	x	J_{12}/cm^{-1}	J_{34}/cm^{-1}	J_{13}/cm^{-1}	J_{14}/cm^{-1}
2.14	0.01	− 35.0(5)	− 71.6(5)	16.6(5)	13.4(5)

The fit procedure was based on the least squares Simplex routine given by Olsson [7]. The criterion to end the fit procedure was the minimum of the expression

$$\Delta = \sum (\chi_{\text{calc}} - \chi_{\text{obs}}) \,. \tag{4}$$

The agreement between the experimental and calculated values is shown in Fig. 2; the resulting magnetic parameters are presented in Table 2. The calculated susceptibilities are listed in Table 1 too.

The magnetic parameters are similar to that of (B) [4], in accordance with the comparable susceptibility function of temperature. Comparison of the molecular structures of both modifications shows nearly the same geometry too. Nevertheless there are small differences which will be discussed in a following paper in more detail [5].

There is no influence of the trichloromethane molecules in the magnetic behaviour of the title complex, in agreement with the fact that no hydrogen bridge over the trichloromethane molecules could be found [2].

Acknowledgement

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