

Figure 2. Total intensity of light scattering vs temperature.

temperatures prevents more detailed correlation of the light scattering results with the nature of the structural changes at the phase transition.

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MONOTHIO- β -DIKETONE DERIVATIVES OF INDIUM, GERMANIUM AND TIN

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MONOTHIO- β -diketones as ligands are quite different from β -diketones. The consequence of gradual replace-

ment of oxygen by sulphur can be illustrated by examining the complexes of the thio-analogue. In contrast to the later transition metals, the chemistry of main group and early transition elements with monothio- β -diketone is very little known¹⁻³. The present communication reports our attempts to prepare and characterise some indium(III), germanium(IV), tin(II) and tin(IV) complexes of a few monothio- β -diketones⁴⁻⁶.

Reactions were carried out under anhydrous conditions in dry nitrogen atmosphere. Solvents were dried by standard methods. Monothio- β -diketones R'CSC₂COR'' (R' = Ph, Me; R'' = Ph, Me, C₆H₄Me-P, C₆H₄Br-P) were synthesised using usual procedures^{2-4,7} by Claisen condensation. InCl₃ and GeCl₄ were purchased from Fluka. SnCl₄ was also prepared by the normal procedure⁸. Anhydrous SnCl₂ was obtained from SnCl₂·2H₂O by the standard method⁹.

The m.p. of the compounds was determined in sealed capillary tube. Elemental analyses (Ge, In¹⁰, Sn and S) were carried out gravimetrically¹¹. IR spectra were recorded as Nujol mulls using KBr pellets and polythene sheet in the range 4000-200 cm⁻¹ on Perkins Elemer 621 spectrometer. PMR spectra were recorded on EM-360 60 MHz in CDCl₃ with TMS as an internal standard. Molecular weights were determined cryoscopically in benzene.

(a) Preparation of dichloro bis(monothio- β -diketonato) Ge(IV) complexes

GeCl₄ and the monothio- β -diketone were mixed in dry hexane (~50 ml) in 1:2 molar ratio and the mixture refluxed for 30 hr under nitrogen atmosphere and cooled. The contents were filtered and the solid was washed with dry hexane. The details are tabulated in table 1.

(b) Preparation of bis(monothio- β -diketonato) Sn(II) and Sn(IV) complexes

In a solution of SnCl₂ in absolute methanol stoichiometric amounts of ligand and potassium acetate (sodium acetate in case of SnCl₄) in abs. methanol were added dropwise while stirring. Stirring was continued for 3 hr at room temperature (25°C). Solid products separated out, were filtered and washed with abs. methanol and recrystallized from chloroform/methanol (1:3) mixture. Details are given in table 1.

(c) Preparation of bis- and tris(monothio- β -diketonato) indium(III) complexes

In a solution of anhydrous InCl₃ in abs. methanol, stoichiometric amounts of the ligand and sodium

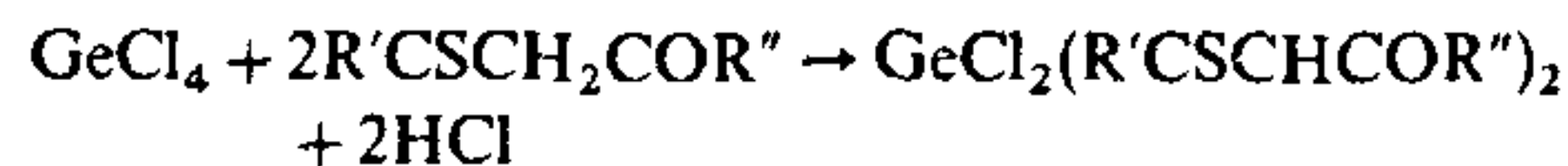
Table 1 Reactions of metal halides with monothio- β -diketones

MCl _n	Reactants (g)		Molar ratio	Reaction condition (h)	Colour of the compounds	M.P. (°C)	% Analysis found (calcd.)		Molecular weight found (calcd.)
	R' -	R'' =					M	S	
GeCl ₄	Ph	Ph	1:2	A(30)	Yellowish orange	140(d)	12.45 (11.66)	10.25 (10.30)	C
GeCl ₄	Ph	Me	1:2	A(30)	Purple	115(d)	14.36 (14.96)	12.77 (13.16)	C
InCl ₃	Ph	Ph	1:3	B ^a (3)	Yellow	177-180	14.77 (13.80)	11.84 (11.54)	902 (831.8)
InCl ₃	Ph	-C ₆ H ₄ Me-P	1:3	B ^a (3)	Yellow	-	12.60 (13.14)	10.85 (10.98)	793 (873.8)
InCl ₃	Me	Ph	1:3	B ^a (3)	Yellow	145-148	18.81 (17.77)	15.66 (14.87)	631.9 (645.8)
InCl ₃	Ph	-C ₆ H ₄ Br-P	1:3	B ^a (3)	Yellow	182	11.14 (10.75)	9.038 (8.98)	
InCl ₃	Ph	Ph	1:2 1:1	B ^a (3) B ^a (3)	Yellow	110-112	18.66 (18.27)	10.24 (10.19)	1379 (1256)
SnCl ₂	Ph	Ph	1:2	B ^b (3)	Yellowish orange	224-230	19.72 (19.89)	10.29 (10.73)	C
SnCl ₂	Ph	Me	1:2	B ^b (3)	Orange	d	23.52 (24.40)	13.77 (13.43)	C
SnCl ₂	Ph	-C ₆ H ₄ Me-P	1:2	B ^b (3)	Orange	240	19.18 (19.00)	10.91 (10.24)	C
SnCl ₂	Me	Ph	1:2	B ^b (3)	Orange	d	24.82 (24.90)	13.68 (13.43)	C
SnCl ₄	Ph	Ph	1:2	B ^a (3)	Yellow	202-204	17.50 (17.76)	9.60 (9.58)	C

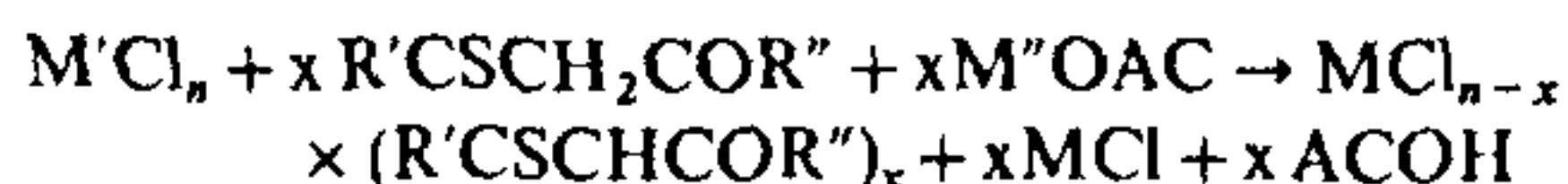
A. Heated under reflux. B. Stirred at room temperature in the presence of required acetates (a = Sodium acetate, b = Potassium acetate). C. The data could not be obtained due to the poor solubility.

acetate in abs. methanol were added dropwise while stirring and the stirring continued for ~ 3 hr at room temperature (~ 25°C). Solid products separated out were filtered and washed with abs. methanol and recrystallized from chloroform/methanol (1:3) mixture. Details are given in table 1.

The complexes as in table 1 were synthesized by the reaction of metal chlorides with monothio- β -diketones directly or in the presence of potassium or sodium acetate in suitable solvents.



(where R' = Ph; R'' = Ph and Me)



$n = 3, \text{M}' = \text{In}, x = 2-3, \text{M}'' = \text{Na}; n = 2,4 \text{M}' = \text{Sn}, x = 2, \text{M}'' = \text{K};$

All these complexes are crystalline solids with yellow to orange colours except GeCl₂(PhCSCHCOMe)₂ which is violet. All are soluble in chlorinated solvents (except

CCl₄). Ge(IV) complexes are insoluble in benzene and Sn(II) complexes sparingly soluble in benzene.

Infrared spectra of these complexes have been helpful in understanding the mode of bonding and also the geometry of the few complexes. The principal bands *i.e.* $\nu(\text{C} \cdots \text{O})$, $\nu(\text{C} \cdots \text{C})$ and $\nu(\text{C} \cdots \text{S})$ of the monothio- β -diketones have been assigned previously¹⁻³. In these complexes the ligand shows bidentate behaviour as shown by a drop in $\nu(\text{C} \cdots \text{O})$ and $\nu(\text{C} \cdots \text{C})$ frequencies respectively at 1580-60 cm⁻¹ and 1545-40 cm⁻¹ (in comparison to the 1600-1590 cm⁻¹ and 1570-1550 cm⁻¹ in the ligand). An intense band at 1250-1230 cm⁻¹ which also occurs in the free ligands in the same region has been assigned to $\nu(\text{C} \cdots \text{S})$ possibly coupled with C \cdots C stretching mode; this involves the coupling vibrational mode for a system of the type -S \cdots C \cdots C \cdots C which is quite possible for the chelate containing resonating double bond characteristics in the ring.

Ge(IV) complexes investigated here are stable for few days in the solid state but are decomposed when kept for a long time. We have reported the Ge(IV)

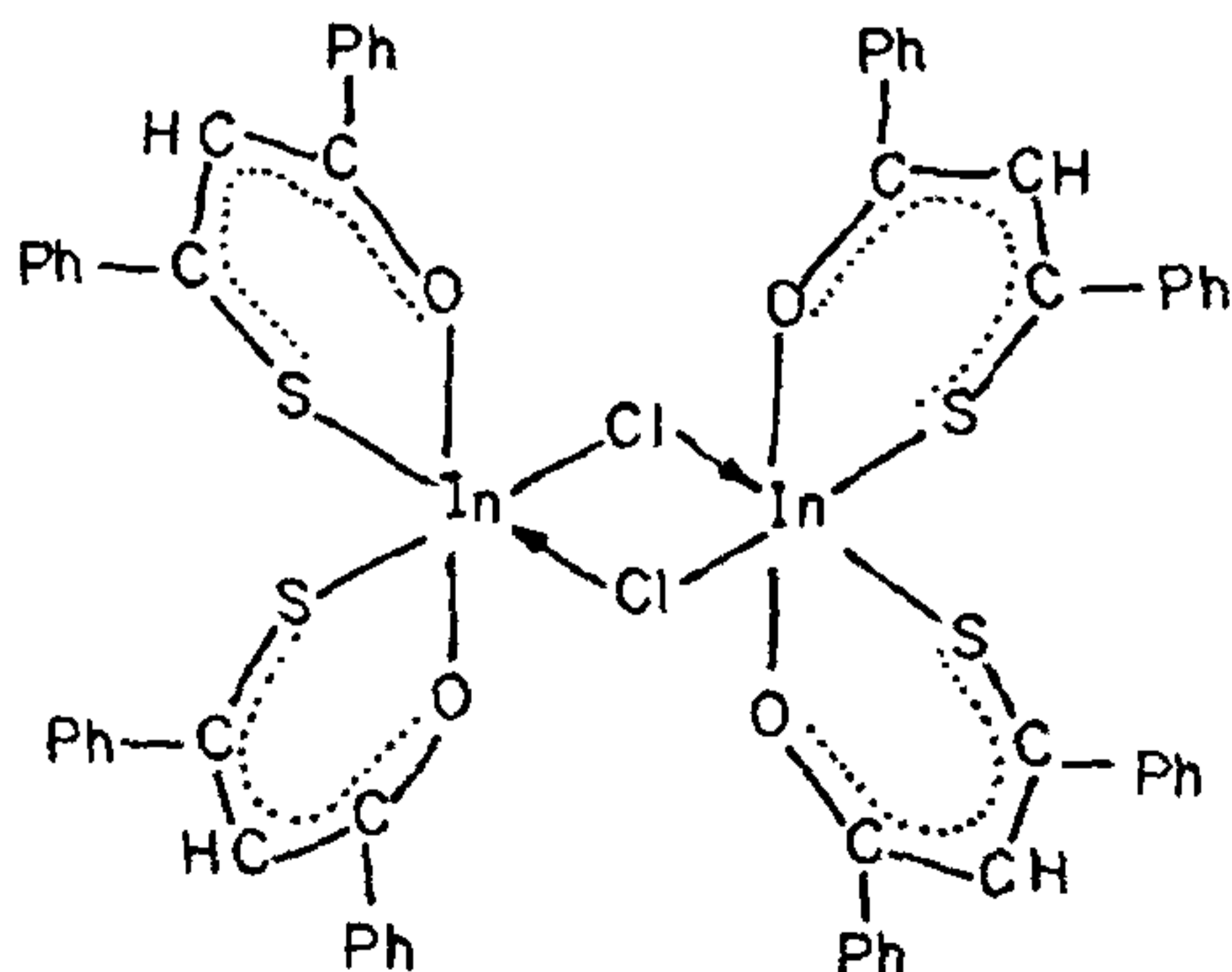
complexes with ligands having thiophenyl group

(Ph-C-S), but our attempts to prepare complexes with

ligands having thiomethyl group (Me-C-S) failed. Their IR spectra in addition to the three characteristic bands mentioned above, show bands at $530\text{--}503\text{ cm}^{-1}$ and $460\text{--}435\text{ cm}^{-1}$ assignable to Ge-O and Ge-S¹⁰ stretching modes respectively. Also the band at $290\text{--}270\text{ cm}^{-1}$ is assigned to Ge-Cl asymmetrical stretching mode. Similarly dichloro bis(monothiodibenzoylmethanato) tin(IV) complex exhibit bands at $\sim 440\text{ cm}^{-1}$ and $\sim 300\text{ cm}^{-1}$ and have been assigned to Sn-O stretching and Sn-Cl asymmetrical stretching modes respectively. In Sn(II) complexes absorption due to $\nu(\text{Sn-Cl})$ mode is absent. The intense band at $\sim 370\text{ cm}^{-1}$ arises due to $\nu(\text{Sn-S})$ absorption in all the Sn(II) and Sn(IV) complexes. A single signal in the PMR spectrum of $\text{GeCl}_2(\text{PhCSCHCOMe})_2$ due to $\text{CH}_3\text{-C(O)}$ group is observed.

Indium tris(monothio- β -diketonato) complexes appeared to be octahedral. Reaction of InCl_3 with the ligands in 1:1 or 1:2 molar ratio ended up with bis-product only which is found to be dimeric. Presumably the dimeric structure involves chlorine bridges as shown below. Absorption due to $\nu(\text{In-Cl})$ mode is observed at $\sim 315\text{ cm}^{-1}$ which is consistent with the position reported for $\text{InX}_2(\text{acac})\text{L EtOH}^{13}$. The absorption at $\sim 370\text{ cm}^{-1}$ present in the ligand becomes very intense. A band observed at 420 cm^{-1} can be assigned to $\nu(\text{In-O})$ mode¹³.

The dipole moments of these complexes are being studied which could throw light on the clustering behaviour of sulphur atom on the coordination sites of the proposed structure.



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OCCURRENCE OF GROWTH RINGS ON THE HARD PARTS OF SCHIZOTHORAX CURVIFRONS HECKEL.

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A GOOD deal of literature is on record for decoding the age by the study of hard parts viz scales, opercula, otoliths and vertebrae from India¹⁻⁷ but such studies have been extremely limited on Kashmir fishes⁸⁻⁹. There is no record of utilizing hard parts for the determination of age and growth of *Schizothorax*