

TABLE 1—ANALYTICAL AND PHYSICAL DATA

Sl. no.	Compd.	Colour	M.p. °C	Analysis % : Found/(Calcd.)		AM Ω ⁻¹ cm ² mol ⁻¹	μ _{eff} B.M.
				N	Metal		
1.	[Cu(C ₁₄ H ₁₆ O ₂ N ₂)Cl] ^a	Brown	176	7.65 (7.82)	17.50 (17.74)	13.6	1.70
2.	[Ni(C ₁₄ H ₁₆ O ₂ N ₂) ₂]	Yellowish green	198°	9.50 (9.71)	10.02 (10.17)	6.7	3.0
3.	[Co(C ₁₄ H ₁₆ O ₂ N ₂) ₂]	Yellowish brown	200°	9.51 (9.71)	10.03 (10.20)	4.0	4.82
4.	[Cu(C ₁₄ H ₁₆ O ₂ N ₂)Cl] ^b	Light brown	181	7.33 (7.52)	17.00 (17.07)	13.1	1.8
5.	[Ni(C ₁₄ H ₁₆ O ₂ N ₂) ₂]	Yellowish green	205°	9.04 (9.26)	9.54 (9.70)	5.1	3.12
6.	[Co(C ₁₄ H ₁₆ O ₂ N ₂) ₂]	Dark brown	209°	9.04 (9.26)	9.61 (9.70)	5.2	4.70

^a Cl % : 9.80 (9.91). ^b Cl % : 9.31 (9.54). ° Decomposed.

for octahedral geometry¹⁶. In the electronic spectra of these complexes, two bands are mainly observed at ~9 000 and ~24 000 cm⁻¹, assigned to ν₁ and ν₃ transitions, respectively, considering a O_h symmetry. Two shoulders ⁴T_{1g}(F)→²T_{1g}, ²T_{2g} (~18 000 cm⁻¹) and ⁴T_{1g}(F)→⁴A_{2g}(F) (~19 000 cm⁻¹) may be considered either due to the splitting of ν₃, in many components or they may be because of appearance of ν₂ transitions¹⁷. The ratio of ν₂/ν₁ (1.95–2.2) suggests the shoulders ~19 000 cm⁻¹ as ν₂ transitions for these complexes.

In ligands, AHCE and AHCP, the band around 1 620 cm⁻¹ is assigned¹⁹ to ν_{C=N} (azomethine) vibrations. The ligands with one primary amino group is expected to show two bands in the region 3 100–3 400 cm⁻¹ due ν_S(NH₂) and ν_{as}(NH₂) vibrations²⁰. The presence of a phenolic group in such compounds makes it difficult to differentiate between ν_{NH₂} and ν_{OH} vibrations since both absorb around the same frequencies. Thus, a band around 3 200 cm⁻¹ has been attributed to a combination of ν_{NH₂}+ν_{OH} vibrations. In the complexes, the ν_{C=N}, ν_{NH₂}+ν_{OH} vibrations have undergone a negative shift by 50–75 cm⁻¹, indicating the coordination of the azomethine, primary amino and phenolic OH groups of the ligands. This view is further supported by the appearance of bands corresponding to ν_{M-N}(525–550) and ν_{M-O}(450–470 cm⁻¹). In the complex nos. 1 and 4 (Table 1), metal halogen bands are also present as indicated by the appearance of bands²¹, ν_{M-Cl}(340–370 cm⁻¹).

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Complexes of Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) and Dioxouranium(II) with Thiophene-2-aldehydethiosemicarbazone

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METAL complexes of thiosemicarbazides have been known for their pharmacological applications¹. Significant antitubercular², fungicidal³ and antiviral⁴ activities have been reported for thiosemicarbazides and their derivatives. Extensive studies on the investigation of metal complexes of thiosemicarbazones have been undertaken in recent years. The present study describes the synthesis and

characterisation of complexes of Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and UO_2^{II} with thiosemicarbazone obtained by condensing thiophene-2-aldehyde with thiosemicarbazide.

Experimental

Thiophene-2-aldehyde (Fluka) and thiosemicarbazide (Fluka) were used to synthesise the semicarbazone (TATSC). Metal acetates were of AnalaR grade, while the solvents were of reagent grade.

Preparation of ligand (TATSC): Thiophene-2-aldehyde (9.2 cm³) in ethanol (60 cm³) was gradually added to a solution of thiosemicarbazide (9.10 g) in ethanol (100 cm³), and the mixture was refluxed on a steam-bath for 3 h and left overnight. A yellowish brown solid separated, was filtered, washed with ethanol and ether and dried over calcium chloride under reduced pressure. The product (yield 80%) was insoluble in water but soluble in ethanol. Analytical data are presented in Table 1.

Metal complexes with TATSC: To TATSC (2.96 g) dissolved in ethanol (60 cm³), aqueous-ethanolic solution containing $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ / $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (2.00 g) / $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (1.60 g) / $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (1.76 g) / $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (2.12 g) / $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (3.40 g) was gradually added with constant stirring. The mixture was refluxed on a water-bath for ~2 h and left overnight. Coloured solid complexes separated out from the solution in 80–85% yield. The products were filtered, washed with ethanol and ether, and air-dried. The complexes were insoluble in hot water but soluble in ethanol.

Analytical data are presented in Table 1. Infrared spectra in the range 4 000–200 cm⁻¹ were recorded on a Beckman Aculab 10 spectrophotometer using KBr pellets. Diffuse reflectance spectra in the range 220–1 000 nm were obtained using a

Carl-Zeiss VSU-22 spectrophotometer. Magnetic susceptibilities of complexes at 303 K were determined by Gouy's method. Thermogravimetric data were obtained by heating the complexes at the rate of 10° min⁻¹ in air upto 800°.

Results and Discussion

The analytical data of the complexes (Table 1) indicate 1 : 2 metal–ligand stoichiometry. μ_{eff} value (4.60 B.M.) for the Co^{II} complex corresponds to three unpaired electrons as reported for tetrahedral Co^{II} complexes⁸. The electronic spectrum showed one intense band at 590 nm and one weak band at 520 nm corresponding to transitions ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, respectively, which also supported tetrahedral geometry around the d⁷ Co^{II} ion⁸. The Ni^{II} complex was diamagnetic, suggesting a square-planar structure of the complex⁷. One intense band (440 nm) observed in the diffuse reflectance spectrum of the complex for the transitions ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$, ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$ also supported square-planar geometry. The μ_{eff} value of 1.86 B.M. for Cu^{II} complex corresponds to one unpaired electron. Square-planar structure of the complex was confirmed^{8,9} by the presence of one band (480 nm) in the reflectance spectrum corresponding to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transition. Zn^{II} , Cd^{II} and UO_2^{II} complexes were all diamagnetic. The electronic spectral measurements of the complexes were not useful.

The presence of bands at 1 540, 1 460, 1 320 and 810 cm⁻¹ in the ir spectrum of TATSC (Table 2) suggests that it exists in thione form in the solid state. In the ir spectra of the complexes, bands assigned to N–C–N, C=S and NH–C=S disappear and new bands for the azine (C=N–N=C) and C–S groups appear, indicating chelation of the metal ion through azine nitrogen and the thio sulphur of the ligand. A negative shift of 20–25 cm⁻¹

TABLE 1—ANALYTICAL DATA AND PHYSICO-CHEMICAL PROPERTIES OF TATSC AND ITS COMPLEXES WITH Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} AND UO_2^{II}

Compd.	Colour	Decomp. Temp. (°C)		Analysis % : Found/(Calcd.)			
		Starting	Completion	Metal	C	H	N
$\text{O}_6\text{H}_7\text{N}_3\text{S}_2$	Yellow	192*	—	—	39.10 (38.91)	3.84 (3.78)	22.58 (22.70)
$\text{Co}(\text{O}_6\text{H}_6\text{N}_3\text{S}_2)_2$	Black	260	720	19.72 (18.80)	34.02 (33.72)	2.94 (2.81)	19.58 (19.67)
$\text{Ni}(\text{O}_6\text{H}_6\text{N}_3\text{S}_2)_2$	Black	280	680	13.64 (13.75)	33.96 (33.74)	2.85 (2.81)	19.34 (19.68)
$\text{Cu}(\text{O}_6\text{H}_6\text{N}_3\text{S}_2)_2$	Brown	240	760	14.52 (14.72)	33.80 (33.36)	2.77 (2.78)	19.38 (19.46)
$\text{Zn}(\text{O}_6\text{H}_6\text{N}_3\text{S}_2)_2$	Yellow	280	760	14.98 (15.08)	33.48 (33.22)	2.80 (2.76)	19.36 (19.38)
$\text{Cd}(\text{O}_6\text{H}_6\text{N}_3\text{S}_2)_2$	White	240	680	23.21 (23.39)	29.90 (29.97)	2.58 (2.49)	17.32 (17.48)
$\text{UO}_2(\text{O}_6\text{H}_6\text{N}_3\text{S}_2)_2$	Yellow	320	—	42.22 (42.31)	22.76 (22.57)	2.05 (1.88)	13.04 (13.06)

* M.p.

TABLE 2—INFRARED SPECTRAL BANDS (cm⁻¹) OF TATSC AND ITS COMPLEXES AND TENTATIVE ASSIGNMENTS

TATSC (L)	Co(L ₂)	Ni(L ₂)	Cu(L ₂)	Zn(L ₂)	Cd(L ₂)	UO ₂ (L ₂)	Assignment
1 650	1 630	1 625	1 630	1 620	1 625	1 630	C=N stretch ^a
—	1 590	1 600	1 580	1 590	1 585	1 590	C=N-N=C stretch ^b
1 540	—	—	—	—	—	—	N-C-N stretch ^c
1 460	—	—	—	—	—	—	C=S stretch ^d
1 320	—	—	—	—	—	—	NH-C=S stretch ^e
1 030	1 050	1 045	1 050	1 045	1 045	1 050	N-N stretch ^f
810	—	—	—	—	—	—	C=S stretch ^g
—	720	725	715	720	720	725	C-S stretch ^h
—	455	460	455	460	470	455	M-N stretch ⁱ
—	290	280	275	280	290	285	M-S stretch ^j

^a Ref. 7. ^b Ref. 11. ^c Ref. 12. ^d Ref. 13. ^e Ref. 14. ^f Ref. 15. ^g Ref. 16. ^h Ref. 17. ⁱ Ref. 6. ^j Ref. 17.

in the stretching frequency of C=N in the ligand observed in the complexes also indicates the involvement of azomethine nitrogen in complexation and is supported by a positive shift of 15–20 cm⁻¹ in the N-N stretching frequency of TATSC when it coordinates with the metal ions. Appearance of new bands due to M-N and M-S stretching vibrations in the spectra of the complexes further supports coordination of the metal ion to the bidentate ligand through azomethine nitrogen and thio sulphur.

Thermogravimetric studies indicate that the metal complexes do not contain any water and that they are thermally quite stable. Decomposition started at relatively higher temperature and was complete above 680° (Table 1). The thermal stability of the complexes were in the following order for metal ions, UO₂^{II} > Ni^{II} ~ Zn^{II} > Co^{II} > Cu^{II} ~ Cd^{II}.

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Stability Constants of some Bivalent Metal Ion Chelates of Schiff Bases derived from 2,4-Dihydroxybenzaldehyde

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POTENTIOMETRIC studies have been carried out on metal chelates of UO₂^{II}, Cu^{II}, Co^{II}, Ni^{II} and Zn^{II} with 2,4-dihydroxybenzylidene thiosemicarbazone and 2,4-dihydroxybenzylidene phenylhydrazone. The proton-ligand and metal-ligand stability constants have been determined by the Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti¹, at 30±0.1° and ionic strength 0.1 M in 75:25 (v/v) dioxan-water medium.

Experimental

The two ligands (A) 2,4-dihydroxybenzylidene thiosemicarbazone and (B) 2,4-dihydroxybenzylidene phenylhydrazone were synthesised by refluxing equimolar quantities of 2,4-dihydroxybenzaldehyde and the respective amines in ethanol. The products were repeatedly crystallised to obtain analytically pure samples. The purity was tested by tlc and elemental analysis (Table 1).