



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Characterization, Kinetic measurements and Toxicity of Group(iv) Metal Complexes with Schiff bases

Akramullah Khan

Department of Chemistry Purnia College, Purnia-854301

ABSTRACT

Adducts of group (iv) metal chloride with Schiff bases derived from, sulphadiazine and salicylaldehyde (I), thiophene 2-asdhyde (II) and 4- dimethylaminobenzaldehyde (iii) have been characterized on the basis of TLC, IR, NMR, UV- visible spectroscopy, elemental analysis, conductance measurements and molecular weight determinations. The Schiff base by chloride ion generated by various nucleophiles have also been carried out at room temperature. A probable mechanism of substitution has been proposed. The toxicity of the Schiff. The LD₅₀ value for cockroaches and % growth inhibition of the fungi show greater efficacy for the complexes than the Schiff bases.

Key Words: Schiff base, Chelation, LD₅₀

INTRODUCTION

Schiff bases derived from amide, amines and aromatic aldehydes are important due to their dual behavior. They behave as chelating agent¹⁻⁴ on one hand and important biocide on the other⁵⁻⁹. In continuation of our earlier work^{5-10, 11}, we are reporting the synthesis of Schiff bases derived from sulphadiazene (I), thiophene 2-aldehyde (II) and 4, dimethylaminobenzaldehyde (III). The complexes with Sn (iv), Ge (iv), Ti (iv) and Zr (iv) have been characterized by elemental analysis, IR, NMR, UV-visible spectroscopy, conductance measurements and molecular weight determination. Kinetic measurement of the adducts of Schiff bases (I, II and III) in presence of nucleophiles namely, C₆H₅COCL, CH₃COCL, SOCL₂ in DMF shows an increase in conductance with time, the specific rate constants K₁ and K₂ for substitution of chloride ion by base molecule have been calculated. The toxicity of the Schiff bases and their complexes have been evaluated against insects and fungi.

EXPERIMENTAL SECTION

SiCl₄, SnCl₄, Ti Cl₄, (B D H), GeCl₄ (Koch Light), sulphadiazene (Wilson), salicylaldehyde, thiophene 2-aldehyde, 4, dimethyl aminobenzaldehyde (E. Merck), benzoylchloride, acetyl chloride, thioxy chloride and DMF (Ruide1) were used as such, the IR spectra (600-4000)cm⁻¹ were recorded on a perkin Elmer 621 spectrophotometer in KBr disc and nujal mull (600-250 cm⁻¹). The NMR spectra were recorded on a Varian A.60.D instrument in deuterated DMSO and UV- visible spectra were recorded on a pye Unicam PU8800. The conductivity measurements were made on an Elico conductivity bridge type CM-82T. The molecular weights were determined by viscosity measurement method in DMF using an Ostwald viscometer. Metals were estimated gravimetrically as metal oxide.

Synthesis of the Ligand

Sulphadiazene (10 m mol) dissolved in 50-50% ethanol and acetone mixture was mixed with salicylaldehyde (I), thiophene 2-aldehyde (II) and 4, dimethyl aminobenzaldehyde (III). The resulting mixture was refluxed on a water bath for 2-3 hrs to yield coloured crystals or amorphous powders. These were filtered, washed with ethanol and dried in vacuo.

Synthesis of the complexes

Schiff bases I, II and III (10m mol) in DMF were mixed with (10m mol) of meter tetra chloride in CCl_4 and stirred for 6 to 10 hrs until an amorphous solid was obtained. This was kept overnight and filtered. The complexes were washed with DMF and dried in vacuo.

For the determination of specific rate constants, K_1 and K_2 millimolar solutions of the complexes and those of nucleophiles were prepared in DMF. The conductance of the complexes: nucleophiles in different molar ratio was measured immediately as function of time after an interval of five minutes for an hr and after 24 hrs to obtain molar conductance at infinite dilution (a_∞).

Toxicity

Experiments were done houseflies (*Musca domestica nobulo*) and cockroaches (*Periplaneta Americana*). The concentration of the Schiff bases (I, II and III) and those of the complexes was selected in 5-9 ppm region. Five to ten insects were taken in each case and the insects were kept under constant observation. A control set was also run simultaneously. Their percent mortality after every 24 and 96 hrs was noted. The LD_{50} was calculated in terms of probit.

RESULTS AND DISCUSSION

The analytical data of the ligands and complexes (Table-1) showed the formation of (MCl_4L) type complexes where $\text{M} = \text{Si}(\text{iv}), \text{Ge}(\text{iv}), \text{Sn}(\text{iv}), \text{Ti}(\text{iv})$ and $\text{Zr}(\text{iv})$ and $\text{L} = \text{Schiff bases I, II and III}$. The molecular weights determined by viscosity measurements in DMF are close to the theoretical values. The molar conductance of millimolar solutions of the complexes in DMF lie in the range of non-electrolytes and suggest them to be covalent. ($3.1\text{-}4.5 \text{ ohm}^{-1} \text{ cm}^{-1} \text{ mol}^{-1}$).

NMR Spectra of Schiff bases 1

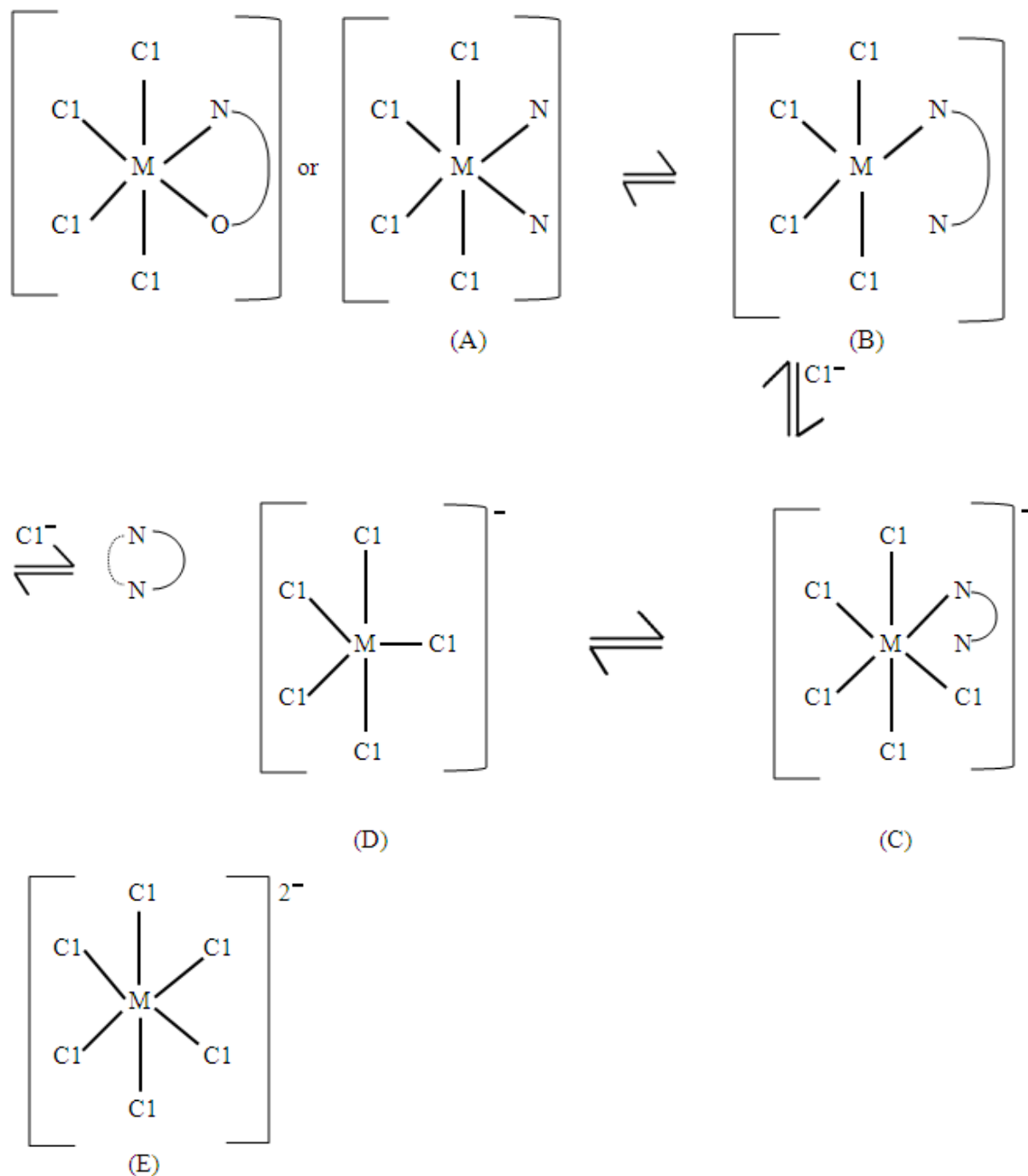
The NMR spectra of I, II and III were recorded in deuterated DMSO. A broad singlet observed at $\delta 10.52$ ppm and $\delta 10.25$ ppm in the spectra of the Schiff base and are assignable to hydrogen bonded OH and NH proton. The former gets shifted to the lower side ($\delta 12.80$ ppm) in the complexes. This shows coordination of the metal atom through phenolic oxygen of the Schiff base. However the larger remains unchanged showing the non involvement of the NH proton in coordination. The singlets in the Schiff base at $\delta 8.82$ ppm are assigned to the azomethine proton and shows a downfield shift ($\delta 9.15$ ppm) in the case of the complexes. It is probably due to the electronic drift from nitrogen atom to the central metal atom to a coordinate covalent bond.

NMR spectra of Schiff base II and III

A broad singlet at $\delta 10.24$ ppm in the Schiff bases are due to NH proton and shifted to $\delta 10.85$ ppm in the complexes. It is due to the formation of coordinate bond between the metal and the Schiff bases as a consequence of electronic drift from nitrogen atom to the central metal ion. The Schiff bases display a complex multiplet in the range $\delta 6.52\text{-}\delta 8.80$ ppm for azomethene¹⁶ proton and aromatic protons respectively.

IR spectra of Schiff base I

Two broad bands in the range $3120\text{-}3450 \text{ cm}^{-1}$ are due to hydrogen bonded OH and NH group of the Schiff base. The band due to OH groups shows a positive shift suggesting the coordination of the Schiff base through phenolic oxygen¹. However, the other bond remains unchanged showing the non involvement of NH group in coordination. The ν (C=N) in the Schiff base appear at $1600\text{-}1620 \text{ cm}^{-1}$ shows a positive shift of 20 cm^{-1} in the complexes indicating the involvement of azomethine nitrogen¹⁷ atom in coordination¹. Strong bond in the Schiff base at 1280 cm^{-1} is assigned to ν (C-O) of the phenolic group and are shifted to higher wave number in the case of the complexes suggesting the coordination through phenolic oxygen atom the ν (C-C) ν (C-N) and ring vibrations at $1095, 1170$ and 1560 cm^{-1} respectively, also appear in the same region of spectrum of the Schiff base and the complexes.



The reaction of chloride ion with $[\text{SnCl}_4 \leftarrow \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}]$ or $[\text{SnCl}_4 \leftarrow \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix}]$ may follow two paths.

- (1) The first order dissociation of the Schiff base from the complex followed by rapid addition of chloride ion.
- (2) The second path is a second order reaction with direct chloride ion attack followed by rapid addition of another chloride ion.

IR SPECTRA OF Schiff base II and III

Unlike I, the Schiff II and III do not contain phenolic group. The coordination of metal through nitrogen atom of the Schiff base results in the weakening of ν (N-H) bond followed by a decrease in ν (C=N), one of the bands get shifted

to higher wave number after complication suggesting the coordination through nitrogen atom. The other frequencies are insignificant and occupy the same position in the free and chelated ligands. The (M-X) bonds are stronger than those of (M-N) bonds and lie at lower wave number.

UV- visible spectra

The absorption spectra of Schiff bases and its complexes in DMF showed absorption largely in the UV region, as the solutions are almost color less owing to extremes dilution. The bands in UV region below (300 nm) appear due to π - π^* transition of lone of electron present on the nitrogen of Schiff bases. This bond undergoes a red shift after coordination as a consequence of metal ligand interaction. The shift of absorption band to a lower wave number (known as chelating effect) is usually of the order of few percent. A general red shift of n - π^* transition would be observed for the complexes with respect to free Schiff bases.

Kinetics and Mechanism of Substitution

The study of the kinetics of substitution of the Schiff bases (I, II and III) complexes by chloride ions generated by nucleophilic reagents provides the following reaction mechanism.

However in our case it has been found to follow first order SN^1 mechanism. The rate of increase in conductance during substitution indicates that the chloride ion is stronger nucleophiles than Schiff base or the solvent. The breaking of one of the two bonds in the Schiff base complex by chloride ion resulting in the formation of $(SnCl_6)^{2-}$ as final product, indicates an increase in conductance after 24 hrs, the pathway shown, however, involves a trigonal

bipyramidal intermediate¹³⁻¹⁴. The dissociation of $(\begin{matrix} N \\ \diagup \\ N \end{matrix} \text{---} SnCl_5)^-$ in step (C) seems to be faster than corresponding dissociation in step (B) because of the negative charge on the former which assists the breaking of

metal ligand bond. However, an equilibrium point is attained after 24 hrs. The dissociation of $(\begin{matrix} N \\ \diagup \\ N \end{matrix})$ in step (B) is

slower process and hence it is rate determining step. The first order plots consist of two intersecting line suggesting that there are two different rate determining steps, the first corresponds to reaction (B) and second to reaction (C).

From this study it has been concluded that the substitution of chloride ion follow (1st order) SN^1 mechanism and on the basis of rate constant value, the nucleophiles may be arranged in decreasing order



Table-1: Analytical data, melting point, and molecular wt. of Schiff bases and their complexes.

Schiff Base (Complexes)	m.p.(°C)	Found (Calc.)%					Molecular Wt. Found (Calc.)
		C	H	N	S	Cl	
C ₁₇ H ₁₄ N ₄ SO ₃ (I)	256	57.75(57.61)	4.00(3.98)	15.91(15.81)	9.03(9.04)		374(354.43)
(C ₁₇ H ₁₄ N ₄ SO ₃)SiCl ₄	296	39.10(38.93)	2.70(2.69)	10.78(10.78)	6.15(6.11)	27.10(27.07)	540.00(524.43)
(C ₁₇ H ₁₄ N ₄ SO ₃)GeCl ₄	d.298	36.20(35.92)	2.50(2.48)	9.90(9.84)	5.68(5.63)	24.99(24.95)	578(568.93)
(C ₁₇ H ₁₄ N ₄ SO ₃)SnCl ₄	285	33.30(33.19)	2.31(2.29)	9.14(9.10)	5.24(5.21)	23.12(23.08)	625.00(615.03)
(C ₁₇ H ₁₄ N ₄ SO ₃)TiCl ₄	d.310	37.65(37.57)	2.61(2.59)	10.32(10.29)	5.92(5.89)	26.13(26.09)	555.00(544.22)
(C ₁₇ H ₁₄ N ₄ SO ₃)ZrCl ₄	d.230	34.85(34.74)	2.42(2.40)	9.64(9.53)	5.48(5.45)	24.19(24.16)	590.00(587.56)
Cl ₅ H ₁₂ N ₄ S ₂ O ₂ (II)	260	52.45(52.31)	3.53(3.51)	16.30(16.26)	18.62(18.59)		350.00(344.37)
(Cl ₅ H ₁₂ N ₄ S ₂ O ₂)SiCl ₄	250	35.20(35.21)	2.38(2.35)	2.82(2.72)	12.48(12.46)	27.63(27.60)	520.00(514.46)
(Cl ₅ H ₁₂ N ₄ S ₂ O ₂)GeCl ₄	d.250	32.35(32.22)	2.18(2.16)	2.52(2.5)	11.50(11.47)	25.44(25.40)	560.00(558.96)
(Cl ₅ H ₁₂ N ₄ S ₂ O ₂)SnCl ₄	245	29.87(29.77)	2.00(1.99)	2.35(2.31)	10.62(10.59)	23.50(23.46)	615.00(605.06)
(Cl ₅ H ₁₂ N ₄ S ₂ O ₂)TiCl ₄	230	28.50(28.40)	1.92(1.90)	2.23(2.20)	11.13(10.11)	22.42(22.35)	640.00(634.25)
(Cl ₅ H ₁₂ N ₄ S ₂ O ₂)ZrCl ₄	d.230	31.28(31.18)	2.11(2.09)	2.55(2.42)	11.12(11.10)	24.61(24.58)	580.00(577.59)
Cl ₁₉ H ₁₉ N ₅ SO ₂ (III)	242	59.95(59.82)	5.05(5.02)	18.40(18.36)	8.43(8.40)		385.00(5381.41)
(Cl ₁₉ H ₁₉ N ₅ SO ₂)SiCl ₄	282	42.48(41.37)	3.49(3.47)	12.72(12.69)	5.84(5.81)	25.77(25.74)	558.00(551.50)
(Cl ₁₉ H ₁₉ N ₅ SO ₂)GeCl ₄	d.295	38.89(38.28)	3.23(3.21)	11.76(11.74)	5.40(5.37)	23.85(23.80)	600.00(596.00)
(Cl ₁₉ H ₁₉ N ₅ SO ₂)SnCl ₄	d.260	40.05(39.94)	3.37(3.35)	12.30(12.25)	5.64(5.61)	24.88(24.85)	580.00(571.29)
(Cl ₁₉ H ₁₉ N ₅ SO ₂)TiCl ₄	d.210	35.63(35.53)	3.00(2.98)	10.92(10.90)	5.00(4.98)	22.14(22.11)	650(642.10)
(Cl ₁₉ H ₁₉ N ₅ SO ₂)ZrCl ₄	256	37.23(37.12)	3.13(3.11)	11.42(11.39)	5.24(5.21)	23.15(23.10)	620.00(614.63)

Toxic Effects

From the values of LD₅₀ (Table 2) it has been observed that the Schiff bases and their complexes are toxic to house flies and cockroaches in as much as low concentration as 10 ppm.

The antifungal activities of the Schiff bases and their complexes are evaluated against *A. flavus* & *A. niger* in 1-2% concentration range. It is demonstrated from % inhibition data that the chelates of II are more toxic than those of I and III (Table-2).

Table-2: (I) % Mortality and LD50 of Cockroaches with corresponding concentration of the Schiff bases and its Complexes.

Ligand / Complexes	Log Conc.in ppmx100	% Morality Ligand / Complexes	Probit Value	LD50 in ppm, Ligand / Complexes
SB(I) / COMPLEXES	2.90	30 / 40	4.4756 / 4.7467	10.00 / 8.91
	2.95	40 / 50	4.7467 / 5.0000	
	3.00	50 / 60	5.000 / 5.2533	
	3.04	60 / 70	5.2533 / 5.5244	
	3.07	70 / 80	5.244 / 5.8416	
	2.90	40 / 50	4.7467 / 5.0000	
SB(II) / COMPLEXES	2.95	50 / 60	5.0000 / 5.2533	8.91 / 7.94
	3.00	60 / 70	5.2533 / 5.5244	
	3.04	70 / 80	5.5244 / 5.8416	
	3.07	80 / 100	5.8416 / -----	
SB(III) / COMPLEX	2.90	20 / 30	4.1584 / 4.4756	10.96 / 10.00
	2.95	30 / 40	4.4756 / 4.7467	
	3.00	40 / 50	4.7467 / 5.0000	
	3.04	50 / 60	5.0000 / 5.2533	
	3.07	60 / 70	5.2533 / 5.2544	

(II) % Inhibition Data, (A)	Aspeegillus flavus & (B) Concentration %	Aspeegillus niger % Inhibition (A)	(B)
Schiff base (I) / Complexes	1.0	57 / 59	57 / 63
	1.5	60 / 63	60 / 66
	2.0	63 / 68	63 / 70
Schiff base (II) / Complexes	1.0	60 / 62	63 / 65
	1.5	62 / 68	65 / 69
	2.0	68 / 75	69 / 73
Schiff base (III) / Complexes	1.0	50 / 60	55 / 65
	1.5	60 / 65	60 / 70
	2.0	65 / 70	70 / 75

REFERENCES

- [1] Birader NS, Karajali GV, Roddababasangouder VL and Aminabhavi TM, *Ind. J. Chem.* 24A, 620 (1985).
- [2] Poddar SN, Das NS, Das AD, *Ind. J. Chem.* 19A, 567 (1980).
- [3] Varshney A and Tondon JP, *synth. React. Inorg. Met. Org. chem.* 16, 1371 (1986).
- [4] Doretti L, Sitaram S, Madalosso F, Baudoli G, Paolucci G, *J. Inorg. Nucl. Chem.*, 42, 1060 (1980)
- [5] Siddiqui KS, Kureshy RI, Khan NH, Tabassum S and ZAIDI, *Inorganica Chem.*
- [6] Castlewr R, Luitt N and Pal C, *J. Am. Chem. soc.* 71, 228 (1949).
- [7] Brauneger H and Ingle P, *J. Pharm, Zeietralbh*, 101, 319 (1962)
- [8] Butler C and Ingle P, *J. Pharm, Pharmacol, B*, 806 (1954).
- [9] Freeman S, *Anal. Chem.* 25, 1750 (1953)
- [10] Khan LA, Siddiqui KS, Khan NH, Kureshy RI and Zaidi SAA, *Ind. J. chem.* 26A 969 (1987)
- [11] Margerum DW and Morgeuthaler LP, *J. Am. Chem. Soc.* 84, 706 (1962).
- [12] Clark HC, O' BreiuRJ & Trotter J, *Proc. Chem. Soc.*, 85 (1963)
- [13] Beahi Ir, Mc-Quillan G.P. and Hulmer, *Chem Ind.* 1429 (1962).
- [14] Beahi IR and Gilson T, *J. Chem. Soc.* 2585 (1961).
- [15] S. Manivanna, A. Manimaran, et.al. *J. Indian Chem.. Soc.* Vol. 85, October 2008, PP 988-995.
- [16] R. Karvembu, S. Hemalatha, R. prabhakaran and K. Natrajan, *Inorg. Chem. Coun.* 2003, 6, 486.
- [1] K.P. Balasubramanian, R. Karvembu, V. Chinnei Samy and K. Natranjan, *Trans. Met. Chem.* 2004, 27, 644
- [17] L.S. Sabirna, V. Muresan, S.Sabirna and N. Muresan. *Ind. Chem. Soc.*, Vol. 82, 2005, 389-392.

[18] Omar, M.M., Mohammad G.G, hindy, A.M.M., *J. Therm. Anal. Col.* **2006**, 86(2), 315- 325.