

Synthesis, Characterization & Toxicity of Complexes of 2,2-Disubstituted Thiazolidin-4-one with Group (IV) Metal Chlorides

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Some 2,2-disubstituted thiazolidin-4-one complexes of the type $(R_2C_3H_2NSOCl)_2M$ or $(R'R''C_3H_2NSOCl)_2M$ where R = cyclopentanone; $R'R''$ = 2,2-methyl, propyl, 2,2-diethyl group; M = Si(IV), Ge(IV), Sn(IV), Ti(IV) and Zr(IV) have been characterized by TLC, NMR and IR spectroscopic data, conductance measurements and molecular weight determinations. The complexes appear to have an octahedral geometry and are non-electrolytes in DMSO solution. The toxicity of the ligands and their complexes has been investigated against insects and fungi.

Substantial work has been done on thiazolidin-4-ones and their derivatives¹⁻⁴. They have assumed importance both as chelating agents and biocides⁵⁻¹⁰. In continuation of our earlier communications^{11,12},

we are reporting here the characterization and toxicity of the complexes of cyclopentanone-, 2,2-methyl, propyl- and 2,2-diethyl-thiazolidin-4-ones with some group(IV) metal chlorides. To evaluate insecticidal and fungicidal activities, experiments were done on cockroaches (*Periplaneta americana*) and fungi (*Aspergillus niger*, *Aspergillus flavus* and *Alternaria porii*).

Cyclopentanone, diethyl ketone, methyl, propyl ketone, mercaptoacetic acid, ammonium carbonate (Fluka, AG), benzene and metal salts (BDH) were used as received. The IR spectra (250-4000 cm^{-1}) were recorded on a Beckman spectrophotometer in KBr disc and nujol mull. The NMR spectra in deuterated DMSO were recorded on Varian A60 D. The conductivity measurements were made on an Elico conductivity bridge type CM-82T in DMSO. The molecular weights were determined by the viscosity method using Ostwald viscometer. For evaluation of fungitoxicity, the agar plate technique was employed.

Synthesis of 2,2-disubstituted thiazolidin-4-one

A mixture of ketone (0.05 mol), mercaptoacetic acid (0.14 mol) and ammonium carbonate (0.15 mol) dissolved in dry benzene was refluxed for 60

Table 1—Analytical, Melting Point and Molecular Weight Data of Thiazolidin-4-one Complexes

	m.p. (°C)	Found (Calcd.), %				Molec. Weight (g)
		C	H	N	S	
$(C_7H_{11}NSO)$ (I)	159	53.50(53.55)	7.02(7.06)	8.88(8.92)	20.38(20.42)	155.35(157.00)
$(C_7H_{10}NSOCl)_2Si$	156	40.86(40.90)	4.85(4.90)	6.77(6.81)	15.52(15.59)	405.32(411.08)
$(C_7H_{10}NSOCl)_2Ge$	260	37.08(37.14)	4.42(4.45)	3.07(3.09)	14.13(14.16)	449.85(452.72)
$(C_7H_{10}NSOCl)_2Sn$	180	33.47(33.51)	3.89(4.01)	5.52(5.58)	12.73(12.78)	498.35(501.69)
$(C_7H_{10}NSOCl)_2Ti$	160	38.99(39.02)	4.63(4.67)	6.47(6.50)	14.85(14.88)	428.38(430.90)
$(C_7H_{10}NSOCl)_2Zr$	210	35.42(35.45)	4.22(4.25)	5.86(5.90)	13.48(13.52)	470.89(474.32)
$(C_7H_{13}NSO)$ (II)	65	52.82(52.87)	8.20(8.24)	8.76(8.80)	20.15(20.16)	157.60(159.00)
$(C_7H_{12}NSOCl)_2Si$	80	40.45(40.51)	5.32(5.36)	6.70(6.74)	15.40(15.44)	413.90(415.08)
$(C_7H_{12}NSOCl)_2Ge$	85	36.78(36.81)	5.23(5.29)	6.10(6.13)	14.00(14.04)	452.80(456.72)
$(C_7H_{12}NSOCl)_2Sn$	75	33.20(33.25)	4.73(4.78)	5.50(5.53)	12.63(12.68)	503.62(505.69)
$(C_7H_{12}NSOCl)_2Ti$	110	38.63(38.66)	5.54(5.56)	6.41(6.44)	14.70(14.74)	432.50(434.90)
$(C_7H_{12}NSOCl)_2Zr$	115	35.12(35.16)	5.02(5.05)	5.83(5.85)	13.36(13.40)	475.00(478.22)
$(C_7H_{13}NSO)$ (III)	155	52.83(52.87)	8.22(8.24)	8.74(8.80)	20.13(20.16)	156.82(159.00)
$(C_7H_{12}NSOCl)_2Si$	60	40.46(40.51)	5.33(5.36)	6.70(6.74)	15.41(15.44)	412.95(415.08)
$(C_7H_{12}NSOCl)_2Ge$	70	36.76(36.81)	5.26(5.29)	6.11(6.13)	14.02(14.04)	453.90(456.72)
$(C_7H_{12}NSOCl)_2Sn$	66	33.22(33.25)	4.76(4.78)	5.49(5.53)	12.64(12.68)	502.00(505.69)
$(C_7H_{12}NSOCl)_2Ti$	250	38.60(38.66)	5.51(5.56)	6.42(6.44)	14.70(14.74)	431.82(434.90)
$(C_7H_{12}NSOCl)_2Zr$	230	35.10(35.16)	5.03(5.05)	5.83(5.85)	13.34(13.40)	473.61(478.22)

hr. This benzene solution was washed thrice with water, 1 M NaOH and ultimately with water. It was dried over anhydrous sodium sulphate. Benzene was removed through suction when a crystalline product was obtained.

Preparation of the complexes

Cyclopentanone-(I), 2-2-methyl, propyl-(II) and 2,2-diethyl (III)-thiazolidin-4-ones (0.02 mol) dissolved in 20 ml of ethanol were mixed with the metal tetrachloride (0.01 mol). The resulting mixture yielded amorphous solids after continuous stirring for 48 hr at room temperature. The com-

plexes were filtered, washed with ethanol and dried *in vacuo*.

Toxicity

In order to evaluate the insecticidal and fungicidal activities, experiments were performed by the methods described in previous communications^{11,12}. The value of LD₅₀ of the cockroaches and % inhibition in growth of the fungi were calculated.

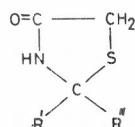
The ligands show a monobasic bidentate behaviour. The analytical data (Table 1) show the formation of L₂MCl₂ type complexes where M = Si

Table 2—%Inhibition Data for (a) *Alternaria Pori* (b) *Aspergillus flavus* (c) *Aspergillus niger* and % Mortality and LD₅₀ values for (d) Cockroaches with the Corresponding Concentrations of Thiazolidin-4-one Complexes

Ligand/Complex	Conc. (%)	Inhibition (%)	Log conc. (ppmx 100)	%Mortality	Probit value	LD ₅₀
(a) Ligand/Complex (I)	1	57/59	—	—	—	—
	1.5	60/63				
	2	63/68				
Ligand/Complex (II)	1	50/60				
	1.5	60/65	—	—	—	—
	2	65/70				
Ligand/Complex (III)	1	60/62				
	1.5	62/68	—	—	—	—
	2	68/75				
(b) Ligand/Complex (I)	1	56/59				
	1.5	60/63	—	—	—	—
	2	63/69				
Ligand/Complex (II)	1	58/59				
	1.5	59/64	—	—	—	—
	2	64/70				
Ligand/Complex (III)	1	60/63				
	1.5	63/67	—	—	—	—
	2	67/74				
(c) Ligand/Complex (I)	1	57/59				
	1.5	59/63	—	—	—	—
	2	63/69				
Ligand/Complex (II)	1	58/60				
	1.5	60/65	—	—	—	—
	2	65/70				
Ligand/Complex (III)	1	60/64	—	—	—	—
	1.5	64/69				
	2	69/75				
(d) Ligand/Complex (I)	—	—	2.90	30/40	4.47/4.74	10.00/8.91
			2.95	40/50	4.74/5.00	
			3.00	50/60	5.00/5.25	
			3.04	60/70	5.25/5.52	
			3.07	70/80	5.52/5.84	
Ligand/Complex (II)	—	—	2.90	40/50	4.74/5.00	
			2.95	50/60	5.00/5.25	
			3.00	60/70	5.25/5.52	8.91/7.94
			3.04	70/80	5.52/5.84	
			3.07	80/100	5.84/—	
Ligand/Complex (III)	—	—	2.90	20/30	4.15/4.47	
			2.95	30/40	4.47/4.74	
			3.00	40/50	4.74/5.00	10.96/10.00
			3.04	50/60	5.00/5.25	
			3.07	60/70	5.25/5.52	

(IV), Ge (IV), Sn (IV), Ti (IV), Zr (IV) and L=ligands. The molar conductances ($0.5\text{--}2.8\text{ Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) of millimolar solutions of these complexes in DMSO indicate that they are covalent in nature. The molecular weights determined by viscosity measurements in DMSO are close to the theoretical values (Table 1).

The proton NMR spectra were recorded in DMSO- d_6 . A broad singlet at $\delta 9.1$ corresponding to NH proton in the ligands does not appear in the complexes showing the replacement of the amino hydrogen. The $-\text{CH}_2$ proton signal in the case of ligands and their complexes is observed in the range $\delta 3.5\text{--}\delta 3.7$. Methyl, propyl, ethyl and



- I; $\text{R}'\text{R}'' = \text{Cyclopentyl}$
 II; $\text{R}'\text{R}'' = \text{Methyl, propyl}$
 III; $\text{R}'\text{R}'' = \text{Ethyl, ethyl}$

cyclopentyl proton signals have been observed in the range $\delta 0.7\text{--}\delta 3.5$.

All the 2,2-disubstituted thiazolidin-4-ones have three potential coordination sites. However, for steric reasons all the sites may not be coordination active. A strong ligand band observed at 3180 cm^{-1} , assigned to $\nu(\text{N-H})$, does not appear in the spectra of complexes showing the replacement of amino hydrogen by metal atom which is also supported by quantitative analysis of chlorine in the complexes. It is known that in molecules containing both C=O and C-N if the coordination occurs through carbonyl oxygen the $\nu(\text{C=O})$ generally decreases^{13,14} with a consequent increase in $\nu(\text{C-N})$. Conversely, if nitrogen is coordinated, $\nu(\text{C-N})$ decreases followed by an increase in $\nu(\text{C=O})$. On the contrary, if both are coordinated there is very little shift in $\nu(\text{C=O})$ and $\nu(\text{C-N})$. In the present case the $\nu(\text{C=O})$ mode shows a small negative shift of 10 cm^{-1} on complexation. Two medium intensity bands at 1280 and 1340 cm^{-1} in the free ligands, assigned to $\nu(\text{C-N})$, are shifted to higher wave numbers showing the involvement of nitrogen atom in coordination. New bands of medium intensity at $440, 685, 425, 540, 550\text{ cm}^{-1}$ in the complexes have been assigned to $\nu(\text{Si-N}), \nu(\text{Ge-N}), \nu(\text{Sn-N}), \nu(\text{Ti-N})$ and

$\nu(\text{Zr-N})$ respectively; while the $\nu(\text{M-Cl})$ bands lie in this region, they are not sharp. The (M-O) stretching frequency lies in the range $440\text{--}965\text{ cm}^{-1}$. It is ascertained from these studies that of the three donor sites only nitrogen and carbonyl oxygen are coordination active.

The sulphur compounds have inherent pesticidal property and, hence, it seemed worthwhile to investigate the fungitoxicity and insecticidal behaviour of the present compounds. The insecticidal activities of thiazolidin-4-ones and their complexes in terms of LD_{50} are given in Table 2. On the basis of the mortality data the ligands may be arranged in the descending order to their toxicities: $\text{II} > \text{I} > \text{III}$.

All thiazolidin-4-ones and their complexes have been screened for their antifungal activities. It has noted that the compounds containing methyl group cause an increase in fungicidal properties (Table 2). The fungitoxicity of the ligands follows the order $\text{III} > \text{I} > \text{II}$ which is exactly the reverse to that found for insects. However, it is important to note that the toxicity of thiazolidin-4-ones is enhanced on chelation.

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