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Synthesis, Nuclear Magnetic Resonance and Infrared Studies of Zinc(II) and Cadmium(II) Complexes of Thiosemicarbazones Derived from Fluorenone and *p*-Anisaldehyde

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Fluorenone (FTSCH) and *p*-anisaldehyde (ATSCH) thiosemicarbazones react with zinc(II) and cadmium(II) acetates forming M:L 1:2 complexes, characterized by IR, ^{1}H and ^{13}C NMR spectra and elemental analyses. The coordination mode of the ligands is discussed and four-coordinate, pseudo-tetrahedral structures are suggested.

Key words: zinc(II), cadmium(II), thiosemicarbazone, fluorenone, *p*-anisaldehyde, IR, ^{1}H, ^{13}C NMR spectra

Zinc(II) ion is essential for all forms of life and several zinc(II) containing metaloenzymes have been identified [1–2]. Further, the zinc(II) ion has been found to be of catalytic importance in enzymatic reactions [3]. Zinc(II) – sulfur interactions are of great interest in biochemical systems, due to the presence of sulfur at the active sites of several enzymes, vitamins and proteins [4]. The ability to coordinate *via* sulfur is enhanced for cadmium, whose toxic properties could be related to strong cadmium(II)–sulfur bond [5]. Moreover, chelating sulfur donors are actually under study as antidotes in cadmium(II) poisoning [6–7]. The enhancement of antitumour activity of some thiosemicarbazones in the presence of zinc(II) [8] and cadmium(II) [9] ions has been reported. Several reports dealing with crystal and molecular structure [10–13], spectroscopic [14–18] and biological properties [19–22] of thiosemicarbazones and their metal complexes have been published. Few reports on metal complexes of fluorenone [23–26] and *p*-anisaldehyde [27–32] thiosemicarbazone are also available. Interesting applications of thiosemicarbazone compounds have encouraged us to search for new complexes of these ligands. Spectroscopic properties of zinc(II) and cadmium(II) complexes with fluorenone and *p*-anisaldehyde thiosemicarbazones, abbreviated as FTSCH and ATSCH, respectively (Fig. 1), are described. One of these complexes [Zn(FTSC)$_2$] has been prepared previously [25], but only selected NMR resonances were listed. We decided to include this compound here in order to present its full NMR spectra compared with those of other complexes.

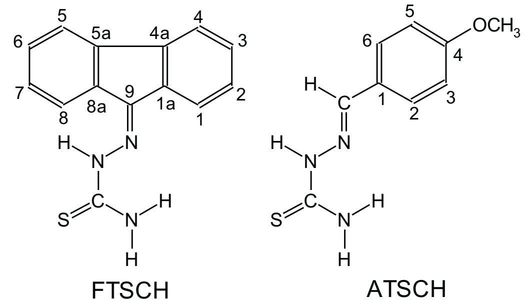

Figure 1. Structure and atom numbering of FTSCH and ATSCH molecules.

EXPERIMENTAL

Syntheses: The preparation of the FTSCH and ATSCH ligands was published in [33]. For preparation of complexes, the ligand (20 mmol) was dissolved in ethanol (50 cm^3) by heating on water-bath for 30 min. Ethanolic solution of respective metal acetate (10 mmol in 20 cm^3) was added to the ligand solution and the resultant mixture was heated at reflux for 2 hrs. After heating, it was allowed to stand at 25°C. The complexes were filtered off and washed with ethanol, diethyl ether and dried over silica gel.

Measurements: Carbon, hydrogen and nitrogen were analyzed using a Coleman Analyzer at Regional Sophisticated Instrumentation Center, CDRI, Lucknow, India. The IR, ^1H and ^{13}C NMR spectra were recorded as reported earlier [26]. The stability of the complexes dissolved for NMR spectroscopy in DMSO-*d6* was verified by the IR spectra measured in the 1600–1100 cm^{-1} region, where the solvent shows a few, low intensity bands, and absorptions observed for solid state complexes were detected.

RESULTS AND DISCUSSION

For uncoordinated ligands, several tautomeric forms are possible as has been shown in Fig. 2. All these forms can be verified by the IR spectroscopy, where the respective ν(SH) and ν(NH) stretching vibrations are very characteristic and absorb in different regions. In the case of both ligands, the ν(SH) band, expected at about 2500 cm^{-1}, is absent, but the ν(NH) mode is located between 3260 and 3300 cm^{-1}, indicating that these compounds exist in thione form in the solid state [34]. Also the ^1H NMR spectra of FTSCH and ATSCH do not show a signal at about 4 ppm [35] attributed to the SH proton. Further, the ^{13}C NMR spectra, which exhibit carbon signal due to C=S group at about 180 ppm, also support the thione form. However, the π-bonding system attributed mainly to the C=S linkage may be delocalized over neighboring bonds causing some conformational restrictions like that concerning the rotation around the C–NH_2 bond. Such delocalization of π electrons has been found for the thiosemicarbazide, where the calculated π-bond orders for C=S (0.518), C–NH_2 (0.547) and C–NH (0.551) bonds indicate their partial double character. Also the computed stretching force constants for C=S (3.0 mdyn·$Å^{-1}$) and C–N (6.25, and 5.55 mdyn·$Å^{-1}$) support this conclusion [36]. In the same work, the computed π-bond order for the NN group was 0.11 supporting the assumption that in the N–N group is a σ-bond. On the basis of the above information, the hydrazone form could be assigned

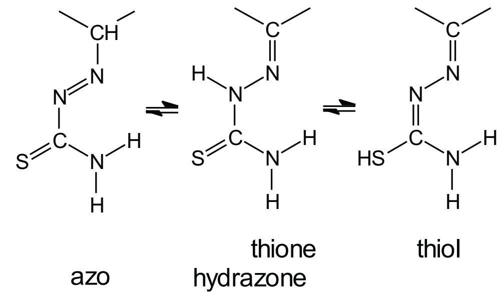

Figure 2. Tautomeric forms of thiosemicarbazone moiety.

to free ligands with sulfur and nitrogen atoms as potential metal binding centers. These coordination abilities of the title ligands as well as the structures of formed complexes will be discussed.

Infrared spectra: Selected IR spectral bands along with their tentative assignments based on previously reported data [26] are given in Table 1. In the region above 3100 cm^{-1}, the ligands show three distinct IR bands corresponding to coupled nitrogen-hydrogen stretching vibrations. Upon metal coordination, some changes are observed in this region. The middle band, resulting predominantly from the ν(NH) vibrations, disappears, suggesting the deprotonation of the thiosemicarbazone group during coordination. Observed splitting of the highest energy mode may be due to different hydrogen bonding of two amine groups present in the complex molecules. Three IR bands observed for the ligands at about 1600, 1490 and 1430 cm^{-1} have been previously attributed to the thiosemicarbazone moiety modes [26]. In the case of three complexes, these bands change positions, supporting the significant electron delocalization in the ligand CNNC skeleton during complexation. Since the 1598 cm^{-1} transition is generated mainly by the $\delta(NH_2)$ vibration, the mentioned hydrogen bonding may also influence the number of bands observed in discussed region for FTSC complexes. Bands with predominant ν(CS) vibrations are located in the FTSCH and ATSCH spectra at 851 and 821 cm^{-1}, respectively. Again, for three complexes, these bands shift after coordination to lower energy at about 710 cm^{-1}, confirming the change into the carbon–sulfur bond order from double bonding in the ligands toward single in the complexes. Similar effect was reported for other zinc(II) and cadmium(II) complexes with thiosemicarbazones [37]. The exceptional spectral behavior is observed for the $[Zn(ATSC)_2]$ complex, where most of the discussed bands are less affected by metal coordination. This phenomenon suggests a different ligand coordination mode, especially the smaller frequency lowering of the ν(CS) vibrations indicates that the double C=S bond is preserved in this complex. In the far-IR region, the complexes show new vibrational bands located at wavenumbers comparable with those previously attributed to ν(M-N) and ν(M-S) modes [25]. The above data suggest that FTSCH with both metals and ATSCH with cadmium(II) form coordination bonds *via* iminyl nitrogen and thiolate sulfur atoms.

Table 1. Selected IR bands[(a)] [cm^{-1}] of the ligands and complexes.

Mode	FTSCH	[Zn(FTSC)$_2$]	[Cd(FTSC)$_2$]	ATSCH	[Zn(ATSC)$_2$]	[Cd(ATSC)$_2$]
ν(NH$_2$) +	3410s	3480m, 3340m	3475m, 3360m	3407m	3420m	3490m, 3370m
ν(NH)	3262m			3293m		
	3156m	3170w		3159w	3170w	
δ(NH$_2$) +	1598s	1610sh	1605sh	1607s	1610s	1615s
ν(CN)		1600s	1595s			
		1570m	1560sh			
	1490m	1560w	1490m	1475m	1475m	1490m
	1433s	1430s	1420s	1449m	1450m	1480m
ν(CS)	851m	710m	705m	821s	815m	715m
ν(M-N)		405m	405m		470w	410w
ν(M-S)		350w	345w		300w	325w
		320m	330w			

(a)s – strong, m – medium, w – weak, ν – stretching, δ – bending.

^{1}H NMR spectra: All ^{1}H NMR spectra have been recorded in DMSO-d6. A spectral comparison of the ligands and complexes leads to the following conclusions. The signals at 10.80 or 11.33 ppm, attributable to the N–NH proton, disappear from the spectra of all complexes (Table 2). Two ^{1}H signals of the NH$_2$ group appear between 7.9 and 8.7 ppm in the spectra of the ligands indicating hindered rotation of the amine group due to partially double character of the respective C–N bond. For three complexes these signals are combined into single, broad signal (Fig. 3), suggesting the free rotation of the NH$_2$ group as a result of the C(S)–NH$_2$ bond order lowering on coordination. However, two distinct signals are observed in the spectrum of [Zn(ATSC)$_2$] at 8.57 and 8.82 ppm, what supports the existence of partially double bond for the C(S)–NH$_2$ group even after deprotonation. This could be only possible if the thione form of the ligand is preserved in the complex.

Table 2. ^{1}H NMR chemical shifts[(a)], δ [ppm *vs* TMS].

^{1}H[(b)]	FTSCH	[Zn(FTSC)$_2$]	[Cd(FTSC)$_2$]	ATSCH	[Zn(ATSC)$_2$]	[Cd(ATSC)$_2$]
C$\underline{H}_3$				3.70 (s)	4.30 (s)	3.74 (s)
C(1)$\underline{H}$	8.00 (d)	7.70 (d)	8.12 (d)			
C(2)$\underline{H}$	7.29 (t)	6.90 (t)	7.30 (t)	7.70 (d)	8.28 (d)	7.65 (d)
C(3)$\underline{H}$	7.47 (t)	7.35 (t)	7.40 (t)	6.90 (d)	7.48 (d)	6.89 (d)
C(4)$\underline{H}$	7.76 (d)	7.61 (d)	7.83 (d)			
C(5)$\underline{H}$	7.76 (d)	7.88 (d)	8.02 (d)	6.90 (d)	7.48 (d)	6.89 (d)
C(6)$\underline{H}$	7.47 (t)	7.43 (t)	7.47 (t)	7.70 (d)	8.28 (d)	7.65 (d)
C(7)$\underline{H}$	7.38 (d)	7.17 (t)	7.34 (t)			
C(8)$\underline{H}$	7.83 (d)	9.17 (d)	9.07 (d)			
C$\underline{H}$=N				7.98 (s)	8.51 (s)	8.05 (s)
N–N$\underline{H}$	10.80 (s)			11.33 (s)		
C–N$\underline{H}_2$	8.70 (s)		8.65 (br)	8.14 (s)	8.82 (s)	7.85 (s)
	8.40 (s)	8.02 (br)		7.92 (s)	8.57 (s)	

(a)Signal multiplicity is given in parentheses; s – singlet, d – doublet, t – triplet, br – broad.
(b)Atom numbering is shown in Fig. 1.

^{13}C NMR spectra: Most of the ^{13}C NMR signals observed in the complex spectra preserve positions close to those of the ligands (Table 3). For the compounds with fluorenone group, the exceptions are signals assigned to the C(S) and C(9) carbon atoms. The C(S) carbon signal is shielded in the zinc(II) and cadmium(II) complexes

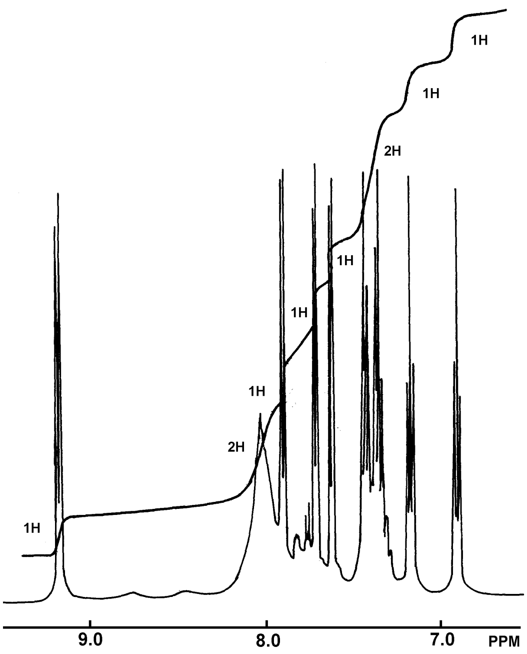

Figure 3. ^{1}H NMR spectrum of [Zn(FTSC)$_2$].

with respect to the free ligand, suggesting the change of the C=S group to the thiol one, upon coordination. The signal for C(9) is deshielded in the spectra of both complexes. Such deshielding effect has been reported for other thiosemicarbazone complexes [26], supporting the electron density change within the C(9)=N group as a result of the metal–nitrogen bond formation. The above effect is partially extended on fluorene group, but observed differences between ligand and complex signal positions diminish rapidly as the respective carbon atoms are located further from the coordinating C=N group. The appearance of two signals for C=S, C=N and other carbon atoms in the spectra of [Cd(FTSC)$_2$] suggests the presence of two isomeric forms of the complex. For the second ligand and its complexes, an upfield shift for C=S (176.79 ppm) and downfield shift for CH=N (144.32 ppm) have been observed in the spectrum of [Cd(ATSC)$_2$]. In contrast, the carbon resonances due to C=S and CH=N groups are both shifted to downfield in the spectrum of [Zn(ATSC)$_2$]. These results support the different coordination mode of ATSCH in its two complexes studied here.

Conclusion: From the elemental analyses, the complexes prepared here could be formulated as ML$_2$. The ^{1}H and ^{13}C NMR spectral measurements provide a valuable data to propose the coordination mode of FTSCH. It appears that FTSCH acts as mononegative bidentate chelating agent, coordinating through iminyl nitrogen and thiolate sulfur atoms. Considering the above data and the bulkiness of the ligand molecules, we postulate the pseudo-tetrahedral central atom surroundings for FTSCH complexes (Fig. 4). Similar conclusion can be formulated for the [Cd(ATSC)$_2$] complex . Different spectral behavior of the [Zn(ATSC)$_2$] complex suggests that the coordination may take place *via* deprotonated nitrogen and thione sulfur atoms. If these two atoms will act as metal binding centers, the four-membered chelate ring may be formed. Despite the internal strain, such structure is possible as has been reported for the [Tl(CH$_3$)$_2$(ATSC)] crystal [31]. However, the data collected here are not sufficient to definitely confirm this structure.

Table 3. ^{13}C NMR chemical shifts$^{(a)}$, δ [ppm *vs* TMS].

^{13}C$^{(b)}$	FTSCH	[Zn(FTSC)$_2$]	[Cd(FTSC)$_2$]	ATSCH	[Zn(ATSC)$_2$]	[Cd(ATSC)$_2$]
$\underline{C}H_3$				55.44 (q)	55.89 (q)	55.26 (q)
$\underline{C}$ (1)	131.3 (d)	132.14 (d)	132.39, 130.92	126.62 (s)	127.80 (s)	128.01 (s)
$\underline{C}$ (1a)	129.1 (s)	130.18 (s)	129.24, 128.96			
$\underline{C}$ (2)	120.7 (d)	120.32 (d)	119.83, 119.78	114.39 (d)	115.20 (d)	114.10 (d)
$\underline{C}$ (3)	127.9 (d)	128.41 (d)	127.94, 127.38	129.20 (d)	129.90 (d)	128.49 (d)
$\underline{C}$ (4)	122.4 (d)	122.21 (d)	122.47, 122.20	161.06 (s)	162.50 (s)	160.17 (s)
$\underline{C}$ (4a)	141.5 (s)	140.12 (s)	141.19, 141.05			
$\underline{C}$ (5)	122.4 (d)	122.21 (d)	120.48, 120.06	129.20 (d)	129.90 (d)	128.49 (d)
$\underline{C}$ (5a)	139.4 (s)	140.12 (s)	139.55, 139.25			
$\underline{C}$ (6)	126.7 (d)	126.69 (d)	127.94, 126.69	114.31 (d)	115.25 (d)	114.10 (d)
$\underline{C}$ (7)	119.0 (d)	119.84 (d)	119.40, 119.30			
$\underline{C}$ (8)	130.3 (d)	131.45 (d)	130.64, 129.97			
$\underline{C}$ (8a)	136.7 (s)	133.32 (s)	136.82, 134.96			
$\underline{C}$ (9)	145.5 (s)	152.59 (s)	150.08, 145.50			
$\underline{C}$H=N				143.38 (d)	144.10 (d)	144.32 (d)
$\underline{C}$ = S	180.2 (s)	175.94 (s)	179.62, 174.77	177.81 (s)	179.69 (s)	176.79 (s)

[a] Measurement in DMSO-d6; signal multiplicity is given in parentheses with abbreviations: s – singlet, d – doublet, q – quartet.

[b] Atom numbering is shown in Fig. 1.

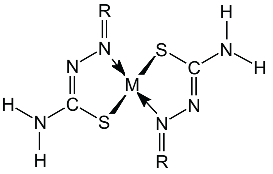

Figure 4. Molecular structure of the FTSCH complexes and [Cd(ATSC)$_2$].

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REFERENCES

1. Tandon S.S., Chander S., Thomson L.K., Bridson J.N. and McKee V., *Inorg. Chim. Acta,* **219,** 55 (1994).
2. Sigel H. (Ed), *Metal Ions in Biological Systems:* Vol. 15: M. Dekker, NY, 1983.
3. Ferrari M.B., Fava G.G., Pelizzi C. and Tarasconi P., *J. Chem. Soc. Dalton Trans.*, 2153 (1992).
4. Prince R.H., *Adv. Inorg. Radiochem.,* **22**, 349 (1979).
5. Fraglia G., Graziani R., Guo Z., Casellato U. and Sitran S., *Inorg. Chim. Acta,* **192**, 17 (1992).
6. Casas J.S., Sanchez A., Bravo J., Gracia-Fontan S., Castellano E.E. and Jones M.M., *Inorg. Chim. Acta,* **158**, 119 (1989).
7. Romero-Molina M.A., Gutierrez-Valere M.D., Lopez-Garzon R., Salas-Peregrin J.M., Arriortua M.I. and Zuniga F.J., *Inorg. Chim. Acta*, **136**, 87 (1987).
8. Solaiman D., Saryan L. and Petering D.H., *J. Inorg. Biochem.*, **10**, 135 (1979).
9. Atassi G., Dumont P. and Harteel J.C., *Eur. J. Cancer*, **15**, 451 (1979).
10. Ferrari M.B., Fava G.G., Leporati E., Pelizzi C., Tarasconi P. and Tosi G., *J. Chem. Soc. Dalton Trans.*, 2455 (1986).
11. West D.X., Lockwood M.A., Liberta A.E., Chen X. and Willet R.D., *Trans. Met. Chem.,* **18**, 221 (1993).
12. Battaglia L.P., Ferrari M.B. and Boggia R., *Inorg. Chim. Acta,* **215**, 85 (1994).
13. West D.X., Bain G.A., Butcher R.J., Jasinski J.P., Li Y. and Pozdniakiv R.Y., *Polyhedron,* **15**, 665 (1996).
14. Singh B. and Srivastava U., *Trans. Met. Chem.,* **13**, 205 (1988).
15. Yulan Z., Hui W., Pengfei X. and Shaozu W., *Synth. React. Inorg. Met-org. Chem.*, **24**, 1479 (1994).
16. Reddy P.S.N. and Agarwala B.V., *Synth. React. Inorg. Met-org. Chem.*, **17**, 585 (1987).
17. Singh B. and Mohan H., *J. Indian Chem. Soc.*, **63**, 692 (1986).
18. Mohan M., Sharma P. and Jha N.K., *Inorg. Chim. Acta,* **107**, 91 (1985).
19. Logan J.C., Fox M.P., Morgan J.H., Makohon A.M. and Pfau C.J., *J. Gen. Virol.*, **28**, 271 (1975).
20. Levinson W.E. and Helling R., *Antimicrob. Agents. Chemother.*, **9**, 160 (1976).
21. Heinisch L. and Tresselt D., *Pharmazie,* **32**, 582 (1977).
22. Mikelens P., Woodson B. and Levinson W.E., *Bioinorg. Chem.*, **9**, 469 (1978).
23. Laly S. and Parameshwaran G., *Asian J. Chem.*, **3**, 142 (1991).
24. El-Sonbati A.Z., El-Sayed M., Mabrouk M. and Megahed H.E., *Trans. Met. Chem.*, **16**, 280 (1991).
25. El-Sheleil A. and El-Sonbati A.Z., *Trans. Met. Chem.*, **17**, 420 (1992).
26. Akinchan N.T., Akinchan R. and Drożdżewski P.M., *Polish J. Chem.*, **74**, 1221 (2000).
27. El-Asmy A.A.m Morsi M.A. and El-Shafei A.A., *Indian J. Chem.,* **26A**, 766 (1987).
28. Thimmaih K.N., Lloyd W.D. and Chandrappa G.T., *Inorg. Chim. Acta,* **106**, 81 (1985).
29. Agrawal B.V. and Reddy P.S.N., *Trans. Met. Chem.,* **13**, 187 (1988).
30. Kinthada Prakash M.M.S., Prabhakar L.D., Reddy L.D. and Venkata D., *Inorg. Chim. Acta*, **141**, 179 (1988).
31. Casas J.S., Castellano E.E., Macias A., Rodriguez-Arguelles M.C., Sanchez A. and Sordo J., *J. Chem. Soc. Dalton Trans.,* 353 (1993).
32. Thimmaiah K.N., Chandrappa G.T. , Rangaswamy and Jayarama, *Polyhedron*, **3**, 1237 (1984).
33. Akinchan N.T., Akinchan R., Ibok U.J., Battaglia L.P., Corradi A.B. and Drożdżewski P., *J. Cryst. Spectr. Res.*, **22**, 741 (1992).
34. Akinchan N.T., West D.X., Yang Y.H., Salberg M.M. and Klein T.L., *Trans. Met. Chem.*, **20**, 481 (1995).
35. Ali M.A., Haroon C.M., Nuzimuddin M., Majumdar S.M.M., Trafder M.T.F. and Khair M.A., *Trans. Met. Chem.*, **17**, 133 (1992).
36. Manogaran S. and Sathyanarayana D.N., *J. Mol. Struct.*, **96**, 73 (1982).
37. Balkrishanan K. and Aravindakshan K., *J. Ind. Chem. Soc.*, **68**, 187 (1991).