REACTIVITY OF SULPHADRUG METAL COMPLEXES WITH GROUP IV METAL HALIDES AND SOME BIOACTIVE ORGANIC BASES

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Abstract

New heterobimetallic complex of Si, Ge, Sn, Ti & Zr(IV) with Cu(II) containing Schiff base of Sulphapyridine have been prepared. All the complexes have been characterized by IR, UV/Vis, EPR Spectroscopy, elemental analysis, magnetic moment and molar conductance measurements. The group(IV) metal achieve octahedral coordination in each case.

Introduction

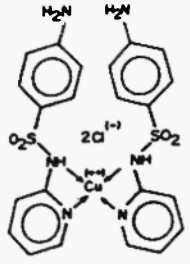
It is known that when sulphadrug is ingested it forms Schiff base in the body system before being assimilated. Possibly the formation of Schiff base facilitates the absorption of the drug[1-10]. The Metallated Schiff base can further act as an electron donor species which easily bind metal ions affording bimetallic complexes. In the present work of Cu(II) Schiff base complex has been further allowed to react with group(IV) metal tetrachlorides and bis (trimethyl silyl) amine to achieve heterobimetallic complexes.

Experimental:

Si, Ge, Sn, Ti and Zr(IV) tetrachloride, bis (trimethylsilyl) amine (Fluka), o-hydroxy benzaldehyde (E.Merck), $CuCl_2.2H_2O$ (BDH) and sulphapyridine (Sigma) were used as such. The IR spectra (4000-200 cm^{-1}) were recorded on Perkin Elmer 621 spectrophotometer in KBr and nujol. UV/Vis spectra were run on Pye UNICAM PU 800 spectrophotometer in DMSO. The EPR spectra were recorded on Bruker ESP-300 X-band spectrometer. The conductivity measurements were made in DMF on an Elico conductivity bridge type CM-82T. Elemental analysis were done on Perkin-Elmer 240B-Microanalyser. Estimation of chloride were done by standard gravimetric method[11].

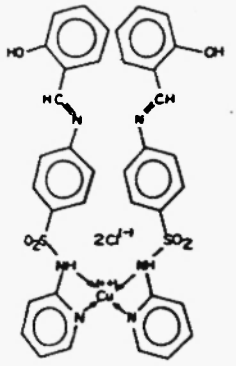
Synthesis of Complex (A)

Sulphapyridine (0.02 mol) and hydrated $CuCl_2$ (0.01 mol) in ethanol (30 mL) was refluxed for two h and left overnight, when fine green crystals separated out. They were washed with ethanol and dried in vacuo. Yield 70% M.P. 185°C, %C 44.77 (44.90);%H 3.68(3.71), %N 14.00 (14.12) and %S 5.33 (5.48).



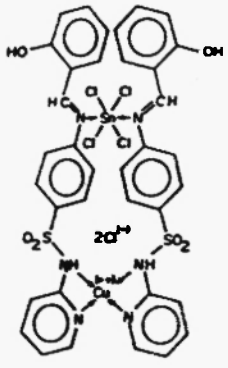
Synthesis of Complex (B)

Complex A(0.01 mol) dissolved in DMF (10 mL) was refluxed with o-hydroxy benzaldehyde for three h. The resulting mixture was cooled and 5ml hexane was added and left overnight at zero°C which yielded yellowish green amorphous powder. The compound was washed with ethanol, flushed with ether and dried in vacuo. Yield 60%, M.P. 200°C, %C 51.61 (51.89), H, 3.58 (3.62), N, 10.03(10.15).



Heterobimetallic complexes of Group(IV) tetrachlorides.

To the solution of B (0.01 mol) in hot MeOH/ DMF (20 mL) was added Group(IV) chloride (0.01 mol) in 1:1 ratio. The mixture was refluxed for three hr and left at room temperature for six h when amorphous coloured compounds were obtained. They were washed with ether and dried in vacuo.



Heterobimetallic complexes of bis (trimethylsilyl) amine

Solution of B (0.01 mol) in hot MeOH/DMF mixture (20 mL) was treated with bis (trimethylsilyl) amine and left at room temperature for about six h. When yellow product was obtained. It was washed with hexane and dried in vacuo. Yield 40% M.P. 289-91°C %C 52.84(53.10), %H 6.25(6.36), %N 10.27 (10.30).

Results and Discussion

On the basis of elemental analysis the complexes may be formulated as $[Cu(SB)_2]Cl_2$ and $[Cu(SB)_2M'Cl_4]Cl_2$ where (M'=Si, Ge, Sn, Ti and Zr). They are thermally stable and insoluble in common organic solvents. Their molar conductance in DMF lies in the range (95-112 ohm^{-1} cm^2 mol^{-1}) and non electrolyte (45-55 ohm^{-1} cm^2 mol^{-1}) in case of bis(trimethyl silyl) amine.

$$[Cu(sp)_2]Cl_2 + 2\ \underset{\text{benzaldehyde}}{\text{o-hydroxy}} \xrightarrow[-2H_2O]{\text{DMF}} \underset{\text{(B)}}{[Cu(SB)_2]Cl_2}$$
(A)

$$[Cu(SB)_2]Cl_2 + M'Cl_4 \xrightarrow[110°C]{\text{MeOH/DMF}} [Cu(SB)_2M'Cl_4]Cl_2$$

$$[Cu(SB)_2]Cl_2 + \underset{\text{bis (tmsa)}}{\text{bis(trimethyl silyl)amine}} \xrightarrow[-2HCl]{\text{MeOH/DMF}} [Cu(SB)_2\ bis(tmsa)_2]$$

Table 1 - Analytical data of Heterobimetallic Complexes

Complex	Colour	M.P.°C	% Calc. (Found) (C)				
			C	H	N	S	Cl
$[(SB)_2Cu.SiCl_4]Cl_2$	Yellow	215	42.85 (43.02)	2.97 (3.03)	8.33 (8.44)	6.34 (6.45)	20.83 (21.60)
$[(SB)_2Cu.GeCl_4]Cl_2$	Light orange	220-222	40.04 (40.44)	2.85 (2.99)	7.98 (8.10)	6.08 (6.28)	
$[(SB)_2Cu.SnCl_4]Cl_2$	Yellow	227-230	39.34 (39.60)	2.73 (2.84)	7.65 (7.73)	5.82 (5.92)	
$[(SB)_2Cu.ZrCl_4]Cl_2$	Orange	235-240	40.32 (40.55)	2.80 (2.90)	7.84 (7.98)	5.97 (6.10)	
$[(SB)_2Cu.TiCl_4]Cl_2$	Orange	238-241	42.02 (42.30)	2.91 (2.99)	8.17 (8.28)	6.22 (6.34)	

* SB = $(C_{18}H_{15}N_3SO_3)$

Table - 2. I.R. Spectra of the Schiff base and Heterobimetallic Complexes

Complexes		νNH		νC=N	νC-N+NH νC-C	νM-CL	M - N
		cm^{-1}		cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
$[Cu(sp)]_2Cl_2$ A		3250 m 3100 m		1630 m 1610 s (pyridyl)	1570 m 1510 m 1500 m 1470 m	330 s	285 m
	νC-O Cm^{-1}		νOH Cm^{-1}		1410 s 1357 m		
$[Cu(SB)_2]Cl_2$ B	1280 s	3130 m	2820 m 2750 m	1630 m 1610 m	1535 m 1505 m 1460 m 1450 m	310 s	285 m
$[Cu(SB)_2SiCl_4]Cl_2$	1280 m	3120 m	2820 m	1630 s 1584 m	1385 m 1360 m 1405 m 1460 m 1380 m	310 s 343 s	285 m 410 m
$[Cu(SB)_2bis(tmsa)_2]$	1280 s	3153 m	2885 m	1627 s 1600 s	1533 m 1457 s 1384 s 1360 m		285 m 405 m

I.R. Spectra

The Schiff bases containing OH have absorption bands in the range 3570-3450 cm^{-1}. In this case a broad band appears at 2830 cm^{-1} due to intramolecular hydrogen bonding. In addition, a band at 2730 has also been observed. These absorptions remain unaltered showing noninvolvement of OH in coordination. Two sharp bands in the spectrum of (B) at 1280 cm^{-1} ascribed to ν(C-0), remain almost unchanged which indicates that it does not participate in coordination. The band at 1390 cm^{-1} is due to CH absorption. The ν(C=N) at 1610-1635 cm^{-1} in copper sulphapyridine complex appears in very narrow region. Sharp bands appearing at 1610, 1630 and 1140 cm^{-1} respectively imply that both the pyridyl nitrogen and azomethine nitrogen are involved in coordination[12-16].

Electronic Spectra

Intense charge transfer bands appearing in 245 - 275 nm region in all the cases have been observed. The weaker bands in the visible region have been used to indicate the geometries of these complexes.

A broad weak band at 820 nm in the case of copper(II) has been assigned to $^2T_{2g} <\!\!-\!\!-\!\!- {}^2E_g$ transition for d^9 system which approximately corresponds to 10Dq value and is influenced by Jahn Teller effect. The magnetic moment value (1.55 BM) and electronic spectrum are consistant with a distorted octahedral geometry[17] for copper(II) ion in case of bis (trimetyl silyl).It has also been supported by the $g_{\perp}$, (2.256 & 2.263) and $g_{||}$ (2.057 & 2.046) values in the EPR spectra of complex bis(tmsa) which corresponds to a distorted octahedral geometry for Cu(II) ion.

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