

Low Temperature Measurement of Magnetic Susceptibilities of Some Bis Amino Acids Copper(II) Complexes.

N.G.MANGRIO* AND W.E.SMITH
*Department of Pure and Applied Chemistry,
 University of Strathclyde Glasgow G1 1XL
 Scotland, U.K.*

(Received 12th April, 1988)

Summary: The magnetic measurements below 80K are difficult to obtain but can be useful in the determination of structure. A Gouy balance was developed and tested from room temperature down to 18K. Measurements on some bis-amino acid copper(II) complexes indicated ideal magnetically dilute behaviour. Tutton's salt of manganese indicated Curie Weis law behaviour over the entire temperature range.

Introduction

Figgis [1] predicted that μ_{eff} of planar Cu(II) complexes falls in the rang 1.7 to 1.9 B.M; and that of tetrahedral complexes at 1.9 to 2.1 B.M. Lower magnetic moments thus occur due to metal-metal interactions either by direct exchange or by indirect exchange through the ligands. The scope of the method is increased by a consideration of the temperature dependence. Since the strength of both antiferromagnetic and ferromagnetic coupling can be guaged by the temperature at which bonding evidently commences [2,3].

Insufficient low temperature measurements are available on the biological model systems such as copper amino acids complexes partly because of the complexity of the technique. Villa and Hatfield have shown that a dimer-tetrakis bis L-tyrosinato discopper has a triplet ground state. The spins of the two copper (II) ions within each dimer are coupled. When the temperature is lowered weak antiferromagnetic behaviour is obtained [4]. Bis histamine copper (II) perchlorate has a magnetic moment of 1.9 B.M. at 25°C suggesting that there was no metal-metal interaction. The arrangement of histamine is square planner to copper (II) atoms with perchlorate groups in the trans position vertical to the plane [5]. The Cu(II) complexes of tyrosine, Cu L(NO₃)₂ and Cu L₂

(H₂O) have magnetic moments of 2.00 and 2.1 B.M. respectively suggesting no metal-metal interaction and approximately octahedral configuration for the complexes [6].

Experimental

The complexes were prepared according to the reported literature [1] for (I)bis alaninato copper (II) [4], ii) bis tyrosinato copper (II) dinitrate dihydrate [6] iii) Tuttons salt of manganese (II). The chemicals used were of Analar grade. Cobalt Mercury thiocyanate was used as Calibrant, because it does not decompose, nor absorb moisture easily and packs well. It's susceptibility at 20°C is 16.44x10⁻⁶ c.g.s. decreasing by 0.05x10⁻⁶ per degree temperature rise near room temperature [3].

Instrumental

The most common, simplest, reliable and robust Gouy balance system was tested and developed to record low temperature magnetic moments. It can measure susceptibilities down to 18K. The accuracy of the balance was $\pm 0.1 \mu\text{g}$.

An NMR tube (18 cm) with tight fitting cap was used to hold the sample lower. Through the cap, a 72

* Present address : Institute of Chemistry, University of Sind, Jamshoro, Pakistan.

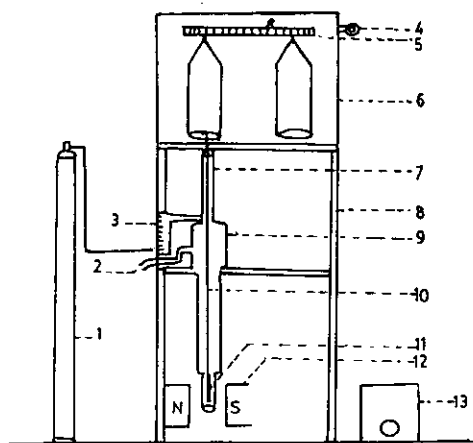


Fig. 1: Diagrammatic view of temperature dependent Gouy balance. 1. Gas Cylinder, 2. Trolley, 3. Rotameter, 4. Weights, 5. Beam and Rider, 6. Balance, 7. Glass tube, 8. Stand, 9. Displex Head, 10. Thread, 11. Sample, 12. Magnets and 13. Current supply.

cm long cotton thread was passed. The other end of the thread was hooked under the left hand pan of the balance. The tube was filled 11.0 cm from the foot, by adding small amount of material and tipping on the bench for complete and tight packing. An ordinary glass tube (whose diamagnetic corrections at different temperature were recorded) was also used to measure magnetic moments any different magnetic current of 1,2, and 4 amperes. This tube was slightly paramagnetic below 50K due to impurities in the glass.

The foot of the tube was suspended at different heights in the magnetic field. A diagrammatic view of the balance and cryostat is given in figure 1. The balance was fixed on stage and on the lower platform, the cryostat rests on three adjustable bolts so that the sample tube compartment hangs between the two magnetic poles. The electromagnet is fixed. A glass shield was placed in front of the suspended tube to prevent draughts from the exposed part of the thread affecting the measurements.

The empty tube was weighed IN and OUT of the field at the same temperature and these measurements were used to determine the magnetic susceptibility of the complexes down 18K. The change in weight of the standard Hg (Co(CNS)₄ and complexes

(Specimen)IN and OUT of the field at room temperature and down to 18K are calculated according to the formula:

$$\mu_{\text{eff}} = 2.84 \sqrt{X_m^{\text{Corr}}} \times T(\text{K})$$

μ_{eff} = effective magnetic moments.

$$X_m^{\text{Corr}} = X_m - \text{Diamagnetic Correction.}$$

T(K) = Temperature.

Gas Flow

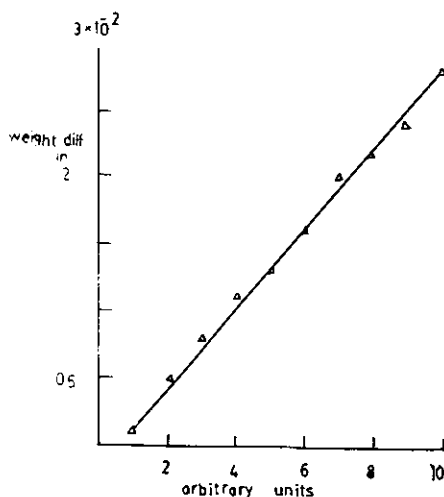


Fig. 2: Gas flow rate for nitrogen gas showing the effect of flow rate on apparent weight.

When the temperature was lowered a stream of Nitrogen gas (99% pure B.O.C) was passed into the sample compartment in order to prevent condensation of impurities. The gas flow was controlled by a rotameter and needle valve. At the time of actual measurement the gas flow was turned down (since higher flow rates had an appreciable effect on the weight measurement). Fluctuations formed by this technique were within the range of instrumental error Fig. 2. Similarly helium gas (99% pure B.O.C) was used from 120K down-wards.

The weight of the empty tube increased by 0.0059g at 120K and as the temperature was lowered the weight went down by 0.0035g. The weight was

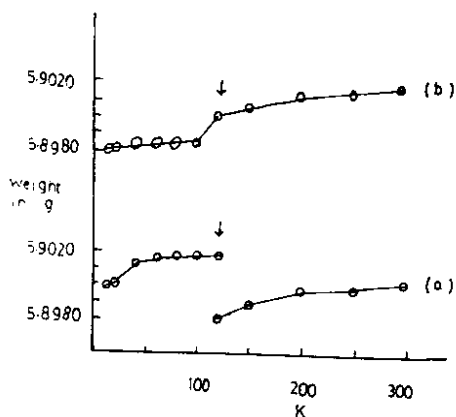


Fig. 3: The changes in weight of the empty tube a. Out of the field, b. in the field as the temperature is lowered. Arrow indicates change from Nitrogen to Helium Gas.

stable for period of hours at 18K. A difference in weight was observed when the heavy gas was changed for nitrogen to helium due to the difference in buoyancy (Fig. 3).

The cooling was achieved by a closed cycle cyrogen system with a heater of (Air products Displex Model CS-202). The temperature at the cold end of the cooler and on the actual cold tail differ by 4-8K. This was checked at 25 points in an actual run between 300 to 18K.

Calibration

Room temperature calibration was made by Hg ($\text{CO}(\text{SCN})_4$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ while Tutton salt of $\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ powder was used as calibrant for the entire range of temperature. It is one of the few compounds for which the temperature dependence of the susceptibilities is known down to 18K and which does not show any anomalous behaviour.

Results and Discussion

Tuttons salt of manganese ($\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) has a magnetic susceptibility which obeys the Curie Weiss law. Figure 4 illustrates the degree of experimental scatter to be expected from measurements taken on the balance. It is somewhat higher than measurements taken with more sophisticated apparatus but is sufficiently ac-

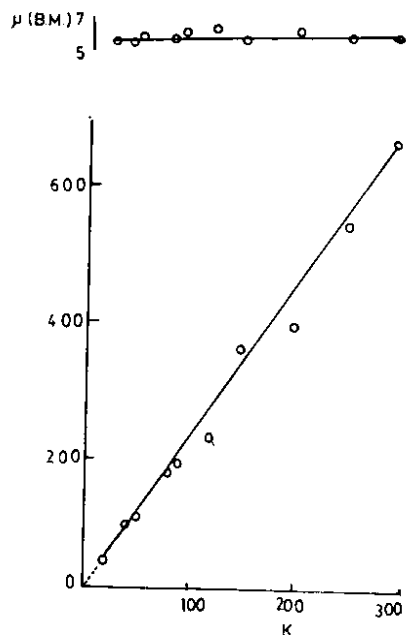


Fig. 4: The inverse molar susceptibility and magnetic moments of $\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ between 294K and 18K.

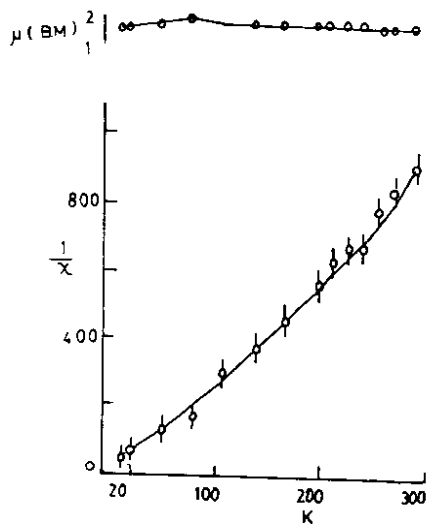


Fig. 5: Temperature dependence of the inverse molar susceptibility and magnetic moments of bis-tyrosinato copper(II) from 294K to 13K measured with internal thermocouple.

curate and is much easier to use than most equipment operating down to 20K.

The magnetic moment of bis-tyrosinato Cu(II) reported by McAullif & Murray [6] at room temperature was 2.0 while Villa and Hatfield obtained 1.89 B.M. [4]. The structure of amino acid copper (II)

complexes would suggest that there may be some magnetic interactions between the copper caused by super exchange involving the carboxylate group which occupies the fifth coordinate position of the copper while the rest of the coordination sites of that molecule coordinate to another copper. Our results are similar to those of Villa and Hatfield and indicate an anomaly in the temperature dependence below 50K as did their results. Therefore there seems to be some exchange effect possibly caused by the carboxylate Fig. 5.

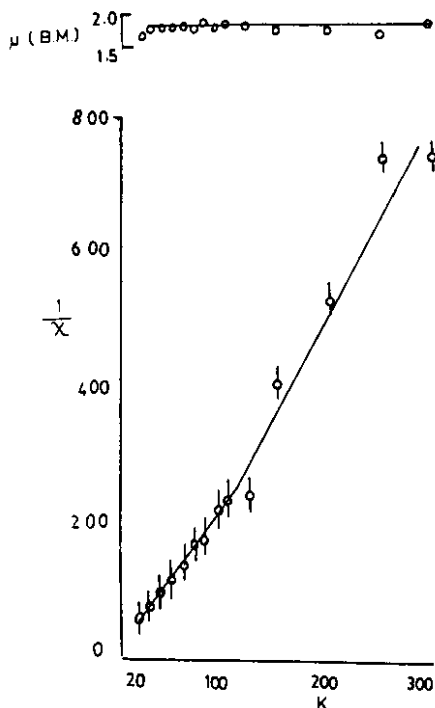


Fig. 6: Temperature dependence of the inverse molar susceptibility and magnetic moments of bis alaninato copper(II) from the temperature 294K to 18K.

In case of bis alaninato copper (II) (Fig. 6) no such evidence suggesting exchange can be deduced from the crystal structure and indeed the room temperature magnetic moments of 1.87 B.M. is higher and the temperature dependence close to the Curie Weiss law. There is some scatter in the results which might indicate a very low temperature anomaly but some curvature is to be expected with copper compounds due to a contribution to the magnetic susceptibility from the temperature independent

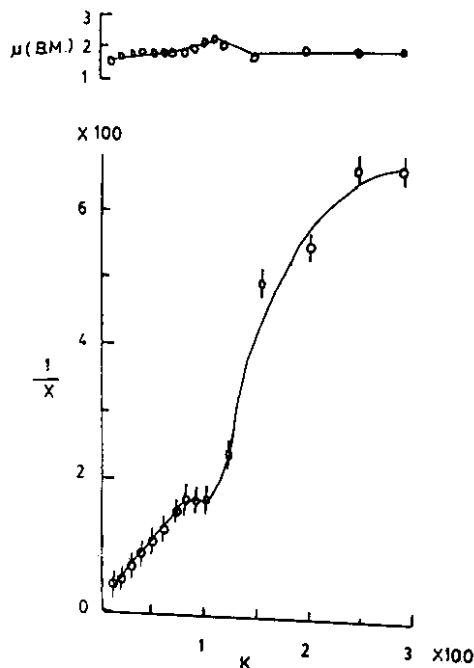


Fig. 7: Temperature dependence of the inverse molar susceptibility and magnetic moments of bis histidinato copper(II) dinitrate dihydrate from the temperature 294K to 13K measured with internal thermocouple.

term resulting from the E ground state of undistorted copper(II). Errors in the individual points are lower at low temperature due to the greater change in mass recorded.

The magnetic moments of bis-histidinato copper (II) di-nitrate dihydrate would suggest that the magnetic behaviour would simply be due to one unpaired electron in an isolated copper (II) ion. In fact, as the temperature dependent magnetic susceptibilities, demonstrate, the magnetic behaviour is complex (Fig. 7). In particular there seems to be curvature in the region 150 to 250K and another change between 80-100K. This latter effect is greater than that found by the other compound and is unlikely to be due solely to instrumental problems such as flow gas changes (Fig. 2). Information is not available about any changes in crystal structure caused by temperature effects in these crystals, but it would appear that an ordinary effects does occur in the case of the complex which is not present in the others studied.

References

1. B.N. Figgis "Introduction to Ligand Fields" Inter-Science Publ; 248 (1967).
2. F.A.Gotton, and G.Wilkinson *Adv.inorg.Chem.* 3rd ed. N.Y.Willey Intso. 535 (1972).
3. A.Earnshaw, "Introduction to Magneto-Chemistry" Academic Press London, N.Y. (1966).
4. J.F.Villa, W.E.Hatfield, *Inorg.Chem.* 11, 1331 (1972).
5. T.Nortia, *Soumen, Kemi* 1332 245 (1959).
6. C.A.McAuliffe, S.G.Murray *Inorg.Chim.Acta* 7, 171 (1973).