

**Characterisation of metal complexes:** The uv absorption band of the ligand remained almost unchanged in the spectra of the metal complexes. It is, therefore, evident that no structural alteration of the ligand occurred during complexation. In the ir spectra of the metal complexes, the strong band of the ligand at  $2\ 230\text{ cm}^{-1}$  remained almost unchanged in position and intensity. This indicates the absence of any bond formation between the metal ion and the cyano function of the ligand. The band at  $1\ 685\text{ cm}^{-1}$  due to hydrogen bonded ester carbonyl of the ligand disappeared in the spectra of the metal complexes. Instead, a new band appeared at  $\sim 1\ 655\text{ cm}^{-1}$  in the spectra of all the metal complexes. This band can be assigned to the stretching of the metal bonded carbonyl group<sup>9</sup>. The absence of the broad band of the ligand at  $2\ 800\text{--}3\ 400\text{ cm}^{-1}$  in the spectra of complexes, indicate the replacement of the NH proton by the metal ion as in structure 1b. Weak bands at  $\sim 3\ 050$  (aromatic C-H) and  $\sim 2\ 850\text{ cm}^{-1}$  (aliphatic C-H) are also observed in the spectra of all the metal chelates. In the spectra of the cobalt(II) complex a broad band is observed at  $3\ 590\text{ cm}^{-1}$  due to its coordinated water. Ir spectra of all the metal complexes showed a medium intensity band at  $\sim 550$  (M-N) and a band at  $\sim 420\text{ cm}^{-1}$  (M-O)<sup>6</sup>.

Further evidence for the bonding mode of the ligand is provided by the <sup>1</sup>H nmr spectra of the diamagnetic nickel(II) complex. Thus, the low-field signal of the ligand at  $\delta 12.95$  disappeared in the spectra of the complex, which indicates the replacement of the NH proton during metal chelation. Thus, the ir and <sup>1</sup>H nmr spectra strongly support the monobasic bidentate nature of the ligand, leaving the cyano function free as in 1b.

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## Coordination Complexes of Chromium(III), Manganese(II), Iron(III), Cobalt(II) and Nickel(II) with some Tri-, Tetra- and Hexadentate Schiff Bases

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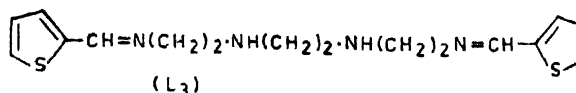
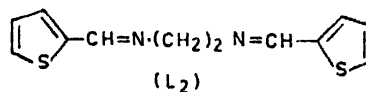
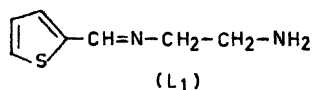
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THE present paper reports a series of eighteen complexes of Cr<sup>III</sup>, Mn<sup>II</sup>, Fe<sup>III</sup>, Co<sup>II</sup> and Ni<sup>II</sup> with the Schiff base ligands *N*-mono(thiophene-2-aldene)-ethylenedimine (L<sub>1</sub>), *N,N*-bis(thiophene-2-aldene)-ethylenedimine (L<sub>2</sub>) and *N*<sup>1</sup>,*N*<sup>4</sup>-bis(thiophene-2-aldene)triethylenetetramine (L<sub>3</sub>).



Analytical, conductance, magnetic moment and spectral data were explored to elucidate their structure.

## Experimental

**Synthesis of ligands:** The ligands were prepared by reacting the corresponding carbonyl compound with ethylenediamine in 1 : 1 and 2 : 1 molar ratio, while with triethylenetetramine in 2 : 1 ratio only. The isolated ligands were characterised on the basis of analysis, molecular weight, ir and <sup>1</sup>H nmr spectral data (Table 1).

**Synthesis of complexes:** The metal salt (0.01 mole) was suspended in methanol (25 ml) and refluxed with the corresponding ligand (0.01 mol) for 6 h. The complexes were crystallised out from the resulting clear viscous solution by repeated treatment with petroleum ether (b.p. 60-80°). The analytical and physical data of the compounds are given in Table 2.

NOTES

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF LIGANDS

Compd.	M.p. °C	Mol. wt. Found/(Calcd.)	Analysis % : Found/(Calcd.)			$\nu_{max}$ (cm <sup>-1</sup> )			$\delta$		
			O	H	N	NH	C=N	C-S	CH <sub>2</sub>	Azomethine	Thiophene
C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> S(L <sub>1</sub> )	85	128 (154)	55.00 (54.54)	6.86 (6.49)	17.04 (18.18)	3 900	1 660	754	3.18	8.50	7.01 7.15
C <sub>11</sub> H <sub>11</sub> N <sub>2</sub> S <sub>2</sub> (L <sub>2</sub> )	94	208 (248)	59.92 (58.96)	5.08 (4.88)	10.80 (11.29)	—	1 658	750	3.20	8.48	7.02 7.14
C <sub>16</sub> H <sub>22</sub> N <sub>4</sub> S <sub>2</sub> (L <sub>3</sub> )	76	295 (334)	58.92 (57.49)	6.02 (6.59)	16.15 (16.77)	3 280	1 662	758	3.21	8.52	7.03 7.10

TABLE 2—ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compd.*	Analysis % : Found/(Calcd.)		Conductance** $\Omega$ cm <sup>2</sup> mol <sup>-1</sup>	$\mu_{eff}$ B.M.
	M	N		
[Ni(L <sub>1</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	20.01 (20.60)	9.81 (9.86)	248 <sup>a</sup>	3.05
[Ni(L <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ]SO <sub>4</sub>	19.66 (19.01)	8.91 (9.07)	286 <sup>b</sup>	2.99
[Co(L <sub>1</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	19.90 (20.70)	9.96 (9.82)	213 <sup>a</sup>	4.98
[Co(L <sub>1</sub> )(H <sub>2</sub> O) <sub>2</sub> ]SO <sub>4</sub>	18.82 (19.02)	8.86 (9.04)	252 <sup>a</sup>	5.05
[Cr(L <sub>1</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	13.58 (14.18)	6.99 (7.68)	35.65 <sup>c</sup>	4.15
[Fe(L <sub>1</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	15.95 (15.06)	8.18 (7.56)	Insol.	1.98
[Mn(L <sub>1</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	15.78 (16.44)	9.02 (8.38)	200 <sup>a</sup>	1.83
[Ni(L <sub>2</sub> )]Cl <sub>2</sub>	15.68 (15.54)	6.71 (7.41)	217 <sup>a</sup>	0.81
[Ni(L <sub>2</sub> )]SO <sub>4</sub>	14.29 (14.58)	6.58 (6.95)	227 <sup>b</sup>	0.56
[Co(L <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	15.36 (15.59)	7.61 (7.41)	262 <sup>a</sup>	5.45
[Co(L <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ]SO <sub>4</sub>	14.72 (14.62)	7.28 (6.55)	236 <sup>b</sup>	5.08
[Cr(L <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	10.98 (11.75)	6.92 (6.32)	Insol.	4.12
[Fe(L <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	12.16 (12.50)	6.59 (6.29)	Insol.	1.82
[Mn(L <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	12.60 (13.89)	7.28 (6.80)	170 <sup>a</sup>	1.92
[Ni(L <sub>2</sub> )Cl <sub>2</sub> ] <sub>2</sub> ·4H <sub>2</sub> O	9.84 (10.98)	11.02 (10.45)	Insol.	3.28
[Co(L <sub>2</sub> )]Cl <sub>2</sub>	11.49 (12.69)	12.56 (12.07)	278 <sup>a</sup>	5.10
[Fe(L <sub>2</sub> )]Cl <sub>2</sub>	12.90 (11.24)	12.10 (11.25)	250 <sup>a</sup>	1.92
[Mn(L <sub>2</sub> )]Cl <sub>2</sub>	11.65 (11.19)	12.65 (12.17)	Insol.	1.86

\*L<sub>1</sub> = C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>S, L<sub>2</sub> = C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>S, L<sub>3</sub> = C<sub>16</sub>H<sub>22</sub>N<sub>4</sub>S. \*\*In <sup>a</sup>methanol, <sup>b</sup>water, <sup>c</sup>nitrobenzene.

Results and Discussion

The ligands L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> can offer terdentate (S, N, N), tetradentate (S, N, N, S) and hexadentate (S, N, N, N, N, S) chelation to the metal ions. The ligands showed a sharp ir band around 1 660 cm<sup>-1</sup> for azomethine stretch which shifted to 1 570 ± 20 cm<sup>-1</sup> in the complexes indicating coordination of azomethine nitrogen<sup>1</sup>. The  $\nu_{N-H}$  of free ligands L<sub>1</sub> and L<sub>2</sub> at 3 290 ± 10 cm<sup>-1</sup> also showed a negative shift in the complexes indicating coordination of nitrogen<sup>2</sup>. Two new sharp bands at 550 ± 10 and 340 ± 10 cm<sup>-1</sup> in the complexes are assigned as  $\nu_{M-N}$  and  $\nu_{M-S}$ , respectively. The bands at 1 120 and 650 cm<sup>-1</sup> correspond to ionic sulphate groups,

while a sharp band at 508 cm<sup>-1</sup> is due to uncoordinated chloride ion. A broad band at 3 400 cm<sup>-1</sup> along with OH rocking and wagging bands around 900 ± 5 and 700 ± 10 cm<sup>-1</sup> in the complexes of ligands L<sub>1</sub> and L<sub>2</sub> support the presence of coordinated water<sup>3</sup>.

In the <sup>1</sup>H nmr spectra of the ligands, the signal for the azomethine proton at  $\delta$  8.50 shifts towards higher field in complexes at  $\delta$  8.68 indicating donation of lone-pair of electron to the central metal atom. The position of signals due to CH<sub>2</sub> multiplet observed at  $\delta$  3.12–3.20 remain unchanged in the complexes. The two signals centered around  $\delta$  7.01 and 7.22 in free ligand are due to thiophene

ring protons ; and the latter shifts to  $\delta$  7.15 in the complexes indicating the involvement of thiophene ring sulphur atom in coordination.

The Ni<sup>II</sup> complexes of ligand L<sub>2</sub> are diamagnetic and show only one band in the spectra at 16.50 kK assigned to  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  transition. In addition, bands at 8.00–10.50 and 20.00–25.00 kK may be due to  ${}^3B_{1g} \rightarrow {}^3B_{2g} + {}^3E_g$  and  ${}^3B_{1g} \rightarrow {}^3A_{1g} + {}^3E_g$  transitions. These bands as well as the value of  $Dq$  (1 650 cm<sup>-1</sup>) are consistent with a planar geometry<sup>4</sup>. The Ni<sup>II</sup> complexes of ligand L<sub>1</sub> and L<sub>3</sub> on the other hand are paramagnetic ( $\mu_{eff}$  around 3.00 B.M.), and in their spectra three characteristic bands at 25.00, 19.00 and 11.50 kK corresponding to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  transitions are observed. The values of  $Dq$ ,  $B$  and  $\nu_2/\nu_1$  ratio around 1 150, 960 cm<sup>-1</sup> and 1.58, respectively, also confirm octahedral geometry<sup>5</sup>.

The  $\mu_{eff}$  values ( $\approx$ 5.00 B.M.) for the Co<sup>II</sup> complexes are independent of temperature and correspond to three unpaired electrons and an octahedral geometry. Three bands in the electron spectra at 20.00, 16.00 and 8.00 kK are assigned to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  ( $\nu_1$ ),  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  ( $\nu_2$ ) and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  ( $\nu_3$ ) transitions, respectively. The splitting of  $\nu_2$  band as well as the values of  $Dq$  and  $B$  correspond to pseudooctahedral geometry<sup>6</sup>.

The  $\mu_{eff}$  values of Cr<sup>III</sup> complexes (around 3.73 B.M.) were very close to the spin-only value for octahedral symmetry<sup>7</sup>. Characteristic bands are seen at 11.80, 18.17 kK with a shoulder at 23.54 kK ; the latter band and shoulder may be assigned to  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  ( $\nu_1$ ) and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  ( $\nu_2$ ) transition, respectively. These along with the  $Dq$  and  $B$  values which are around 1 820 and 700 cm<sup>-1</sup> correspond to octahedral coordination<sup>8</sup>.

The  $\mu_{eff}$  values of Fe<sup>III</sup> and Mn<sup>II</sup> complexes are around 2.20 B.M. which correspond to their low-spin configuration having one unpaired electron. These complexes show a large number of bands in their electronic spectra around 40.00, 30.00 and 25.00 kK which are all charge transfer in nature. Ligand field transitions have been observed in the form of weak bands corresponding to  $Dq$  and  $B$  values of 3 500 and 720 cm<sup>-1</sup>, respectively, and are consistent with octahedral structures<sup>9</sup>.

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### A Corrosion Study of Welded Steel Specimens in 3% NaCl Media

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VARIOUS types of mild steel and stainless steel in welded forms are used extensively in different metallic structures. A large number of studies have been made on the corrosion of various types of metals and alloys in chloride environment<sup>1-5</sup>. But studies of corrosion of welded steel specimens in chloride media are rather limited<sup>6,7</sup>. Therefore in the present investigation corrosion studies of welded mild steel both cold rolled and hot rolled and stainless steel of the type AISI 304 have been undertaken in 3% NaCl medium to find out the nature and extend of corrosion damage.

#### Experimental

The steel specimens used for corrosion tests were rectangular sheets (25 × 18 × 2 mm) both in case of welded and unwelded forms. The composition of the specimens used is given in Table 1.

For welded specimens, the samples were cut into two pieces and then joined by electrical arc welding or by inert gas welding methods. Subsequently the specimens were polished on successive grades of emery paper and then washed with acetone, dried and weighed. The surface was examined under microscope. After taking the weight the specimens were subjected to electro-chemical polarisation study and for corrosion rate determination.

For the polarisation study, the specimens were taken as working electrodes. The assembly consisted of a H-type cell having a working electrode of a specific area (1 sq cm)<sup>8</sup>.