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Studies on 2-Thiazolidinethione, 2,4-Thiazolidinedione and Ethylene Monothiocarbonate Complexes of Sn(IV), Ti(IV) and Fe(II) Halides

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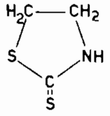
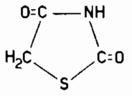
Complexes of the type $SnCl_4\cdot 2L$, $TiCl_4\cdot 2L$ *and* $FeX_2\cdot 2L$ [X = *Cl, Br, I;* L = *2-thiazolidinethione (tzt), 2,4-thiazolidinedione (tzd), ethylene monothiocarbonate (emt)] have been prepared and characterized by elemental analysis, infrared spectra, magnetic moment and conductance measurements. The infrared spectral results indicate that in tzt the amino nitrogen and in tzd and emt the carbonyl oxygen are the donor sites. The group theoretical calculations show that* $SnCl_4$ *and* $TiCl_4$ *complexes are trans octahedral. The magnetic moment values show that all iron complexes are tetrahedral.*

Introduction

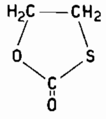
In this communication we have studied the donor behaviour of 2-thiazolidinethione, 2,4-thiazolidinedione and ethylene monothiocarbonate towards Sn(IV), Ti(IV) and Fe(II) halides.



2-Thiazolidinethione
(tzt)



2,4-Thiazolidinedione
(tzd)



Ethylene monothiocarbonate
(emt)

The donor properties of thiazolidinethione have been studied by Singh[1] and De Filippo[2]. Both these authors have drawn different conclusions regarding the site of bonding in this ligand. We have related our discussion with the previous observations of these workers also.

Experimental

Materials and Manipulations

Reagent grade solvents were carefully dried and purified. Tin(IV) and Ti(IV) halides were purified by distilling over phosphorus pentoxide, in a closed system. Anhydrous Iron(II) halides (Alfa Inorganic), thiazolidinethione, thiazolidinedione and ethylene monothiocarbonate (Eastman Organic Chemicals) were used as such from fresh bottles.

All the reagents were handled in a dry box flushed with nitrogen.

Preparation of the Complexes

All the complexes were prepared by direct reaction of the ligand solution with solutions of metal halides in 1:2 molar ratio.

For emt complexes of $TiCl_4$ and $SnCl_4$ both the components were dissolved in cyclohexane and for tzt and tzd complexes dichloroethane was used as solvent. In all these cases complexes were either immediately formed or were formed after stirring for a short while. These were filtered, washed with the solvent and dried under vacuum. The compounds were recrystallised.

In case of iron complexes, the halides were dissolved in small quantity of butanol, and the ligands in large quantity of chloroform. The two solutions were mixed and refluxed for 48 hours. Solid compounds were formed, which were filtered, washed with the solvent and dried under vacuum.

Most of these complexes are soluble in organic solvents, have sharp melting points (Table I), and are non-conducting (Table III). These properties indicate that they are molecular addition compounds.

Physical Measurements

Infrared spectra of the ligands and complexes were recorded on a Perkin–Elmer model 621 as nujol mulls

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TABLE I. Analytical Results of Complexes.

Complexes	Colour	M.P. (°C)	Metal %		Halogen %		Carbon %		Hydrogen %		Sulphur %	
			Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1. $FeCl_2 \cdot 2tzt$	Brownish	180	15.1	15.5	19.5	19.4	19.7	20.0	3.2	2.8	36.4	35.5
2. $FeBr_2 \cdot 2tzt$	Straw	190	12.4	12.3	35.5	35.2	16.4	15.8	1.9	2.2	28.9	28.2
3. $FeI_2 \cdot 2tzt$	Light Brown	154	10.3	10.2	46.4	46.3	12.3	12.9	1.4	1.7	23.8	23.4
4. $SnCl_4 \cdot 2tzt$	Cream	215	23.1	23.7	28.1	28.5	15.0	14.4	2.1	2.0	25.5	26.1
5. $SnBr_4 \cdot 2tzt$	Yellow	197	16.8	16.0	47.1	47.5	10.2	10.6	1.1	0.9	19.3	18.9
6. $TiCl_4 \cdot 2tzt$	Light Brown	108	11.0	11.1	33.2	33.3	12.0	11.7	1.4	1.6	39.7	39.8
7. $FeCl_2 \cdot 2tzd$	Brown	[b]	16.2	16.1	19.3	19.7	14.6	15.0	1.7	1.2	13.7	13.3
8. $FeBr_2 \cdot 2tzd$	Light Brown	[b]	12.5	12.4	35.7	35.5	12.8	13.1	1.8	1.8	22.9	23.2
9. $FeI_2 \cdot 2tzd$	Dark Grey	197	10.9	10.3	46.2	46.7	12.6	13.2	1.6	1.8	11.1	11.7
10. $SnCl_4 \cdot 2tzd$	White	180(d)[a]	23.6	23.9	28.3	28.7	14.3	14.8	1.6	1.3	12.2	12.5
11. $TiCl_4 \cdot 2tzd$	Light Yellow	115	11.2	11.3	33.6	33.5	12.2	11.9	1.6	1.0	14.6	15.1
12. $FeCl_2 \cdot 2emt$	Yellowish White	[b]	16.9	16.7	21.3	21.2	20.8	21.5	2.1	2.4	20.2	19.1
13. $SnCl_4 \cdot 2emt$	White	60	24.0	24.1	30.5	30.3	15.2	15.3	1.6	1.7	12.5	13.6
14. $TiCl_4 \cdot 2emt$	Bright Yellow	114	12.2	12.1	35.9	35.6	22.0	22.5	2.2	2.5	19.4	20.0

[a] d = decomposes. [b] Does not melt up to 300°C.

using CsI optics. Spectra of the ligands were recorded as dilute solutions as well.

Magnetic susceptibility measurements were made on a Gouy balance using cobalt(II) mercury tetrathiocyanate as standard[3]. Diamagnetic corrections were made by the methods outlined by Figgis[4].

The molar conductance measurements of the complexes were made on a Philips conductivity meter type CDM 2d No. 47501 with a conductivity cell Radiometer type CDC 114.

Analysis of the Complexes

The complexes were analysed for C, H, N and sulphur by micro techniques and halogen and metals gravimetrically as silver halides and oxides respectively.

Results and Discussion

Thiazolidinethione Complexes

Thiazolidinethione has three possible donor sites, *viz.* N of NH group, S of C=S group and S of the ring.

To find out the actual donor site we have compared the infrared spectra of the ligands with those of the complexes. Intermolecular hydrogen bonding between NH and S of C=S is present in thiazolidinethione. This has a marked effect on the positions of N–H and C=S bands[1,5,6]. To eliminate this effect we have taken the spectrum of the ligand in dilute chloroform solution for the purpose of comparison.

On comparing the i.r. spectrum of the ligand with those of the complexes (Table II) we observe a negative shift of the order of 200 cm^{-1} in N–H stretching frequencies and a positive shift of the order of 50–90 cm^{-1} in δ(N–H) band. These shifts indicate coordination through nitrogen[1]. These negative shifts could also be due to hydrogen bonding between the halogen of the metal halides and the hydrogen of NH group in the ligand[7,8]. If the negative shift is due to hydrogen bonding its magnitude should differ considerably from chloride to iodide[9]. Such a difference in magnitude of shift is not observed. Moreover the N–H peaks of the complexes are sharp. These observations indicate the absence of hydrogen bonding. Hence it is believed that the negative shift in ν(N–H) stretching frequencies is not due to hydrogen bonding but to coordination through nitrogen. In the far infrared region of the complexes an additional band appears which can be assigned to (Fe–N) or (Sn–N) stretching modes. These bands are in the region of ν(M–N) reported by various workers[5]. The presence of this band further supports bonding through nitrogen of N–H.

The other possible donor sites in 2-thiazolidinethione are sulphur of C=S and sulphur of the ring. We have therefore examined the shifts in these bands also. Unfortunately there appears to be a great uncertainty about the assignment of C=S stretching frequencies. We have however followed the assignments made by Elmore[10]. Accordingly the band at 1295 cm^{-1} has been taken as a mixed band of $\nu(C{=}S)+\delta(NCS)$. This band shows a positive shift which indicates that sulphur of C=S is not involved in coordination. This indirectly supports the linkage through nitrogen.

The band at 697 and 652 cm^{-1} assigned to symmetric and asymmetric C–S stretching frequencies also do not show features of coordination. This shows that ring sulphur is not involved in coordination. The far infrared region also does not show the presence of M–S bands. These observations very clearly show that the nitrogen of N–H is involved in coordination and not the thiocarbonyl or the ring sulphur.

TABLE II. Assignments of Infrared Spectral Bands (cm^{-1}).[a]

Complexes	ν(N–H)	δ(N–H)	ν(C=S) + δ(NCS)	ν(C–S) Asym.	ν(C–S) Sym.	ν(C–N)	ν(C=O) I Asym.	ν(C=O) I Sym.	ν(C=O) II Asym.	ν(C=O) II Sym.	δ(C–O–C)	ν(M–N)	ν(M–O)	ν(M–X)
2-Thiazolidinethione (tzt)														
(Nujol)	3120s	1512s	1294s	697s	652s									
tzt ($CHCl_3$soln.)	3425s	1490s	1295s	697s	652s									
1. $FeCl_2 \cdot 2tzt$	3220sb	1540s	1308s	721m	660s							380s, 335s		310s, 298s
2. $FeBr_2 \cdot 2tzt$	3220sb	1540s	1310s	722s	658s							330s		–
3. $FeI_2 \cdot 2tzt$	3195mb	1560s	1306s	712m	655s							329s		–
4. $SnCl_4 \cdot 2tzt$	3210s	1525s	1298b	705m	660sh							380s b		326w
5. $SnBr_4 \cdot 2tzt$	3218s	1540sb	1315s	720s	661b							380w		310sh
6. $TiCl_4 \cdot 2tzt$	3260sh	1568s	1310s	725s	666s							382w		320sh
2,4-Thiazolidinedione (tzd)														
(Nujol eml.)	3140m	1460s		710s		1376s	1770s	1740s	1675m	1670s				
tzd ($CHCl_3$soln.)	3410s	1570s		710s		1322s	1778s	1740s	1760s	1710s				
7. $FeCl_2 \cdot 2tzd$	3415s	1600s		718s		1338s	1780s	1735s	1675s	1650s			418sh, 405m	290s, 282sh
8. $FeBr_2 \cdot 2tzd$	3400s	1590s		716s		1340s	1775m	1745s	1665s b	1600s b			400m	272s
9. $FeI_2 \cdot 2tzd$	3410s	1613s		727s		1350s	1775m	1742m	1710s	1613s b			432s	–
10. $SnCl_4 \cdot 2tzd$	3422m	1625s		700s		1348s	1775s	1745sh	1666wsh	1620s b			–	–
11. $TiCl_4 \cdot 2tzd$	3417m	1620s		695s		1345s	1780sh	1740s b	1655 m b	1620b			405s	260m
Ethylene monothiocarbonate (emt)														
($CHCl_3$ soln.)				705s				1746sb			1075s			
12. $FeCl_2 \cdot 2emt$				710s				1638w			1082s		442sh, 408sh	310sh, 268s
13. $SnCl_4 \cdot 2emt$				720s				1628sb			1085s		404s	270sb
14. $TiCl_4 \cdot 2emt$				730s				1612s			1090s		453s	270m

[a] s = strong, m = medium, w = weak, b = broad, sh = shoulder.

Our conclusions regarding the site of bonding in tzt are not consistent with the observations of De Filippo[2]. Therefore, we prefer to give a critical discussion of the two results. De Filippo[2] has taken the spectrum of the ligand in nujol and has not given any consideration to the effect of hydrogen bonding on the position of ν(N–H). It is perhaps on this account that he has drawn a faulty conclusion. The assignments of ν(C=S) and M–S bands are always indefinite. Hence conclusions based only upon these two bands cannot be much relied upon.

2,4-Thiazolidinedione Complexes

Thiazolidinedione too has three potential donor sites, *viz.* NH, two carbonyl groups and ring sulphur. In order to find out the actual site of donation we have compared the i.r. spectrum of the ligand with those of the complexes. The ligand spectrum has been recorded in solution to eliminate the effect of hydrogen bonding between the oxygen of the C=O group and H of NH.

Tzd has two carbonyl groups and both are in different environments. Accordingly two bands are observed in the carbonyl stretching region.

On comparing the i.r. spectrum of the ligand with those of the complexes (Table II) we observe a negative shift of the order of 50 to 105 cm^{-1} in one of the C=O stretching frequencies. The bands due to the other carbonyl stretching frequency remain unaffected. This shows that only one carbonyl group is involved in coordination[11,12]. It is however difficult to say which one of two carbonyl groups is the actual donor group.

The shift in ν(N–H), δ(N–H), ν(C–N), ν(C–S) clearly indicate that the nitrogen of amino group is not involved in coordination.

The far infrared region of the complexes shows the presence of an additional band at 405 cm^{-1} in the case of titanium and at 400–432 cm^{-1} in the case of iron complexes. These bands can be assigned to M–O stretching modes[9]. The presence of an M–O band lends direct support to the bonding through carbonyl oxygen.

Ethylene Monothiocarbonate Complexes

Comparison of the spectrum of the ligand with those of the complexes (Table II) shows a strong negative shift in the carbonyl stretching frequency of the ligand. This clearly indicates that the coordination is through the oxygen of carbonyl group. The shifts in ν(C–S) and δ(C–O–C) also indirectly favour coordination through carbonyl group. The presence of an additional band in the range 404–453 cm^{-1} in each complex, which can be assigned to the M–O stretching band, also supports bonding through carbonyl group.

Configuration of the Complexes

To establish the configuration of tin(IV) and titanium(IV) complexes we have assumed different point groups for *cis* and *trans* configuration and have calculated the number of normal modes with their species with the help of group theoretical methods. The results of these calculations clearly show that all the complexes have *trans* configuration.

All the iron complexes are paramagnetic and their magnetic moment values are in the range 4.6–4.9 (B.M.) (Table III). These values clearly show that they are in tetrahedral configuration. A C_{2v} point group has been established for these complexes by comparing the observed and calculated number of bands.

Relation between $\Delta\nu(C=O)$ and Stability Constant (LogK)

With the help of the following equation[13] we have calculated the stability constant of our complexes. The results of which along with the $\Delta\nu$(C=O) are presented in Table IV:

$$\log K = 0.042\,\nu(C{=}O) - 64.428$$

On plotting logK values *vs.*$\Delta\nu$(C=O) we obtained a straight line as shown in Figure 1. This observation is in accord with the previous results[13]. On comparing the logK values of this series of complexes with the logK values of previously reported Sn(IV) complexes[13]

TABLE III. Molar Conductance at 25 °C at Various Molar Concentrations (cm^{-2} mho/mol) and B.M. Values.

Complexes	Solvent	M/128	M/256	M/512	M/1024	Nature	μ_{eff}(B.M.)
1. $FeCl_2 \cdot 2tzt$	Ethanol	18.62	23.53	29.5	32.7	Non-electrolyte	4.82
2. $FeBr_2 \cdot 2tzt$	Ethanol	14.77	20.73	22.92	28.88	Non-electrolyte	4.61
3. $SnCl_4 \cdot 2tzt$	DMF[a]	12.3	18.72	21.86	27.6	Non-electrolyte	4.84
4. $FeCl_2 \cdot 2tzd$	Ethanol	22.62	26.52	30.21	34.13	Non-electrolyte	4.88
5. $FeI_2 \cdot 2tzt$	–	–	–	–	–	Non-electrolyte	4.79
6. $FeBr_2 \cdot 2tzd$	–	–	–	–	–	Non-electrolyte	4.80
7. $FeI_2 \cdot 2tzd$	–	–	–	–	–	Non-electrolyte	4.89
8. $FeCl_2 \cdot 2emt$	–	–	–	–	–	Non-electrolyte	4.91

[a] DMF = dimethylformamide.

TABLE IV. $\Delta\nu$(C=O) *vs.* LogK.

Complexes	$\Delta\nu$(C=O), cm^{-1}	LogK
Thiazolidinedione		
1. $FeCl_2 \cdot 2L$	85	6.12
2. $SnCl_4 \cdot 2L$	94	5.54
3. $TiCl_4 \cdot 2L$	105	5.08
4. $FeBr_2 \cdot 2L$	95	5.50
5. $FeI_2 \cdot 2L$	50	7.39
Ethylene Monothiocarbonate		
1. $FeCl_2 \cdot 2L$	107	4.368
2. $SnCl_4 \cdot 2L$	117	3.948
3. $TiCl_4 \cdot 2L$	133	3.276

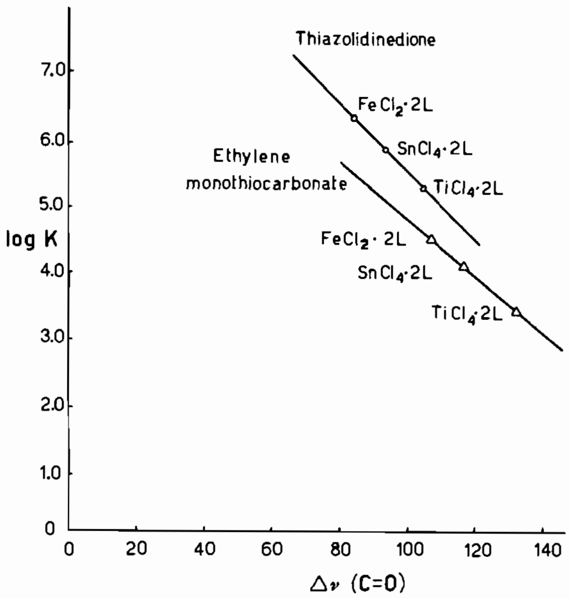

Figure 1. Plot of logK *vs.* $\Delta\nu$(C=O).

we find that the tzd and emt can be given the following position:

Ethylene urea<dimethylformamide<ethylene monothiocarbonate<benzamide<succinamide<thiazolidinedione.

The tzd and emt complexes of Fe(II), Sn(IV) and Ti(IV) chlorides indicate that the Fe(II) has the highest value of logK as compared to Ti(IV) or Sn(IV). This observation is consistent with the established order[14].

Conclusions

(i) Sn(IV), Ti(IV) and Fe(II) halides are linked either to nitrogen or oxygen atoms of the ligands. All these halides are hard acids[15] and the donor atoms (*viz.* nitrogen and oxygen) are hard bases. The interaction between hard acid and hard base is preferred according to HSAB theory[15]. The other possible donor atoms in all the ligands are either thionyl sulphur or the ring sulphur. Sulphur is a soft atom, and will comparatively less prefer a hard atom for coordination.

(ii) Amino nitrogen in tzt and carbonyl oxygens in tzd and emt are the donor atoms. These atoms have the highest electronegativity in their respective molecules, and perhaps this factor helps in increasing the electron density at these sites[6]. Inductive and mesomeric effects also favour increase of electron density at these donor centres.

(iii) The magnitude of shift in carbonyl stretching frequency on complex formation is lower in tzd than in emt. This is perhaps due to the presence of another electron withdrawing carbonyl group in tzd which lowers the electron density on the coordinating carbonyl group.

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References

1 P.P. Singh and R. Rivest, *Can. J. Chem.*, *46*, 2361 (1968).
2 D. De Filippo and C. Preti, *J. Chem. Soc. A*, 1904 (1970).
3 B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
4 B.N. Figgis and J. Lewis, "Modern Coordination Chemistry", Edited by J. Lewis and R.C. Wilkins, Interscience, New York, p. 403 (1960).
5 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, p. 148–149 (1963).
6 P.P. Singh and I.M. Pande, *J. Inorg. Nucl. Chem.*, *34*, 591 (1972).
7 J. Chatt, L.A. Duncanson and L.M. Venanzi, *J. Chem. Soc.*, 2712 (1956).
8 A. Naka, Y. Satto and H. Kuroya, *Bull. Chem. Soc. Japan*, *25*, 331 (1952).
9 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, p. 145 (1963).
10 D.T. Elmore, *J. Chem. Soc.*, 3489 (1958).
11 E.W. Randall, C.M.S. Yoder and J. Zuckerman, *Inorg. Chem.*, *5*, 2240 (1966).
12 R. Rivest, *Can. J. Chem.*, *40*, 2234 (1962).
13 P.P. Singh and I.M. Pande, *J. Inorg. Nucl. Chem.*, *34*, 1139 (1972).
14 F. Basalo and R. Johnson, "Coordination Chemistry", Benjamin, New York, p. 123 (1964).
15 R.G. Pearson, *J. Chem. Ed.*, *45*, 581, 643 (1968).