The Magnetic Susceptibilities of Some Trinuclear Copper(II) Compounds

By **B. N. Figgis** * and **D. J. Martin**, School of Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia

The magnetic susceptibility of four trinuclear compounds of bivalent copper has been measured to very low temperatures. In two cases the measurements extend from room temperature to 4·2 K or below, and in two cases from room temperature to 80 K, with the addition of 4·2 K. The e.s.r. *g*-values for the cupric ion were determined. The results support the model of magnetic exchange between one cupric ion and its neighbours on each side, with no interaction between the latter. They allow a more accurate evaluation of the parameters which characterises the model. *J* is 43 cm^{-1} in one instance and *ca.* 200 cm^{-1} in three others, and *g* varies from 2·04 to 2·17.

THE magnetic susceptibilities of polymeric, particularly dinuclear, cupric compounds have been widely studied. In many instances the measurements have been taken from ambient to about 80 K in temperature. The results have usually been interpreted in terms of magnetic exchange between a small number of cupric ions of spin $\frac{1}{2}$ and *g*-value *ca.* 2·1. In some cases, the theory for a one-dimensional antiferromagnet has been involved. The magnitudes of the exchange integrals (J) between neighbouring cupric ions has usually been so large (*ca.* −300 K) that studies down to 80 K have been able to define the magnetic behaviour of the system adequately.

Harris and his co-workers,[1,2] have described a series of trinuclear cupric Schiff's base compounds of which they have studied the magnetic susceptibilities down to 80 K. They interpreted the results in terms of antiferromagnetic exchange between a central, and each of two neighbouring, cupric ions, with zero exchange between the latter two. That is, in Figure 1, J is negative and finite, and J' is zero. The theory of the magnetic properties of this exchange system was given by Harris and his co-workers, and they deduced the formula † (1). They employed J and g (the average *g*-value for the three cupric ions) as adjustable parameters. They took $N\alpha$, the temperature-independent paramagnetic term, to be $2{\cdot}26 \times 10^{-9}$ SI mol^{-1}, as would be typical for three cupric ions with oxygen and nitrogen ligands.[4] Values for J and g were derived for each compound. The values for J were mostly similar to those observed for dimeric compounds (*ca.* −200 cm^{-1}), but in one case it was distinctly smaller, at *ca.* −40 cm^{-1}. In the latter instance the temperature range, 300—80 K, was not sufficient to characterise the magnetic properties of the system.

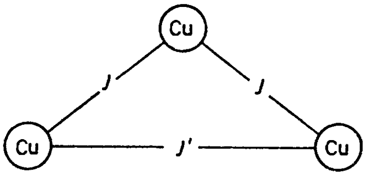

FIGURE 1 The model for magnetic exchange in the trinuclear cupric complexes studied

$$\chi_A = \frac{Ng^2\beta^2\mu_0}{4kT}\cdot\frac{\exp(-2J/kT)+\exp(-2J'/kT)+10\exp(J/kT)}{\exp(-2J/kT)+\exp(-2J'/kT)+2\exp(J/kT)} + N\alpha \qquad (1)‡$$

We have performed measurements of the magnetic susceptibilities of four of these compounds (see Table 3) at lower temperatures, including the one with J *ca.* −40 cm^{-1}. For two of the compounds the temperature range was extended continuously to the helium range, and for the other two a single measurement at 4·2 K was made. These measurements allow a much more complete description of the magnetic behaviour of the system to be made, particularly for the case with the low value of J.

RESULTS AND DISCUSSION

The values of the parameters J and g which we derived for the model are given in Table 1. We also employed $N\alpha = 2{\cdot}26 \times 10^{-9}$ SI mol^{-1}. The magnetic moment, as a function of temperature, is compared with that predicted by the model in Figures 2 and 3. The magnetic susceptibilities found for the compounds at various temperatures are given in Table 2. Except in the case of $Cu(Cues)_2(ClO_4)_2,2H_2O$ in the range 80—100 K our results agree well with the earlier measurements between 80 and 300 K.

TABLE 1

The parameters of the model for magnetic exchange in the compounds studied

	This work		Earlier work [1,2]	
Compound	J/cm^{-1}	g	J/cm^{-1}	g
$Cu(Cues)_2(ClO_4)_2,3H_2O$	−43 †	2·091	−40	2·10
$Cu(Cueha)_2(ClO_4)_2,2H_2O$	−190	2·042	−200	2·13
$Cu(Cups)_2(ClO_4)_2,2H_2O$	−237	2·171	−230	2·12
$Cu(Cupha)_2(ClO_4)_2,3H_2O$	−236	2·104	−240	2·20

† This value fits the data above *ca.* 100 K. See text concerning the behaviour at lower temperatures.

The results substantiate the conclusions of the

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† This equation is a corrected form of equation (5) of ref. 2. The necessity for the correction was discovered in the course of this work and was confirmed by the authors of that reference. They also point out[3] that, because a misprint in the formulae for the coefficients *a* on p. 2190, other expressions given there for molar susceptibilities are in error.

‡ $\mu_0 = 4\pi \times 10^{-7}$ H m^{-1}.

[1] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.

[2] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Chem. Phys.*, 1968, **49**, 2183.

[3] E. Sinn, personal communication.

previous work, in the main. The values of J deduced by Harris and his co-workers[1,2] are very similar to those we have found, and their conclusion that J' is negligible is upheld. Our e.s.r. values for g are typical for cupric complexes with octahedral co-ordination by oxygen and nitrogen ligands.[4] They differ appreciably from those deduced from the magnetic properties alone,[1,2] but not by more than might be expected in view of the fitting procedure there.

TABLE 2

Magnetic susceptibility of the compounds studied at various temperatures (10^{-9} SI/kmol of copper)

$Cu(Cues)_2(ClO_4)_2,3H_2O$																
T/K	305·0	302·1	282·3	260·6	242·7	218·5	194·3	168·1	150·5	129·0	106·1	104·0	80·2	70·0	59·0	48·1
χ_{Cu}	14·52	14·68	15·48	16·58	17·40	19·07	20·86	22·94	24·64	27·16	30·1	30·4	35·0	38·5	43·4	49·1
T/K	43·7	38·8	33·8	29·3	25·3	19·5	15·0	13·0	11·5	9·68	8·08	5·39	4·20			
χ_{Cu}	53·4	59·0	65·2	72·4	82·2	104·2	132·8	152·0	170·7	208·4	246·4	355·6	465			
$Cu(Cueha)_2(ClO_4)_2,2H_2O$																
T/K	293·3	283·8	261·3	239·5	217·1	191·8	167·5	143·2	125·5	100·2	81·0	35·9	30·0	25·4	22·0	9·86
χ_{Cu}	7·73	7·83	8·04	8·35	8·80	9·36	10·29	11·78	13·10	16·30	20·08	44·8	54·4	64·4	73·4	80·3
T/K	17·5	15·5	13·0	11·9	9·30	8·15	6·75	5·77	5·37	4·82	4·41	4·20	3·95	3·60	3·35	2·955
χ_{Cu}	91·1	106·8	126·2	137·5	175·8	197·3	244·2	276·4	295·6	323	356	373	376	413	449	507
$Cu(Cups)_2(ClO_4)_2,2H_2O$																
T/K	302·1	299·5	288·8	273·9	253·4	225·1	201·3	175·5	154·0	139·2	106·2	84·1	4·20			
χ_{Cu}	7·52	7·55	7·66	7·91	8·28	8·87	9·65	10·92	12·19	13·50	18·00	22·84	429			
$Cu(Cupha)_2(ClO_4)_2,3H_2O$																
T/K	303·8	297·5	277·5	248·2	218·5	202·8	174·6	148·3	113·1	80·90	4·20					
χ_{Cu}	7·07	7·07	7·40	7·88	8·43	9·12	10·10	11·70	15·50	22·1	424					

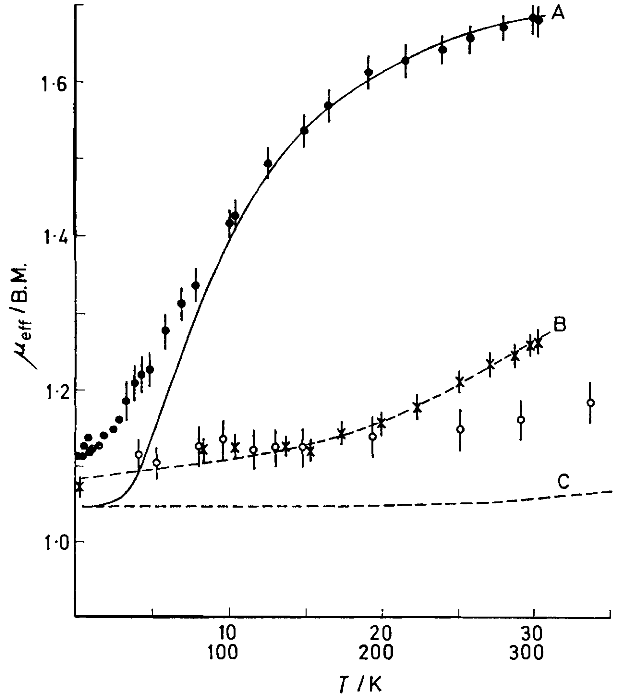

FIGURE 2 Magnetic moment as a function of temperature for ●, $Cu(Cues)_2(ClO_4)_2,3H_2O$, 0—350 K scale; ○, $Cu(Cues)_2(ClO_4)_2,3H_2O$, 0—35 K scale; and ×, $Cu(Cups)_2(ClO_4)_2,2H_2O$, 0—350 K scale. Vertical bars on points indicate approximate limits of error; A, $J = -43$ cm^{-1}, $g = 2·091$, 0—350 K scale; C, $J = -43$ cm^{-1}, $g = 2·091$, 0—35 K scale; and B, $J = -237$ cm^{-1}, $g = 2·171$, 0—350 K scale

The exception to some of these statements concerns the compound with the low value of J, $Cu(Cues)_2(ClO_4)_2,3H_2O$, where the model fails to reproduce the experimental variation of magnetic moment with temperature below *ca.* 100 K. If J' is allowed to be non-zero, whether positive or negative, the agreement between theory and experiment is poorer. The experimental susceptibility rises above that given by the model by as much as 25%, and is 14% high at 4·2 K. The susceptibility obeys the Curie law at very low temperatures. It is easy to see from the form of the expressions for the magnetic susceptibility in the presence of exchange that, for Curie-law behaviour to occur, an odd number of cupric ions must be involved in the interaction. For a fixed negative value of J, the number of cupric ions in the exchange system must be lower in order to raise the susceptibility at a given temperature, but the only odd number less than three is unity, and the susceptibility for an isolated cupric ion

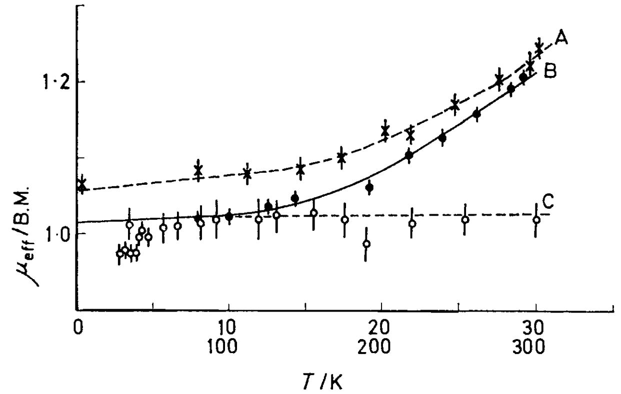

FIGURE 3 Magnetic moment as a function of temperature for ●, $Cu(Cueha)_2(ClO_4)_2,2H_2O$, 0—350 K scale; ○ $Cu(Cueha)_2(ClO_4)_2,2H_2O$, 0—35 K scale; and × $Cu(Cupha)_2(ClO_4)_2,3H_2O$, 0—350 K scale; B, $J = -190$ cm^{-1}, $g = 2·042$, 0—350 K scale; C $J = -190$ cm^{-1}, $g = 2·042$, 0—35 K scale; and A, $J = -236$ cm^{-1}, $g = 2·104$, 0—350 K scale

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[4] E. Konig, Landolt-Bornstein, II, Atomic and Molecular Physics, vol. 2, Magnetic Properties of Co-ordination and Organometallic Transition-metal compounds.

is much too high. The alternative of raising the magnitude of J does not solve the problem, since the susceptibility at temperatures much lower than $|J|$ is independent of J, and destroys the good fit for the data at higher temperatures. No explanation for the discrepancy is available at this stage, and further speculation is not warranted in the absence of a crystal-structure determination.

The fall in the magnetic moment for the compound $Cu(Cueha)_2(ClO_4)_2,2H_2O$ at temperatures below 4 K, obvious in Figure 3, is real and probably reflects a very small inter-molecular exchange interaction.

EXPERIMENTAL

The compounds were prepared by the methods described by Harris and his co-workers.[1,2] Analyses are in Table 3.

TABLE 3

Analytical data for the compounds studied

Found				Calc.		
C (%)	H (%)	Cu (%)	Formula	C (%)	H (%)	Cu (%)
Bis-[*NN'*-ethylenebis(salicylaldiminato)copper(II)]copper(II) perchlorate trihydrate: $Cu(Cues)_2(ClO_4)_2,3H_2O$						
39·1	3·2	19·4	$C_{32}H_{34}Cl_2Cu_3N_4O_{15}$	39·4	3·5	19·5
Bis[*NN'*-ethylenebis(*o*-hydroxyacetopheniminato)copper(II)] copper(II) perchlorate dihydrate: $Cu(Cueha)_2(ClO_4)_2,2H_2O$						
43·7	4·5	18·6	$C_{36}H_{40}Cl_2Cu_3N_4O_{14}$	42·6	4·0	18·8
Bis-[*NN'*-1,3-propylenebis(salicylaldinato)copper(II)]copper(II) perchlorate dihydrate: $Cu(Cups)_2(ClO_4)_2,2H_2O$						
41·3	4·0	19·0	$C_{34}H_{36}Cl_2Cu_3N_4O_{14}$	41·4	3·7	19·3
Bis-[*NN'*-1,3-propylenebis(*o*-hydroxyacetopheniminato) copper(II)]copper(II) perchlorate trihydrate: $Cu(Cupha)_2$-$(ClO_4)_2,3H_2O$						
43·2	4·35	17·95	$C_{38}H_{46}Cl_2Cu_3N_4O_{15}$	43·0	4·4	18·0

Magnetic susceptibility was measured on equipment of the Faraday type. An electromagnet with 100 mm diameter pole pieces shaped to the design of Garber, Henry, and Hoeve [5] was used. The parameters in the design were adjusted so that the pole gap was 45 mm and the maximum field obtainable was about 800 mT. dH^2/dx was *ca.* 10 T^2 m^{-1} at that field strength. Moveable iron shims, *ca.* 10 mm square, at the top of the pole pieces allowed an empirical fine adjustment to obtain as large a region of constant dH^2/dx as possible. The region covered a vertical distance of *ca.* 20 mm for a constancy of 1%.

The sample was suspended from the left-hand side of the beam of a Cahn model RG electromicrobalance, which was contained in a vacuum bottle. The level of sensitivity in weighing which could be obtained varied considerably with temperature and with the pressure in the balance region. Under favourable conditions, for example a high vacuum at 4·2 K or atmospheric pressure at room temperature, it was *ca.* 2×10^{-7} g, near the manufacturers' claim. At operational pressures it fell to perhaps 10^{-5} g at some intermediate temperatures. A pressure of *ca.* 10^{-2} Torr of helium in the sample chamber and balance was found to provide the best compromise between thermal contact from the sample to the chamber and undesirable effects, such as balance noise and convection and conduction of heat from outside, which arose at higher values.

The helium cryostat was of conventional design, with a 45 mm outside diameter tail which fitted between the magnet poles. There was provision for pumping on the helium-bath to obtain temperatures down to *ca.* 2 K. The sample chamber was a copper block of length 150 mm and internal diameter 15 mm. It was separated from the helium-bath by a space in which the pressure of helium gas could be varied. The sample chamber was equipped with an electrical heater and several temperature sensors. Heat was applied to balance the loss across the space to the helium-bath. The sensors available were a germanium resistance thermometer (Texas Instrument Co.), a platinum resistance thermometer (Jepson, Bolton and Co., type E104), a carbon resistance thermometer (Allen-Bradley Co., 47 Ω, $\frac{1}{8}$W), and a gold–iron/constantan thermocouple. Below 60 K the temperature was maintained constant by using the resistance of the germanium thermometer automatically to control the heater current. Between 60 and 300 K temperature was measured by means of the thermocouple. The calibration of the thermocouple was by reference to a series of vapour-pressure thermometers. Below 60 K the temperature was measured by reference to the germanium resistance thermometer.

The most satisfactory method for calibrating the germanium resistance thermometer in the temperature range 4·2—60 K was found to be the measurement of the force on a sample whose magnetic susceptibility accurately obeyed a simple law; $K_2Cu(SO_4)_2,6H_2O$ was chosen. The susceptibility of this compound has been studied between 1·5 and 298 K and obeys a Curie law, with a small temperature-independent term.[6] The accuracy of the calibration varied rather widely with temperature. Near 4 K the accuracy is ±0·02 K. In the region of 10 K, and again near 50 K, the inaccuracy may be as large as ±5% in temperature. Probably, in the lower range, the error results largely from lack of thermal equilibrium with the sample chamber, and in the higher range it follows from insensitivity in the thermometer. Above 80 K the accuracy of determination of temperature was *ca.* 0·3 K. Below 4·2 K temperature was defined by the vapour pressure of the helium-bath, and was accurate to better than 0·01 K.

The magnetic susceptibilities were measured at a field strength of *ca.* 250 mT. At 4·2 K they were also performed at field strengths ranging from 100 to 400 mT, in order to check for ferromagnetic effects. The susceptibilities remained constant within experimental error (*ca.* ±2%) at that temperature. The absolute value of the magnetic susceptibility at ambient temperature was determined by the Faraday method as described previously,[7] and was accurate to about ±2%. Diamagnetic corrections were made according to a standard tabulation.[4]

E.s.r. spectra were recorded on a Varian model V-4502 machine operating at 9·5 GHz, at *ca.* 295 K. The g-values are accurate to *ca.* ±0·002.

[2/372 *Received, 21st February,* 1972]

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[5] M. Garber, W. G. Henry, and H. G. Hoeve, *Canad. J. Phys.*, 1960, **38**, 1595.

[6] J. C. Hupse, *Physica*, 1942, **9**, 633.

[7] L. M. Englehardt and B. N. Figgis, *J. Chem. Soc.* (*A*), 1968, 1258.