

Magnetic Susceptibility of Bis[bis(methoxycarbimido)aminato]copper(II) Complex

R. BOČA, P. BARAN, and L. DLHÁŇ

Department of Inorganic Chemistry, Faculty of Chemical Technology,
Slovak Technical University, SK-812 37 Bratislava

Received 16 April 1993

The magnetic susceptibility of the $[\text{Cu}(\text{N}(\text{C}(\text{NH})\text{OCH}_3)_2)_2]$ complex has been measured within the temperature range from 77 K to 300 K. The AC susceptometer technique has been used for this purpose. The complex obeys the typical Curie—Weiss law so that from the nonlinear regression the Curie constant $C = 0.0163774$ K, Weiss constant $\Theta = -7.74$ K, and the temperature-independent term $\alpha(\text{SI}) = 41 \times 10^{-6}$ have been obtained. The averaged g -factor, $g_{av} = 2.089$ evaluated from the Curie constant, matches well with that obtained from EPR spectra.

Among magnetochemical techniques the AC (alternating current) susceptometry belongs to relatively new methods. It is based on the time development of the alternating magnetic field as

$$H_{ac} = H_0 \cos(\omega t) \quad (1)$$

where H_0 is the amplitude of the magnetic field intensity and ω is the frequency. The magnetization M_{ac} cannot follow the incident field immediately and it is shifted by a phase angle θ , so that

$$M_{ac} = M_0 \cos(\omega t - \theta) = X' H_0 \cos(\omega t) + X'' H_0 \sin(\omega t) \quad (2)$$

Consequently the magnetic susceptibility in alternating fields becomes a complex quantity [1]

$$X_{ac} = X' - iX'' \quad (3)$$

where the real component $X' = (M_0/H_0) \cos \theta$ is the dispersion and the imaginary component $X'' = (M_0/H_0) \sin \theta$ is termed the absorption.

The measurements of the AC susceptibility depend upon several factors among which the following ones adopt a great importance:

- i) proper selection of the frequency (ω) and field (H_0),
- ii) determination of the sample volume (V_s),
- iii) correction to demagnetization,
- iv) subtraction of addenda,
- v) data analysis and mathematical processing.

The subsequent publications on magnetic measurements by our group will follow the procedure described below. For this reason the procedure is presented in more detail. The comparison with standard measurements in static fields is also included.

EXPERIMENTAL

The experiments were done on the commercial AC susceptometer/magnetometer LakeShore, model

7221. The voltage $U_1 (U_2)$ induced in secondary coils represents the recorded quantity. This is influenced by the sample stored in a nylon container and it includes also the offset voltage U_0 . A pair of secondary coils is wound in an opposite direction and this construction permits to subtract the offset voltage, as $U_1 = U + U_0$ and $U_2 = -U + U_0$. Thus the voltage

$$U = (U_1 - U_2)/2 \quad (4)$$

represents the true response of the sample and it is directly proportional to the (volume) susceptibility X

$$U = (1/\beta) V_s f H X \quad (5)$$

Here β is the system calibration coefficient ($\beta = 1.754$, considered as a universal constant), V_s sample volume, f frequency of AC field (variable from 5 to 1000 Hz), H magnetic field amplitude to 800 A m^{-1} .

For precision measurements or when the susceptibility is large, the measured susceptibility X should be corrected for demagnetization effects. This effect has geometrical reasons (internal field in the sample differs from the applied field) and is evaluative from the sample shape. Then the true internal susceptibility is

$$X_{int} = X/(1 - DX) \quad (6)$$

where D stands for the demagnetization factor. The latter is tabulated for cylindrical samples and it is a smooth function of ℓ/d where d means the sample diameter and ℓ its height [2].

The AC susceptibility depends upon the frequency of the applied field. The low-frequency limit

$$\lim_{f \rightarrow 0} X = X_T = \left(\frac{\partial M_{ac}}{\partial H} \right)_T \quad (7)$$

corresponds to the thermal equilibrium and is comparable with the susceptibility measured in static fields (e.g. by Gouy or Faraday balances). The greater the frequency, the lower the susceptibility which

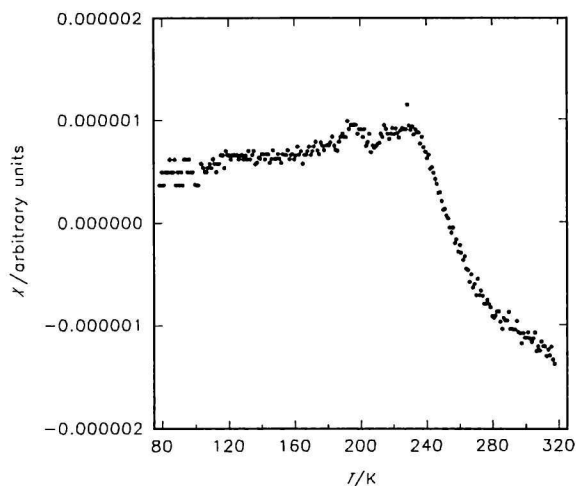


Fig. 1. Addenda A_4 recorded for $f = 666.7$ Hz and $H = 320$ A m^{-1} . Only the real component X' is shown (in arbitrary units).

in the opposite limit approaches the adiabatic value

$$\lim_{f \rightarrow \infty} X = X_S = \left(\frac{\partial M_{ac}}{\partial H} \right)_S \quad (8)$$

The choice of the H and f combination heavily influences the quality of the signal U measured by the nanovoltmeter: high value of the (fH) factor secures that the voltage is read off with small error; small value, on the contrary, may lead to a considerable scattering of experimental data. High value of the (fH) factor may be reached either by high f or H . High f , however, reduces the value of X which departs from the X_T limit and approaches the X_S value. High H , on the other hand, may lead to the declination from the linear M vs. H behaviour and then the magnetic susceptibility is a function of the applied field. Thus it is difficult to select the best of these experimental parameters and therefore the measurements are to be done for several combinations of f and H . As an example the following statements may serve:

i) For strong signal samples (e.g. superconductors, ferromagnets) the values of $f = 125.0$ Hz and $H = 80$ A m^{-1} may be used, since $fH = 10\,000$ A $m^{-1} s^{-1}$;

ii) For medium signal samples (multi-spin paramagnets) the combination like $f = 666.7$ Hz and $H = 320$ A m^{-1} seems to be an appropriate choice, as $fH = 213\,344$ A $m^{-1} s^{-1}$; when the material does not declinate from linear magnetics another choice is relevant, namely $f = 222.2$ Hz and $H = 800$ A m^{-1} , so that $fH = 177\,760$ A $m^{-1} s^{-1}$;

iii) For very low signal samples (diluted paramagnets and antiferromagnets) the $f = 1000$ Hz and $H = 800$ A m^{-1} parameters represent the limiting case and then $fH = 800\,000$ A $m^{-1} s^{-1}$.

The second important factor influencing the measurements is represented by the determination of the

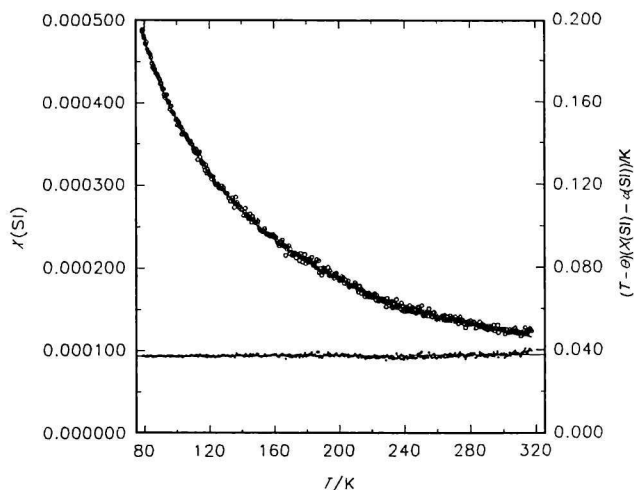


Fig. 2. Volume susceptibility vs. temperature (open circles) for $Ni(en)_3S_2O_3$ complex; 482 points measured at $f = 125.0$ Hz and $H = 80$ A m^{-1} (addenda A_4 subtracted).

sample volume. As far as the demagnetization correction is important the sample shape should be described: the sample diameter and height may be determined taking into account the shape of the sample holder (diameter and the length of the filled space). Moreover, the volume of the sample should be determined as precisely as possible. For powder samples the following procedure has been adopted. The dried and powdered sample has been separated according to the size of particles and a definite fraction of particles size has been used to determine the specific volume. A calibrated glassy holder has been filled by the powdered sample and the specific volume has been calculated as $v = V/m$. The nylon (nontransparent) sample holder has been filled in a similar way and the sample volume is $V_s = m_s (V/m)$, m_s being the sample mass.

As the free sample holder, the support rod, and residual air in the sample holder contribute to the measured voltage, addenda should be used to eliminate this admixture. Several sets of addenda were provided:

i) addenda A_2 corresponds to the air-containing sample holder; this has the highest (paramagnetic) signal;

ii) A_3 means a sample holder filled with the helium gas (the residual oxygen present) and it yields a lower signal;

iii) A_4 is an evacuated sample holder (traces of oxygen still present) producing even lower signal;

iv) A_5 is a highly evacuated sample holder (oxygen absent) and this gives the lowest (diamagnetic) signal.

Let us note that the powdered samples have some residual content of the paramagnetic oxygen between particles and also in the space of the sample holder. Our experience shows that the addenda A_4 or A_3 may

Table 1. Input Experimental Parameters and Calculated Magnetic Parameters for Ni(en)₃S₂O₃

Data set	a	b	c	d
Density ρ /(g cm ⁻³)	0.921			
Sample mass m_s /g	0.13654			
Sample volume V_s /cm ³	0.14825			
Demagnetization factor D (SI)	0.179			
Field parameters:				
frequency f /Hz	666.7	666.7	125.0	125.0
amplitude H /(A m ⁻¹)	320	320	80	80
Addenda $A_n(f, H)$	A_3	A_4	A_3	A_4^a
Mass susceptibility				
χ_p (SI)/(10 ⁻⁹ m ³ kg ⁻¹) at 298 K				
measured value	124.7	128.4	131.3	135.2
best fit 1 value ^b	127.2	130.5	130.8	134.0 ^a
best fit 2 value ^c	127.4	130.6	130.1	133.4
tabulated ^d	140.0			
Curie—Weiss parameters (SI) — best fit 1				
number of points	464	464	482	481
Curie constant C /K	0.036657	0.036892	0.036871	0.037509
Weiss constant Θ /K	- 1.12	- 0.29	+ 2.24	+ 2.26
α term(SI)/10 ⁻⁶	- 5.43	- 3.46	- 4.23	- 3.42
Curie parameters (SI) — best fit 2				
number of points	464	464	482	481
Curie constant C /K	0.036080	0.036741	0.038079	0.038749
α term(SI)/10 ⁻⁶	- 3.70	- 3.01	- 7.91	- 7.20

a) Most reliable results; b) Curie—Weiss law used; c) pure Curie law used; d) in static magnetic field.

successfully describe the situation. A typical characteristics of addenda A_4 is shown in Fig. 1. However, small variation of addenda characteristics with f and H parameters is possible. In reality, addenda is measured in the dual (complex) mode and its voltage (corresponding to the actual combination of f and H) is subtracted from the sample voltage during the data analysis. The recording of addenda has a certain scattering of points. Therefore the corrected file X vs. T may be less smooth than the recorded X vs. T function.

In order to compare the results of the AC susceptometry with tabulated data some magnetochemical standards have been reinvestigated. Fig. 2 shows the X vs. T dependence (corrected to A_4) for the salt of Ni(en)₃(S₂O₃). The calculated data are collected in Table 1. The following relationship holds true

$$\chi_p/(\text{m}^3 \text{kg}^{-1}) = 10^{-3} X(\text{SI})/(\rho(\text{g cm}^{-3})) \quad (9)$$

It can be concluded that the measured data match quite well with those tabulated in literature [3].

The numerical data X vs. T have been used to fit the curve

$$X = C/(T - \Theta) + \alpha \quad (10)$$

using the nonlinear regression and thus the values of the Curie constant C , Weiss constant Θ , and the temperature-independent term α have been obtained. The last term consists of the diamagnetic contribution α_{dia} and the temperature-independent paramagnetism α_{TIP} , i.e.

$$\alpha = \alpha_{\text{dia}} + \alpha_{\text{TIP}} \quad (11)$$

The quality of the regression is best visible from the dependence $(X - \alpha)(T - \Theta)$ vs. T which should be a constant.

RESULTS AND DISCUSSION

The title complex has been prepared as described elsewhere [4]. The complex (violet crystals) has a molecular structure (Fig. 3) with a single unpaired electron per central atom. This is the *raison d'être* of its behaviour as a diluted paramagnet. The magnetic susceptibility has rather low values approaching ca. $\chi_p = 90 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$ at 293 K. Therefore the demagnetization correction loses its significance but the addenda, on the contrary, becomes more important.

The recording of X vs. T dependence has been performed for the same sample two times (data set 1 and 2). Low signal which did not allow an automatic positioning (the finding of the optimum sample position within the secondary coil which produces the maximum voltage) was the reason of this fact. Such an accumulation of data may eliminate the accidental errors.

The measured (volume) susceptibility (data set 1, uncorrected to addenda) follows a smooth curve within the temperature range 80—230 K (Fig. 4). Above this temperature the addenda adopts its quantitative, as well as qualitative importance.

A virtual volume susceptibility is obtained when the addenda A_4 is subtracted (Fig. 5). This procedure,

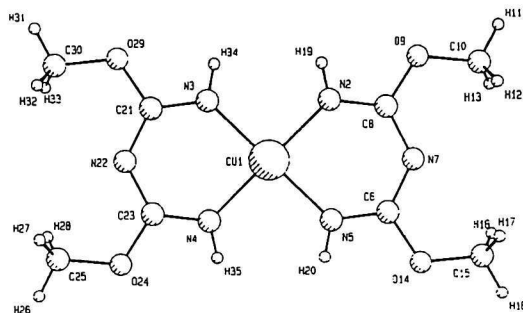


Fig. 3. Molecular structure of $[\text{Cu}(\text{N}(\text{C}(\text{NH})\text{OCH}_3)_2)_2]$ complex.

however, enlarges the scattering of points. After the nonlinear regression (110 points) the Curie–Weiss parameters relaxed to $C = 0.0163774$ K, $\Theta = -7.74$ K, and $\alpha(\text{SI}) = 40.74 \times 10^{-6}$. Results of alternative fittings procedures are collected in Table 2. The X vs. T dependence for the accumulated set of data (data set 1 + 2), corrected to addenda A_3 , is shown in Fig. 6.

Since the complex under study may be considered as an axially symmetric system with $X = (2X_{\perp} + X_{\parallel})/3$, the molar Curie constant, by its definition, is

$$C_{\text{mol}} = [N_A \mu_0 \mu_B^2 S(S+1)/3k] [2g_{\perp}^2 + g_{\parallel}^2]/3 \quad (12)$$

where N_A is Avogadro constant, μ_0 permeability of the vacuum, μ_B Bohr magneton, k Boltzmann constant, g_{\perp} and g_{\parallel} components of the g -tensor. For the spin $S = 1/2$ we get

$$C_{\text{mol}}/(\text{K m}^3 \text{ mol}^{-1}) = 1.178\,550 \times 10^{-6} [2g_{\perp}^2 + g_{\parallel}^2]/3 \quad (13)$$

(in SI units). Thus we can evaluate an “averaged” g -factor as

$$g_{\text{av}}^2 = [2g_{\perp}^2 + g_{\parallel}^2]/3 = 0.848\,50 \times 10^6 C_{\text{mol}}/(\text{K m}^3 \text{ mol}^{-1}) \quad (14)$$

This formula requires the experimental value of the molar Curie constant which is

$$C_{\text{mol}} = CM/\rho \quad (15)$$

where $M = 323.7982$ g mol $^{-1}$ is the molar mass and $\rho = 1.031$ g cm $^{-3}$ density of the powder sample (better to say this is a reciprocal value of the specific volume, $\rho = v^{-1}$). Using this information the molar Curie constant is $C_{\text{mol}} = 5.143\,523 \times 10^{-6}$ K m 3 mol $^{-1}$ and it yields $g_{\text{av}} = 2.089$. This value may be compared with that obtained from EPR spectra of the frozen (100 K) toluene solution of the title complex [5, 6]: g_{av} (EPR) = 2.087 ($g_{\perp} = 2.050$ and $g_{\parallel} = 2.158$).

The molar Curie constant may be used to evaluate the effective magnetic moment

$$\mu_{\text{eff}} = [(3k/N_A \mu_0) \chi'_{\text{mol}} T]^{1/2} = [(3k/N_A \mu_0) C_{\text{mol}}]^{1/2} \quad (16)$$

or in usual units of the Bohr magneton

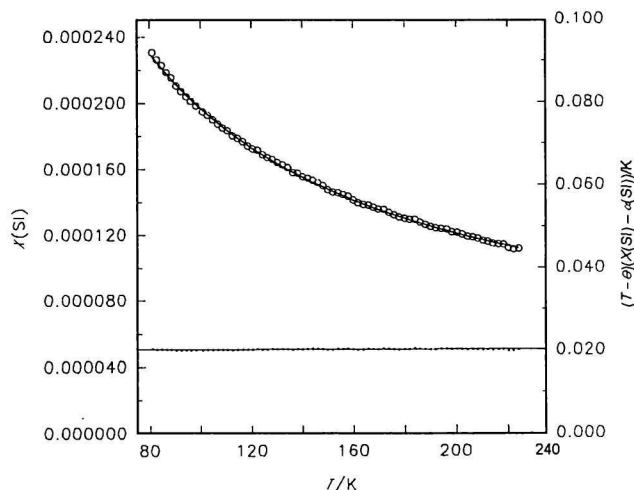


Fig. 4. Volume susceptibility vs. temperature (open circles) for $[\text{Cu}(\text{N}(\text{C}(\text{NH})\text{OCH}_3)_2)_2]$ complex; 73 points measured at $f = 222.2$ Hz and $H = 800$ A m $^{-1}$ (addenda not subtracted).

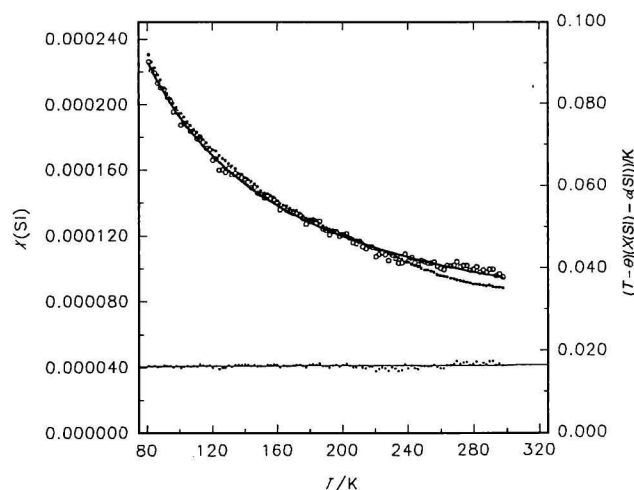


Fig. 5. Volume susceptibility vs. temperature for $[\text{Cu}(\text{N}(\text{C}(\text{NH})\text{OCH}_3)_2)_2]$ complex (data set 1); 108 points measured at $f = 222.2$ Hz and $H = 800$ A m $^{-1}$; filled circles — recorded data; open circles — data corrected to addenda A_4 .

$$\mu_{\text{eff}}/\mu_B = 798 (\chi'_{\text{mol}} T)^{1/2} = 798 C_{\text{mol}}^{1/2} \quad (17)$$

Here χ'_{mol} is the molar susceptibility corrected to the diamagnetism. Then C_{mol} yields the effective magnetic moment of $\mu_{\text{eff}}/\mu_B = 1.810$. The last value is slightly higher relative to the spin only value for a single unpaired electron which is $\mu_{\text{eff}}/\mu_B = 1.73$. An independent measurement on Gouy balances [7] gave the value of $\mu_{\text{eff}}/\mu_B = 1.89$ (293 K).

The temperature-independent term $\alpha(\text{SI}) = 40.74 \times 10^{-6}$ may be used to evaluate the temperature-independent paramagnetic contribution by subtracting the diamagnetic correction α_{dia} . The diamagnetic contribution may be estimated by the usual way — using Pascal constants (see e.g. [3]). Hence the molar contribution becomes $\alpha_{\text{dia}} = -142 \times 10^{-6}$ cm 3 mol $^{-1}$ (in the usually used Gaussian and cgs emu

Table 2. Results on $[\text{Cu}(\text{N}(\text{C}(\text{NH})\text{OCH}_3)_2)_2]$ Complex

Data set	1	1 ^a	1 + 2	1 + 2
Molar mass $M/(\text{g mol}^{-1})$	323.7982			
Density $\rho/(\text{g cm}^{-3})$	1.031			
Sample mass m_s/g	0.14485			
Sample volume V_s/cm^3	0.140			
Demagnetization factor D (SI)	0.163			
Field parameters:				
frequency f/Hz	222.2			
amplitude $H/(\text{A m}^{-1})$	800			
Addenda A_n^b	A_3	A_4	A_3	A_4
Mass susceptibility				
$\chi_p(\text{SI})/(10^{-9} \text{ m}^3 \text{ kg}^{-1})$ at 293.5 K				
measured value	91.15	92.47		
best fit value	90.32	92.25		
Curie—Weiss parameters (SI) — best fit				
number of points	108	110	217	221
Curie constant C/K	0.013245	0.016377	0.015909	0.018406
Weiss constant Θ/K	+ 4.17	- 7.74	- 8.01	- 15.26
α term(SI)/ 10^{-6}	47.33	40.74	39.24	34.62
Effective magnetic moment μ_{eff}/μ_B				
best fit value	1.628	1.810	1.784	1.919
Averaged g -value g_{av}				
best fit value	1.879	2.089	2.059	2.215

a) The best estimates. b) Addenda measured at $f = 666.7 \text{ Hz}$ and $H = 320 \text{ A m}^{-1}$.

units). The total temperature-independent term in these units is

$$\frac{\alpha_{\text{mol}}/(\text{cm}^3 \text{ mol}^{-1})}{(4\pi\rho/(\text{g cm}^{-3}))} = \frac{\alpha(\text{SI})(M/(\text{g mol}^{-1}))}{1018 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}} \quad (18)$$

and finally $\alpha_{\text{TIP}} = \alpha - \alpha_{\text{dia}} = 1160 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The last value, however, is overestimated when compared with the typical values for copper(II) complexes [1].

CONCLUSION

Results on the reinvestigation of the magnetochemical standard $\text{Ni}(\text{en})_3\text{S}_2\text{O}_3$ showed that the AC susceptometry may be successfully applied to diluted paramagnets, particularly to metal complexes with bulky organic ligands. Such a reinvestigation is not a trivial problem, as resulted from the parallel reinvestigations of $\text{HgCo}(\text{NCS})_4$ [8]. The best value of the mass susceptibility $X_p(298 \text{ K}) = 134.0 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$ matches well with the tabulated value of $X_p(298 \text{ K}) = 140.0 \times 10^{-9} \text{ m}^3 \text{ kg}^{-1}$. The above value results from the calculated Curie—Weiss parameters (C , Θ , α) generated through a nonlinear regression to the Curie—Weiss law.

The title compound, bis[bis(methoxycarbimido)-aminato]copper(II) complex, follows the Curie—Weiss law, too; the calculated molar Curie constant $C_{\text{mol}} = 5.143\,523 \times 10^{-6} \text{ K m}^3 \text{ mol}^{-1}$ may be used to enumerate the g_{av} value, i.e. $g_{\text{av}} = 2.089$. The latter value is in harmony with that obtained by the EPR technique. Moreover, the effective magnetic moment at 293 K $\mu_{\text{eff}}/\mu_B = 1.81$ agrees with that obtained by the Gouy balances.

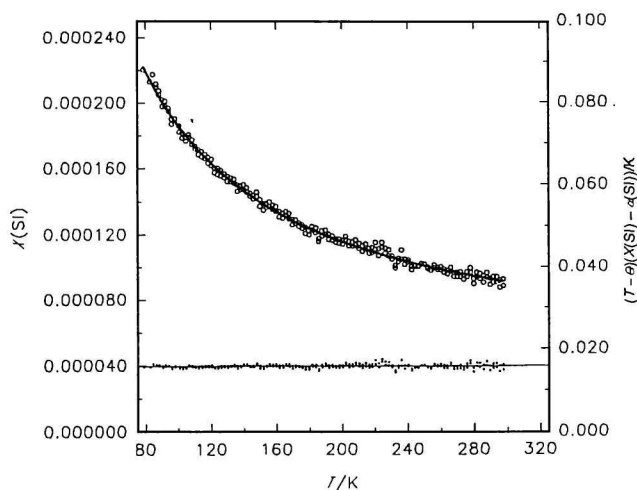


Fig. 6. Volume susceptibility vs. temperature for $[\text{Cu}(\text{N}(\text{C}(\text{NH})\text{OCH}_3)_2)_2]$ complex (data set 1 + 2); 217 points measured at $f = 222.2 \text{ Hz}$ and $H = 800 \text{ A m}^{-1}$; open circles — data corrected to addenda A_3 .

REFERENCES

- Carlin, R. L., *Magnetochemistry*. Springer-Verlag, Berlin, 1986.
- Goldfarb, R. B. and Minervini, J. V., *Rev. Sci. Instrum.* 55, 761 (1984).
- König, E., in *Landolt—Börnstein*, Neue Serie, Bd. II/2, p. 1. Springer-Verlag, Berlin, 1966.
- Kožíšek, J., Hvastijová, M., and Kohout, J., *Inorg. Chim. Acta Lett.* 168, 157 (1990).
- Valko, M., private communication.
- Boča, R., Hvastijová, M., Kožíšek, J., and Valko, M., *J. Am. Chem. Soc.*, submitted for publication.
- Jamnický, M., private communication.
- Nelson, D. and ter Haar, L. W., *Inorg. Chem.* 32, 182 (1993).

Translated by R. Boča