

The nickel alkoxides obtained were filtered and dried *in vacuo* for 2 hr. The filtrate was also dried *in vacuo* to get a white solid which was crystallized from benzene. The compounds obtained are listed in Table 3.

The above results support the formation of insertion products and confirm the bonding through nitrogen in these nickel derivatives, being reported for the first time.

Experiments were carried out under anhydrous conditions. Benzene, methanol and isopropanol were dried by the literature procedures<sup>8</sup>. Phenyl isocyanate (b.p. 164°) and naphthyl isocyanate (b.p. 269°) were distilled twice before use. Nickel was estimated as dimethylglyoxime complex and nitrogen by Kjeldahl method. The alcohol was estimated by an oxidimetric method<sup>9</sup>.

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## A Stereochemical Study of Isomeric Cu(II) Chelates with Salicylamide

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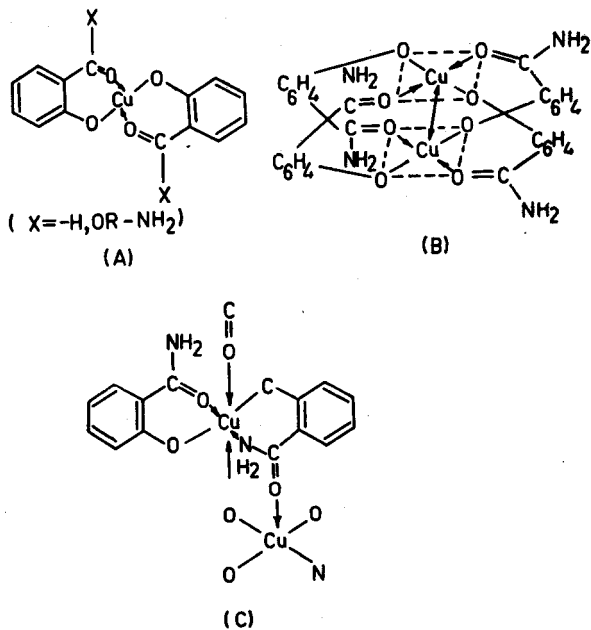
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Reflectance, far IR, cryomagnetic and thermal analysis data on three isomeric chelates of copper(II) with salicylamide have been examined.

SALICYLAMIDE has been reported<sup>1</sup> to form three isomeric complexes with copper(II). On the basis of the room temperature magnetic moment values and IR data (4000-700 cm<sup>-1</sup>) these isomers have been assigned structures A (X=NH<sub>2</sub>), B and C. The present communication deals with their far IR, reflectance, cryomagnetic and thermal analysis data.

Reflectance spectra (200-1000 nm) were taken on a VSU-2P spectrophotometer, far IR spectra on a Perkin-Elmer 621 spectrophotometer, paramagnetic susceptibility were measured according to Gouy method and DTA and TGA studies were carried out with instruments manufactured by P and D Division, FCI, Sindri, India.



The presence of the highest energy bands at 245 nm in the reflectance spectra of all the three chelates may be assigned to  $\pi_4 \rightarrow \pi_6^*$  transition of salicylamidate ion<sup>2</sup>. It occurs at 260 nm in the spectrum of bis-salicylaldehydato copper(II) (A, X=H). The main ligand to metal charge transfer band at ~333 nm is associated with a shoulder at ~415 nm. This shoulder has also been observed in a large number of dimeric copper(II) carboxylates<sup>3-13</sup> as well as monomeric bis-deketonates<sup>14</sup> of copper(II) and has been assigned to charge transfer<sup>9</sup> from the non-bonding, practically pure 2p orbital of oxygen to incompletely filled d-orbital of copper(II) ( $n\pi \rightarrow \sigma^* d_{x^2-y^2}$ ).

The shape of absorption curve of the isomer (A) is different from those of (B) and (C) which are similar in the range 650-800 nm. This may be attributed to the difference in stereochemistry. The isomer (A) may be considered to be the analogue of bis-salicylaldehydato copper(II) (A, X=H). The latter complex has been assigned square coplanar stereochemistry on the basis of single crystal X-ray studies<sup>15</sup>. Swett and Dudek<sup>16</sup> have reported its electronic and EPR spectra and have assigned the main band at 650 nm to the transition  $d_{xy} \rightarrow d_{x^2-y^2}$ . The isomer (A) whose electronic spectrum shows the main absorption band at 625 nm may be assumed to possess the same stereochemistry with CuO<sub>4</sub> chromophore having d-orbital sequence  $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz, yz}$ . The remaining two less intense bands at 575 and 752 nm may be attributed to

TABLE 1 — ELECTRONIC REFLECTANCE SPECTRA OF CHELATES (A), (B) AND (C) IN nm

(A)	(B)	(C)
245	245	245
335	330	330
423	408	425
575	750	570
625	—	680
752	780	715

$d_{xz,yz} \rightarrow d_{x^2-y^2}$  and  $d_{z^2} \rightarrow d_{x^2-y^2}$  transitions respectively. Any attempt at the assignment of the various bands in the region 500-1000 nm present in the absorption spectra of the isomers (B) and (C) is difficult in the absence of X-ray data.

The temperature paramagnetic susceptibility data of the isomers (A) and (B) are given in Table 2. The plot of  $1/\chi_A'$  against T for (A) shows that it obeys Curie-Weiss law ( $\chi_A' = C/T + \theta$ ) with  $\theta$  as 19.9° K and C as 0.498 cgs (least square fit values). Its  $\mu_{eff}$  value varies from 1.93 B.M. at 295.9°K to 1.82 B.M. at 84.2° K. Bis-acetylacetonato copper(II) having  $\mu_{eff}$  values of 1.91 B.M. (ref. 17) and 1.8 B.M. (ref. 18) at 292° and 10°K respectively and showing electronic absorption band at 621 nm<sup>15</sup> has been assigned square coplanar stereochemistry. The magnetic behaviour of the isomer (A) therefore, also supports the previous proposal made on the basis of electronic spectrum. This assignment is also consistent with the conclusion drawn by Hathaway and Billing<sup>19</sup> that the square coplanar stereochemistry can only exist with ligands capable of  $\pi$ -bonding to copper(II), such as oxygen of acetylacetonate ion because of the inherent similarity of the chelate ring of this ion and that of salicylamidate ion. The extent of variation of  $\mu_{eff}$  of (B) with temperature is also in accord with the reported antiferromagnetic character and consequent dimeric nature<sup>1</sup>. Figgis<sup>20</sup> has measured the magnetic susceptibility of chelate (C) between 84°K and room temperature and has reported that the compound obeys a Curie-Weiss law with a  $\theta$  value of about 10°C.

The results of thermal analysis are given in Table 3. TGA data show that the thermal decomposition of all the chelates results in the formation of CuO as residue and is thus consistent with the assigned chemical composition. The TGA and DTA curves reveal the order of decomposition temperatures to be C>A>B.

Far infrared spectra of salicylamide and the chelates have been recorded and the band positions along with their probable assignments are given in Table 4. The bands appearing in the spectrum of

TABLE 3 — THERMAL ANALYSIS RESULTS

Compd	Endothermic minima °C	Decomp. temp. °C	Constant wt of the residue left, %	Wt expected for CuO residue, %
A	120	260	23.0	23.7
B	—	220	24.7	23.7
C	—	280	23.9	23.7

TABLE 4 — ASSIGNMENT OF FAR IR SPECTRA  
(Values in cm<sup>-1</sup>)

Salicylamide	A	B	C	Assignment*
575m	575m	558bs	583m	N-C=O
541s	545m	533sh	521s	$\alpha$ CCC
528s	—	—	—	—
477s	492m	475w	483m	$\phi$ CC
—	429s	425m	438m	$\nu$ (Cu-O)
—	—	402w	—	—
396s	—	—	—	$\beta$ (C-OH)
—	—	—	342s	$\nu$ (Cu-N)
—	308	308	316w	$\nu$ (Cu-O)
—	—	—	263wb	—

\*N-C = O bending vibrations;  $\alpha$ CCC, in-plane benzene ring deformation;  $\phi$ CC, out-of-plane ring deformation, and  $\beta$  in-plane deformation of ring substituent.

salicylamide are assigned following the assignments made by Jakabsen and Bentley<sup>21,22</sup> for related compounds. The absence of the intense band at 396 cm<sup>-1</sup> in the spectra of its chelates is consistent with its assignment as  $\beta$ (C-OH). Fay and Pincavaia<sup>23</sup> have assigned the frequencies in the regions 500-400 cm<sup>-1</sup> and 400-200 cm<sup>-1</sup> in the IR spectra of metal acetylacetonates to be due to  $\nu$ (M-O). They have also observed that the lower frequency band is broad and in some cases accompanied by one or two shoulders. In view of this and the similarity of chelate rings of salicylamidate ion and acetylacetonate ion the strong band at 429, 425 and 438 cm<sup>-1</sup> and a weak broad band at 308, 308 and 316 cm<sup>-1</sup> in the spectra of (A), (B) and (C) respectively, and their absence in the spectrum of the ligand may be attributed to  $\nu$ (Cu-O). A weak broad band at 263 cm<sup>-1</sup> in the spectrum of (C) may also be due to  $\nu$ (Cu-O) corresponding to C=O→Cu bonding to the neighbouring complex molecules. This bond is evidently a weaker bond as compared to the remaining Cu-O bonds of the chelate ring. The appearance of a medium intensity band at 342 cm<sup>-1</sup> in the spectrum of (C) and its absence in those of (A) and (B) may be attributed to Cu-N stretch<sup>24</sup>.

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TABLE 2 — MAGNETIC DATA AT DIFFERENT TEMPERATURES

Temp. (°K)	10% $\chi_g$ (cgs)	10% $\chi_A$ (cgs)	10% $\chi_A'$ (cgs)	$\mu_{eff}$ (B.M.)*
CHELATE A				
84.2	14.1	4730	4893.6	1.82
97.0	12.5	4193	4356.6	1.84
113.4	10.5	3522	3685.6	1.83
153.3	8.03	2694	2857.6	1.87
204.0	5.98	2005	2168.6	1.88
295.9	4.27	1432	1595.6	1.93
CHELATE B				
83.6	0.674	226.1	389.7	0.51
100.0	1.06	355.5	519.1	0.64
115.5	1.31	439.4	603.0	0.75
149.0	1.79	600.5	764.1	0.95
198.0	2.28	764.7	928.3	1.21
296.3	2.49	835.2	998.8	1.54

\* $\mu_{eff} = 2.828 (\chi_A T)^{1/2}$ .

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### Complexes of Sn(IV), Ge(IV), Si(IV) & Ti(IV) Halides with Pyridazine

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Preparation and characterization of complexes of the type  $\text{MX}_4(\text{Pyd})_n$  [for  $\text{M} = \text{Sn}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ;  $n = 1, 2$  and for  $\text{M} = \text{Ge}, \text{Si}, \text{Ti}$ ;  $\text{X} = \text{Cl}$ ;  $n = 2$ ] are reported. The far infrared spectra indicate a *trans*-octahedral environment for the metal ion with both bidentate ( $n = 1$ ) and unidentate ( $n = 2$ ) pyridazine ligands. A polymeric structure involving azine bridging is proposed for the 1:1 complexes.

DIAZINES have been found to act as unidentate or bidentate ligands forming octahedral (monomeric or polymeric) complexes involving azine or/and halogen bridged structures<sup>1-5</sup>. Pyridazine (1,4-diazine) complexes of tin(IV) halides of the type  $\text{SnX}_4$  (pyridazine) and  $\text{SnX}_4(\text{pyridazine})_2$  have recently been reported and a *trans*-octahedral structure involving azine bridging in the 1:1 complexes and a terminal coordination of the ligand in the 1:2 complexes have been proposed<sup>6</sup>. In this paper we report the results of our studies on the pyridazine (1,2-diazine, Pyd) complexes of tetrahalides of group (IV) elements.

Tin(IV) halides were prepared according to standard methods<sup>7</sup>. Pyridazine (Pyd) and metal halides were commercial samples and were used as such. All manipulations were carried out in a dry box.

The infrared spectra were recorded on a Beckman IR-12 spectrophotometer in KBr (4000-650  $\text{cm}^{-1}$ ) and in nujol (650-200  $\text{cm}^{-1}$ ). Conductivity measurements were made on  $\text{Sn(IV)}$  complexes using a Systronix conductivity bridge type 302. Other complexes were insoluble in most of the organic solvents.

Complexes of the type  $\text{MX}_4(\text{Pyd})_2$  were prepared by mixing chloroform solutions of metal salt and the ligand in 1:2 (metal-ligand) ratio. Complexes of the type  $\text{MX}_4(\text{Pyd})$  were prepared by taking metal salt and ligand solutions in 2:1 ratio. In each case a solid product was obtained immediately, which was washed with the solvent and dried *in vacuo*. The characterization data of the complexes are listed in Table 1.

All the adducts except those of  $\text{SnCl}_4$  and  $\text{SnBr}_4$  are highly air- and moisture-sensitive. The molar conductivities of tin complexes in nitromethane ( $10^{-3}\text{M}$ ) are in the range 40-50  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  indicating them to be non-electrolytes<sup>8</sup>.

Tentative geometries of the complexes have been deduced on the basis of far IR spectral studies. The ring vibrations of pyridazine observed at 624, 540 and 368  $\text{cm}^{-1}$  shift to higher frequency region in the complexes due to certain rigidity in the ligand

TABLE 1—COLOUR, MELTING POINTS AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	m.p. (°C)	Calc. (Found), %			
			C	H	N	X
$\text{SnCl}_4(\text{Pyd})_2$	White	295 (d)	22.85 (22.46)	1.91 (2.37)	13.32 (13.40)	33.70 (34.56)
$\text{SnCl}_4(\text{Pyd})$	do	260 (d)	14.11 (14.98)	1.18 (0.90)	8.23 (9.01)	41.63 (40.82)
$\text{SnBr}_4(\text{Pyd})_2$	do	195 (d)	16.05 (15.56)	1.34 (1.32)	9.36 (8.84)	53.39 (52.42)
$\text{SnBr}_4(\text{Pyd})$	Yellow	170 (d)	9.27 (9.98)	0.78 (1.10)	5.41 (5.89)	61.66 (60.12)
$\text{SnI}_4(\text{Pyd})_2$	Dark brown	110	12.22 (12.61)	1.02 (1.29)	7.12 (7.41)	64.55 (65.61)
$\text{SnI}_4(\text{Pyd})$	Dark green	125	6.80 (7.56)	0.57 (0.87)	3.97 (3.98)	71.86 (70.11)
$\text{GeCl}_4(\text{Pyd})_2$	Murky white	154	25.65 (25.62)	2.15 (2.83)	14.96 (15.31)	37.84 (38.01)
$\text{SiCl}_4(\text{Pyd})_2$	White	198 (d)	29.12 (28.91)	2.44 (2.54)	16.97 (17.88)	42.95 (42.40)
$\text{TiCl}_4(\text{Pyd})_2$	Murky white	230 (d)	27.48 (28.00)	2.30 (2.61)	16.02 (16.98)	40.52 (41.83)