

The damped oscillation has the initial value A . For small oscillations, we can write

$$\phi(t) = -Ae^{-bt} + Abte^{-bt} - \frac{CA}{I}te^{-bt} \quad \dots (6)$$

which is evidently transient in character.

REFERENCE

Lewis, J. A., 1962. *Quart. Appl. Maths.*, **20**, 13.

17

LOW TEMPERATURE MAGNETIC INVESTIGATION IN SINGLE CRYSTALS OF SOME PSEUDO-TETRAHEDRAL Cu(II) AND Ni(II) CHELATES

S. LAHIRY, D. MUKHOPADHYAY AND D. GHOSH
(Nee GUHA THAKURTA)

MAGNETISM DEPARTMENT, INDIAN ASSOCIATION FOR THE CULTIVATION
OF SCIENCE CALCUTTA-32, INDIA

(Received August 9, 1968)

Following our magnetic studies (Lahiry *et al.*, 1966, Bose *et al.* 1965) on several tetrahedral copper (II) compounds of the general formula $MX_2 [CuX_4]$ where $M = Cs$, and $(CH_3)_4N$, $X = Cl$, and Br , we now report the preliminary low temperature magnetic investigation of the following chelate complexes :

(i) copper (II) bis (-N-isopropylsalicylaldiminato), (ii) copper (II)-bis (N-*t*-butylsalicylaldiminato) and (iii) nickel (II) bis (N-isopropyl-salicylaldiminato). All these crystals belong to the orthorhombic system, having space group $Pbca$ with $Z = 8$ for the first and the third crystals (Orioli, *et al.* 1966 and Fox *et al.* 1964) and space group $P2_1 2_1 2_1$ with $Z = 4$ for the second (Cheeseman *et al.* 1966). However, from the point of view of magnetic symmetry, in all these cases we can consider them as having only one magnetically inequivalent pair of ions in the unit cells. These complexes having a pair each of oxygens and nitrogens constituting the primary ligand cluster depart appreciably from a regular tetrahedron, the copper (II) complexes being flattened heavily along one of the S_4 axis while the Ni(II) complex may be assumed to have an orthorhombic symmetry. Incidentally this is the first report of single crystal anisotropy investigations in a tetrahedral chelate of Ni(II), the only compounds studied as yet are Ni^{2+} in host lattices of ZnO and CdO (Brumage and Lin 1964).

The crystalline magnetic anisotropies for each of these crystals have been measured in two principal planes in the temperature range 300°K to 68°K and are given in figures (1) and (2). An additional measurement in the third principal plane have been made only at room temperature as a check. The mean susceptibilities K , measured in the same temperature range are given in figure (1) and (2) in terms of P_f^2 the effective ionic moment square given by the usual relation, $P_f^2 = 3K.kT/N\beta^2$. The ionic anisotropies, calculated for the two copper (II) complexes using the angular orientations and the equation.

$$K_{11} - K_{12} = \frac{\chi_c - \chi_a}{\gamma^2 - \alpha^2} = \frac{\chi_a - \chi_b}{\alpha^2 - \beta^2} = \frac{\chi_b - \chi_c}{\gamma^2 - \beta^2}$$

where α, β, γ are direction cosines of the S_4 axis of the complex with the crystal axes a, b, c respectively, are about 350×10^{-6} c.g.s.e.m.u. as compared to about

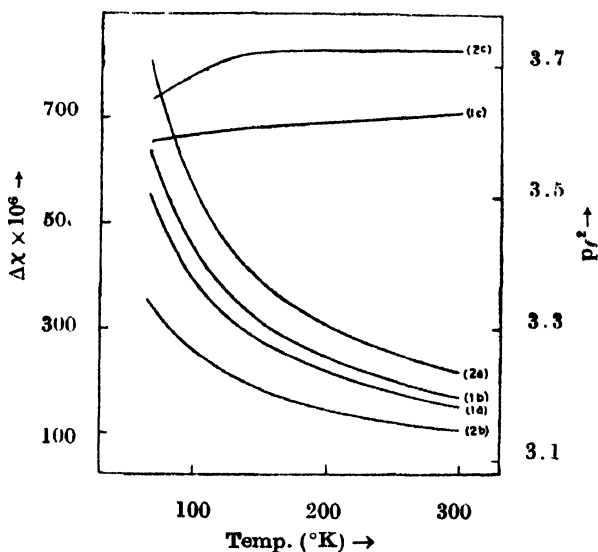


Figure 1. Principal crystalline anisotropies (1a) $(\chi_c - \chi_b) \times 10^6$ (1b) $(\chi_a - \chi_b) \times 10^6$ and (1c) the effective ionic moment square P_f^2 v. s Temperature (°K) curves of Cu(II)-Sal-isopropyl. Corresponding curves (2a) $(\chi_b - \chi_c) \times 10^6$, (2b) $(\chi_b - \chi_a) \times 10^6$ and (2c) P_f^2 refer to Cu(II)-Sal-t-butyl.

500×10^{-6} for some earlier observed tetrahedral complexes. The low value of ionic anisotropy and the mean susceptibility for these copper (II) complexes compared to those found in Cs_2CuCl_4 and $[(CH_3)_4N]_2CuCl_4$ (Lahiry *et al* 1966) is indicative of more flattening of the tetrahedron as also revealed in X-ray analysis, and the predominant effect of covalency expected for these chelates. This is also in good agreement with the preliminary correlation of experimental results with the theory at all temperatures.

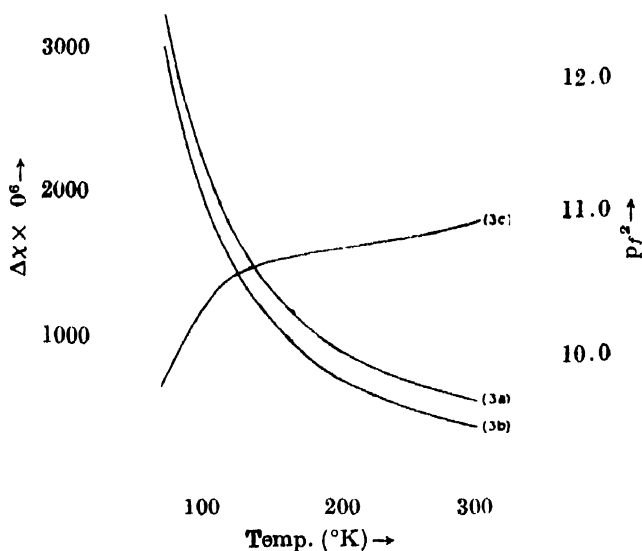


Figure 2. Principal crystalline anisotropies (2a) $(\chi_b - \chi_a) \times 10^6$ (3b) $(\chi_a - \chi_c) \times 10^6$ and (3c) the effective ionic moment square P_f^2 N.S. Temperature ($^{\circ}\text{K}$) curves of Ni(II)-Sal-isopropyl.

Full details of the experimental results and their correlation with theory for all these complexes will be reported in due course.

The authors are grateful to Prof. A. Bose, D.Sc., F.N.I., for his guidance and help.

REFERENCES

- Bose, A., Lahiry, S. and Ghosh, U. S., 1965, *J. Phys. Chem. Solids*, **26**, 1747.
 Brumage, W. H. and Lin, C. C., 1964, *Phys. Rev.*, **134A**, 950.
 Cheeseman, T. P., Hall, D. and Waters, T. N., 1966, *J. Chem. Soc.*, A, 685.
 Fos, M. R., Orioli, P. L., Lingafelter, E. C. and Sacconi, L., 1964, *Acta. Cryst.*, **17**, 1159.
 Lahiry, S., Ghosh, D. and Mukhopadhyay, D., 1966, *Indian J. Phys.*, **40**, 671.
 Orioli, P. L. and Sacconi, L., 1966, *J. Chem. Soc.*, A, 277.