

LOW TEMPERATURE MAGNETIC SUSCEPTIBILITY OF THULIUM SESQUIOXIDE

STUDY of rare-earth sesquioxide has been a subject of considerable interest in recent years. All rare-earths form sesquioxides where their ions are presumed to exist in trivalent state. Antiferromagnetic ordering have been observed^{1, 2} in some of these oxides (Tb_2O_3 , Er_2O_3 , Yb_2O_3 and Dy_2O_3) at low temperatures. To the best of our knowledge the magnetic studies of holmium and thulium and sesquioxide have not yet been reported in literature. In this note we report the magnetic susceptibility and magnetization of Tm_2O_3 from 4.2° K to 270° K. No magnetic ordering have been observed in this compound upto 4.2° K.

Tm_2O_3 with a stated purity of 99.9% was procured from Fluka AG Switzerland. It has cubic (C-type) structure, with room temperature cell parameter $a = 10.488 \text{ \AA}$. It belongs to space group $T_h^7 (Ia\bar{3})$ and has 16 molecules per unit cell³.

The magnetisation of the sample was measured using Foner magnetometer. In this technique sample vibrates perpendicular to a constant and homogeneous magnetic field direction, and the alternating signal induced in a pair of pick up coils is measured and compared to that from a nickel sample. The magnetization of the sample (1 to 50 mg) could continuously be recorded from 4.2 to 300° K at the magnetic field from 0 to 10 kgauss.

The results are shown in Fig. 1. The χ^{-1} vs T curve is a good straight line up to the lowest temperature

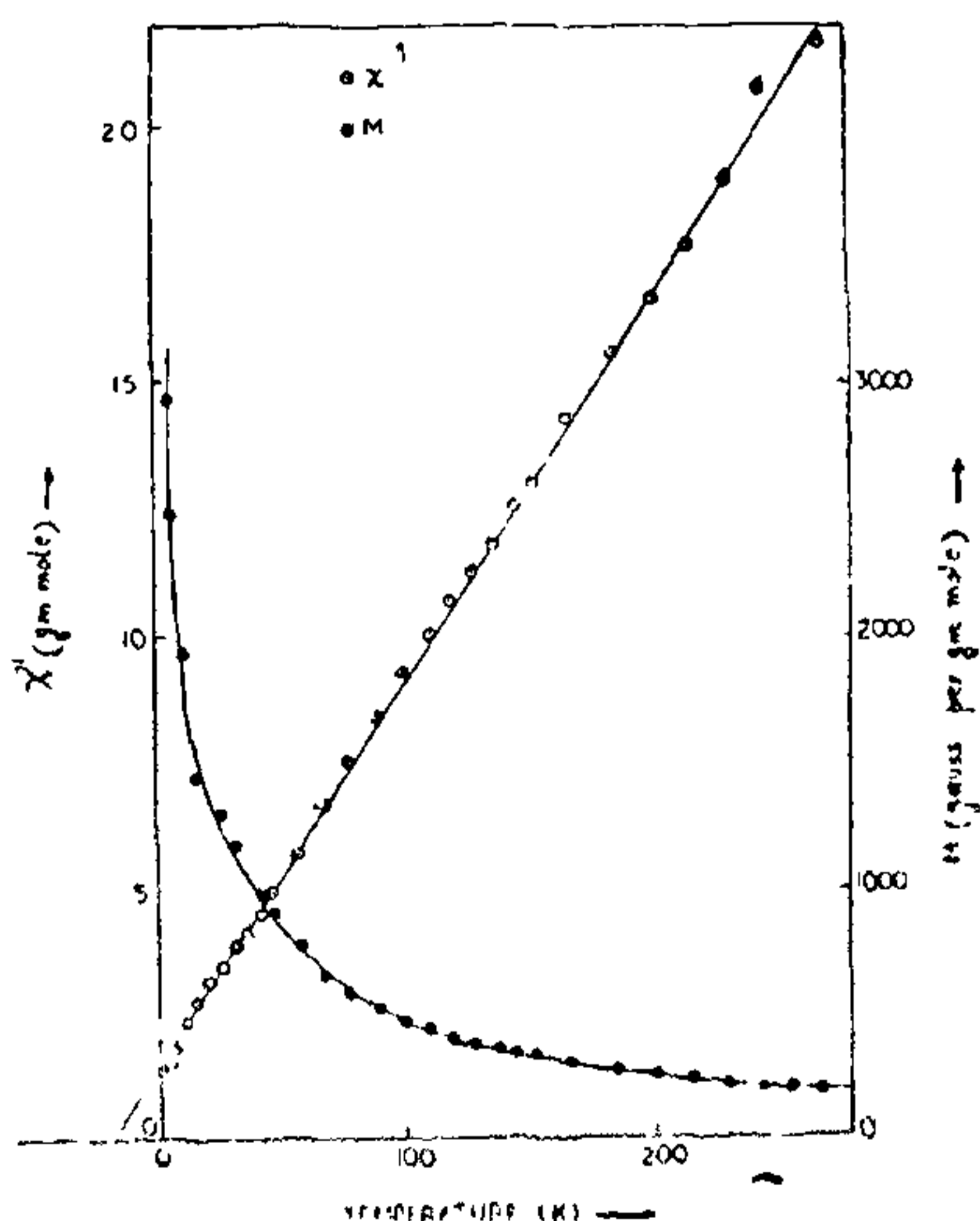


FIG. 1. The magnetisation (M) and the inverse magnetic susceptibility (χ^{-1}) vs temperature (°K) of the powdered sample of Tm_2O_3 .

and thus obeys the Curie Weiss law with Curie constant $C = 13.51^\circ \text{ K/g. mole}$ and paramagnetic Curie temperature $\theta = -20^\circ \text{ K}$. The only magnetic ion in this sample is Tm^{3+} . In the ground state⁴ it has $J = 6$, $L = 5$, $S = 1$. This gives a magneton number [$p^2 = g J(J + 1)$] for this ion as 7.57. Experimental value of p can be obtained from the value of C using the relation⁴

$$p = (3kC/2N\beta^2)^{1/2} \quad (1)$$

where k is Boltzmann constant, N the Avogadro number and β the Bohr magneton. The number 2 is coming in denominator because each molecule contains two Tm^{3+} ions. On computation one gets the experimental value of $p = 7.35$. This value agrees fairly well with the theoretical value.

All the rare-earth sesquioxides studied are antiferromagnetic and hence it is expected that Tm_2O_3 may also be antiferromagnetic. The Curie-Weiss behaviour of χ supports this inference. However a negative value of θ and Curie-Weiss law behaviour can also come purely due to crystal field effect, whose contribution is larger than KT below 100° K even for the cubic symmetry⁴. Thus Curie-Weiss behaviour observed may be the combined effect of crystal field and antiferromagnetic exchange interaction. It can be said with certainty that Tm_2O_3 does not exhibit any magnetic order upto 4.2° K.

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INFRARED SPECTRAL STUDIES OF N-PHENYL AND N, N'-DIPHENYLTHIOUREA COMPLEXES WITH d^{10} METAL IONS

Introduction

THIOUREA class of compounds has not been studied extensively except for the first member, thiourea^{1, 2}. The complexes of thiourea (tu) with $Zn(II)$, $Cd(II)$ and $Hg(II)$ chlorides have already been reported and their infrared spectra studied by Swaminathan and Irving¹. There are reports about the synthesis and infrared spectral studies related to complexes of thioureas with $Ni(II)$ ³, $Co(II)$ ³, $Fe(II)$ ⁴, $Mn(II)$ ⁵ and $Pd(II)$ ⁶

The monosubstituted N-phenyl thiourea (Ptu) and the symmetrically disubstituted N, N-diphenylthiourea (DPtu) complexes with Zn (II), Cd (II) and Hg (II) chlorides have been investigated by us. Amongst these complexes, Ptu and DPtu complexes with ZnCl₂ and HgCl₂ are reported recently⁷. The composition of the complexes is different and the structural assignments are based on the assignments of Yamaguchi⁶.

Experimental

Metal chlorides and other chemicals were of Analar grade. The complexes were prepared by treating the hot metal chloride solution in methanol with a slight excess of hot Ptu solution in the same solvent. The solution was concentrated and cooled in ice. The product was washed with methanol and dried in vacuum.

The above procedure was followed for DPtu complexes, but the complexes crystallise out on concentrating the solution. The complexes were analysed for metal, chloride, nitrogen and sulfur by standard procedures. The analytical data are given in Table I.

comparing the infrared spectra of thiourea with selenourea have assigned a band 630 cm⁻¹ to C-S stretching. In Ptu and DPtu a band at 638 cm⁻¹ and 630 cm⁻¹ respectively could be assigned to CS stretching (Table I). The ν CS (stretching frequency) is reduced by 20-30 cm⁻¹ in the DPtu complexes as in Ptu complexes of Zn (II), Cd (II) and Hg (II). This observation reveals the coordination of substituted thiourea with metal ions through sulphur.

The far infrared spectra of the above metal complexes contain medium strong to strong bands in the region 210 to 290 cm⁻¹ which indicate the existence of M-S band (Table I). These are clearly distinguished from M-Cl stretching vibrations found in the region 270 to 340 cm⁻¹. The band splitting for ν (Zn-Cl) indicates the increased covalency of the bond compared to that of other metal complexes. The appearance of only one band in the case of (HgDPtu₂Cl) and (ZnPt₂Cl₂) indicates vibrational coupling of M-S and M-Cl stretching frequencies. Since divalent Zn, Cd and Hg

TABLE I

Complex	Elemental Analysis				Infrared Frequencies		
	Metal %	Cl %	S %	N %	ν CS	ν M-Cl	ν M-S
Ptu	638 ms
ZnCl ₂ . 2Ptu	14.88 (14.84)	15.98 (16.08)	14.45 (14.55)	12.62 (12.72)	622 m	..	277 s 287 s
CdCl ₂ . 2Ptu	23.18 (23.06)	14.45 (14.55)	13.35 (13.13)	11.60 (11.49)	596 m	319 s	283s
HgCl ₂ . 2Ptu	34.67 (34.82)	12.39 (12.31)	11.00 (11.14)	9.65 (9.73)	592 s	327-331 mb	277 s
DPtu	630 s
ZnCl ₂ . 2DPtu	10.90 (11.03)	12.13 (11.96)	10.77 (10.81)	9.48 (9.45)	610 ms	315 ms 328 ms	290 s
CdCl ₂ . 2DPtu	17.40 (17.58)	11.19 (11.09)	9.81 (10.01)	8.75 (8.76)	601 s	273 s	238 s
HgCl ₂ . 2DPtu	27.60 (27.54)	9.80 (9.74)	8.88 (8.81)	7.66 (7.69)	600 mw	..	261 s

The values in the parenthesis are the calculated values.

s = Strong, ms = Medium Strong, w = Weak, mb = Medium Broad, mw = Medium Weak.

The infrared spectra of the samples were recorded in nujol mull on a Carl-Zeiss UR 10 Spectrophotometer from 4000-400 cm⁻¹ and Beckman I.R. 12 Spectrophotometer from 400-200 cm⁻¹.

Results and Discussion

The complexes have 1:2 stoichiometry and they are colourless and amorphous. Jensen and Nielsen⁸ by

have strong tendency to form tetrahedral complexes, the complexes presently discussed may have tetrahedral stereochemistry.

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A CONVENIENT METHOD FOR THE PREPARATION OF α -ARYLAMINO PHENYL ACETIC ACIDS

McKENZIE and coworkers¹ prepared α -phenylamino phenyl acetic acid by condensing α -halophenyl acetic acid with aniline. We have prepared α -arylamino phenyl acetic acid of the type $C_6H_5 \cdot CH(R)COOH$ where R = phenylamino; *o*-, *m*- and *p*-tolylamino *o*- and *p*-anisylamino; *m*- and *p*-chlorophenyl amino; *p*-bromo and *p*-iodophenyl amino, etc. They have been prepared by hydrolysing α -arylamino phenyl acetonitriles, first by treating with concentrated H_2SO_4 as a result of which amide formation takes place which then gets hydrolysed by aqueous sodium hydroxide solution (10%) to the corresponding acids. This method is found to be convenient and the yield of the products is also very good.

Experimental

(a) Preparation of α -arylamino phenyl acetonitriles

They have been prepared by the method suggested by Sandhu and coworkers². The different substituents R, % yields and the m.p. in °C are as follows:

Aryl, 85, 90°; *o*-tolyl, 79, 75°; *m*-tolyl, 82, 95°; *p*-tolyl, 80, 110°; *o*-anisyl, 85, 68°; *p*-anisyl, 86, 80°; *m*-chloro phenyl, 80, 78°; *p*-chloro phenyl, 78, 70°; *p*-bromo phenyl, 76, 100°; *p*-iodophenyl, 60, 75°. All compounds gave correct N-analysis.

(b) Preparation of α -arylamino phenyl acetamide

α -Phenylamino phenyl acetonitrile (0.025 mole) was dissolved in concentrated sulphuric acid (10 ml)

below 10° and kept for 48 hours at room temperature. Contents were then poured into ice-water and filtered. The filtrate was made alkaline by aqueous sodium hydroxide solution. The product obtained was crystallised from alcohol.

Different substituents R, % yield and the m.p. in °C are as follows:

Aryl, 75, 120°; *o*-tolyl 63, 110°; *m*-tolyl, 60, 100°; *p*-tolyl, 65, 129°; *o*-anisyl, 72, 165°; *p*-anisyl, 74, 105°; *m*-chloro phenyl, 62, 103°; *p*-chloro phenyl, 58, 146°; *p*-bromo phenyl, 70, 174°; *p*-iodophenyl, 74, 172°.

All compounds gave correct N-analysis.

(c) Preparation of arylamino phenyl acetic acid

α -Arylamino phenyl acetamide (0.025 mole) was mixed with aqueous sodium hydroxide solution (10%) and refluxed for 4 hours. It was diluted with ice-water and filtered. The filtrate was then acidified with concentrated hydrochloric acid. The product obtained was crystallised from alcohol.

Different substituents R, % yield and the m.p. in °C are as follows:

Aryl, 55, 179° (Reported 175°); *o*-tolyl, 50, 149°; *m*-tolyl, 53, 145°; *p*-tolyl, 51, 164°; *o*-anisyl 49, 280°(d); *p*-anisyl, 51, 173°; *m*-chloro phenyl, 48, 147°; *p*-chloro phenyl, 45, 175°; *p*-bromo phenyl, 46, 171°; *p*-iodophenyl, 42, 160°.

All compounds gave correct N-analysis.

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MIXED LIGAND COMPLEXES OF COBALT (III) CONTAINING N, N'-TETRAMETHYLENEBIS (SALICYLIDENEIMINE) AND BIDENTATE LIGANDS

IN recent years there has been considerable interest on the transition metal complexes of quadridentate Schiff bases I¹⁻⁴. As the number of the carbon atoms in the methylene bridge increases from $n = 2$ to $n = 3$ or 4 the stereochemistry of the metal (II) complexes [where M = Co (II) and Cu (II)] changes from square planar to tetrahedral⁵⁻⁷. We have recently reported the synthesis and characterisation of cobalt (III) complexes of salt⁸, where saltⁿ = N, N'-trimethylenebis (salicylideneimine). In this preliminary communication we report the syntheses of several new cobalt (III) mixed ligand complexes of saltⁿ and