

## Synthesis, spectral, biological, thermal and cyclic voltammetric studies of some Ni<sup>II</sup> complexes of azodyes derived from 4-amino antipyrine

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Some new Ni<sup>II</sup> complexes of the ligands 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methyl phenyl azo)pyrazol-5-one (CAAPH) and 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-chloro phenyl azo)pyrazol-5-one (CPAAPH) having the compositions [Ni(LH)<sub>2</sub>Cl<sub>2</sub>], [Ni(LH)(Ac)<sub>2</sub>], [Ni(LH)(NO<sub>3</sub>)<sub>2</sub>], [Ni(LH)SO<sub>4</sub>], [Ni(LH)<sub>2</sub>(ClO<sub>4</sub>)]ClO<sub>4</sub>, [Ni(LH)<sub>2</sub>(NCS)Cl], [Ni(L'H)<sub>2</sub>Cl<sub>2</sub>], [Ni(L'H)(Ac)<sub>2</sub>], [Ni(L'H)(NO<sub>3</sub>)<sub>2</sub>], [Ni(L'H)SO<sub>4</sub>], [Ni(L'H)<sub>2</sub>(ClO<sub>4</sub>)]ClO<sub>4</sub> and [Ni(L'H)<sub>2</sub>(NCS)Cl] (LH = CAAPH and L'H = CPAAPH) have been synthesised and characterised by elemental analysis, IR, electronic and <sup>1</sup>H NMR spectra, magnetic and conductance measurements, thermal and cyclic voltammetric studies. The ligands and complexes have been screened for their antibacterial activity against gram positive and gram negative bacteria.

Ni<sup>II</sup> forms a large number of complexes<sup>1</sup> with a wide range of geometries such as six coordinate octahedral (*O<sub>h</sub>*), five coordinate square pyramidal (*C<sub>4v</sub>*) or trigonal bipyramidal (*D<sub>3h</sub>*) and four coordinate square planar (*D<sub>4h</sub>*) or tetrahedral (*T<sub>d</sub>*). A characteristic feature of Ni<sup>II</sup> complexes is that a temperature dependent equilibria can exist between these structural forms, which may be due to the small free energy difference between them. In view of the importance of Ni<sup>II</sup> complexes, we have isolated and characterized some new complexes of two potential multidentate ligands, 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methyl phenyl azo)pyrazol-5-one (cresol azoantipyrine, CAAPH) and 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-chloro phenylazo)pyrazol-5-one (chloro phenol azoantipyrine, CPAAPH) derived from biologically active molecule, 4-amino antipyrine. Both CAAPH and CPAAPH are potential tridentate monobasic ligands<sup>2,3</sup>.

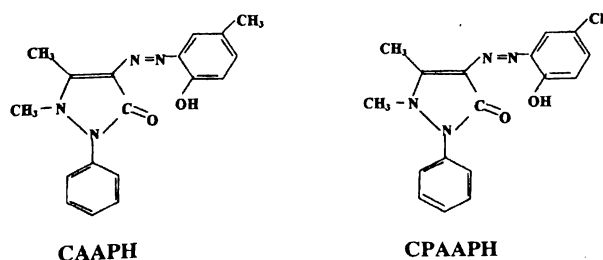


Fig. 1

### Results and discussion

All the chelates (Table 1) are coloured (either brown or dark brown) solids stable in air, non-hygroscopic and amorphous. They are soluble in methanol and ethanol, partially soluble in water and benzene but remain insoluble in ether. The perchlorate complex explodes violently on heating. The analytical data (Table 1) clearly show that the acetate, nitrate and sulphate complexes of both CAAPH and CPAAPH correspond to the composition (NiLX<sub>2</sub>), but the chloride and thiocyanate complexes have the composition [NiL<sub>2</sub>X<sub>2</sub>] while the perchlorate complexes correspond to the formula [NiL<sub>2</sub>X]X, where X = Cl, Ac, NO<sub>3</sub>, SO<sub>4</sub>/2, NCS or ClO<sub>4</sub> and L=CAAPH or CPAAPH. The molar conductance values of the complexes in C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, CH<sub>3</sub>CN and CH<sub>3</sub>OH (Table 1) show that all the complexes except the perchlorate complexes are non-electrolytes. The perchlorate complexes behave as 1 : 1 electrolytes<sup>4</sup>.

In the present investigation, it has been found that the chloride, perchlorate and thiocyanate complexes of Ni<sup>II</sup> with both the ligands show magnetic moments ranging from 3.08 to 3.28 B.M. at room temperature (Table 1) conforming to octahedral geometry. All the other complexes are found to be diamagnetic, indicating square planar geometry<sup>5</sup>.

The infrared spectra of the ligands exhibit a broad

Table 1. Analytical and physical data of the complexes

Complex	Colour	Metal % (Calcd.)	Molar conductance <sup>a</sup> ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )			$\mu_{\text{eff}}$ (B.M.)
			C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	CH <sub>3</sub> CN	CH <sub>3</sub> OH	
[Ni(CAAPH) <sub>2</sub> Cl <sub>2</sub> ]	Brown	7.38 (7.50)	4.2	44.9	31.7	3.28
[Ni(CAAPH)(Ac) <sub>2</sub> ]	Dark brown	11.63 (11.76)	4.1	38.3	29.3	Diamagnetic
[Ni(CAAPH)(NO <sub>3</sub> ) <sub>2</sub> ]	Dark brown	11.56 (11.62)	3.7	43.9	27.5	Diamagnetic
[Ni(CAAPH)(SO <sub>4</sub> )]	Brown	12.21 (12.32)	3.5	37.5	21.3	Diamagnetic
[Ni(CAAPH) <sub>2</sub> (ClO <sub>4</sub> )]ClO <sub>4</sub>	Dark brown	6.22 (6.43)	23.7	131.3	91.7	3.08
[Ni(CAAPH) <sub>2</sub> (NCS)Cl]	Brown	6.74 (7.39)	3.3	53.5	37.5	3.21
[Ni(CPAAPH) <sub>2</sub> Cl <sub>2</sub> ]	Brown	7.18 (7.21)	3.7	64.8	26.7	3.28
[Ni(CPAAPH)(Ac) <sub>2</sub> ]	Dark brown	10.96 (11.36)	4	58.1	24.5	Diamagnetic
[Ni(CPAAPH)(NO <sub>3</sub> ) <sub>2</sub> ]	Dark brown	10.94 (11.18)	3.9	63.7	28.1	Diamagnetic
[Ni(CPAAPH)(SO <sub>4</sub> )]	Brown	11.56 (11.81)	4.2	61.3	27.3	Diamagnetic
[Ni(CPAAPH) <sub>2</sub> (ClO <sub>4</sub> )]ClO <sub>4</sub>	Dark brown	5.89 (6.16)	22.1	128.1	93.5	3.18
[Ni(CPAAPH) <sub>2</sub> (NCS)Cl]	Brown	6.86 (7.04)	3.8	60.9	29.5	3.17

<sup>a</sup>All compounds gave satisfactory C, H, N and anion analysis.

medium intensity band  $\sim 3000 \text{ cm}^{-1}$ , assignable to hydrogen bonded OH group<sup>6</sup>. A very strong band occurring at  $1660 \text{ cm}^{-1}$  in the spectra of the ligands is attributed to  $\nu\text{C}=\text{O}$  of pyrazolone ring<sup>7</sup>. Also a band observed  $\sim 1450 \text{ cm}^{-1}$  in both the ligands may be attributed to the vibrational stretching of  $-\text{N}=\text{N}-$  group<sup>8</sup>. The bands observed  $\sim 3000 \text{ cm}^{-1}$  in the spectra of the ligands are found to be absent in their complexes. Instead, a new broad band  $\sim 3400 \text{ cm}^{-1}$  appeared in the spectra of the complexes, indicating the presence of free  $-\text{OH}$  group and its non-involvement in complexation. The  $\nu\text{C}=\text{O}$  is shifted to  $\sim 1590 \text{ cm}^{-1}$  in all the complexes providing evidence for the participation of this group in coordination to the metal. Also the vibrational band at  $1450 \text{ cm}^{-1}$ , assigned to  $\nu\text{N}=\text{N}$  in the spectra of the ligands is shifted by about  $20 \text{ cm}^{-1}$  in the spectra of all the complexes confirming

the coordination through one of the azo group nitrogens. Thus the ligands exhibit a neutral bidentate behaviour in all the complexes, coordinating through the  $>\text{C}=\text{O}$  and the  $-\text{N}=\text{N}-$  groups only.

For the perchlorate complexes,  $\nu_3$  and  $\nu_4$  appear as strong and medium intensity bands  $\sim 630$  and  $1140 \text{ cm}^{-1}$  respectively, indicating a monodentately coordinated perchlorate group. The medium intensity band observed  $\sim 925 \text{ cm}^{-1}$  in the spectra of the perchlorate complexes confirms this fully<sup>9</sup>.

The  $N$ -coordinated nature of the thiocyanate<sup>10</sup> group is indicated by the  $\nu\text{C}-\text{N}$  ( $\sim 2080 \text{ cm}^{-1}$ ),  $\nu\text{C}-\text{S}$  ( $\sim 780 \text{ cm}^{-1}$ ) and  $\delta\text{NCS}$  ( $\sim 470 \text{ cm}^{-1}$ ). The IR spectra of the nitrate<sup>11</sup> complexes are suggestive of monodentately coordinated nitrate group ( $\nu_4 \sim 1500$ ,  $\nu_1 \sim 1350$  and  $\nu_2 \sim$

1000  $\text{cm}^{-1}$ ). Also the IR spectra of acetate complexes exhibit a strong band at 1570  $\text{cm}^{-1}$  and a medium intensity band at 1330  $\text{cm}^{-1}$ , which can be attributed to  $\nu_{\text{C=O}}$  and  $\nu_{\text{C-O}}$  respectively of acetate group. The position of these vibrations and their separation by 240  $\text{cm}^{-1}$  are as seen for unidentate coordination of acetate group<sup>12,13</sup>.

Regarding the sulphate complexes, the infrared spectral bands  $\sim 1210$ , 1150 and 1070  $\text{cm}^{-1}$  are assigned to  $\nu_3$  of chelating bidentate sulphate group. Also the bands shown by the complexes  $\sim 990$  and 620  $\text{cm}^{-1}$ , which are absent in the spectra of both ligands are assigned to  $\nu_1$  and  $\nu_4$  of sulphate group, coordinated to the metal as a chelating bidentate group<sup>14</sup>.

The electronic spectral bands of the complexes in methanol together with the tentative assignments are discussed in detail<sup>15</sup>. The electronic absorption spectra of octahedral  $\text{Ni}^{\text{II}}$  complexes show three transitions  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ , which are observed  $\sim 25000$ , 17000 and 11000  $\text{cm}^{-1}$  respectively<sup>16,17</sup>. The  $d-d$  transition for square planar complex, observed usually  $\sim 16600$  is attributed<sup>18</sup> to  ${}^1A_{1g} \rightarrow {}^1B_{1g}$ . The complexes  $[\text{Ni}(\text{CAAPH})\text{X}_2]$  and  $[\text{Ni}(\text{CPAAPH})\text{X}_2]$  (where  $\text{X} = \text{Ac}, \text{NO}_3$ ) and  $[\text{Ni}(\text{CAAPH})\text{SO}_4]$  and  $[\text{Ni}(\text{CPAAPH})\text{SO}_4]$  show strong absorption band  $\sim 16660$   $\text{cm}^{-1}$ , which can be attributed to the spin allowed transition  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  of square planar  $\text{Ni}^{\text{II}}$  complexes<sup>19</sup>. The electronic spectral bands of the remaining  $\text{Ni}^{\text{II}}$  complexes under investigation are suggestive of octahedral geometry for them. The broad band  $\sim 17240$   $\text{cm}^{-1}$  observed in all these complexes is assigned to  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  transition of octahedral  $\text{Ni}^{\text{II}}$ . The band observed around  $\sim 25000$   $\text{cm}^{-1}$  is attributed to the transition  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ . The transition  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  could not be seen in the spectra of the present complexes.

${}^1\text{H}$  NMR spectrum<sup>20</sup> of the ligand CAAPH shows three singlets which correspond to the methyl protons and are observed at  $\delta$  2.2, 2.7 and 3.4. The signal due to five aromatic protons of the antipyrine phenyl ring appeared as a multiplet between  $\delta$  7.6 and 7.58 and that due to cresol protons is observed as a multiplet between  $\delta$  6.7 and 7.3. The signal due to phenolic proton appeared as a hump at  $\delta$  5.2. In the  ${}^1\text{H}$  NMR spectrum of CPAAPH, the signal due to two methyl protons are observed as

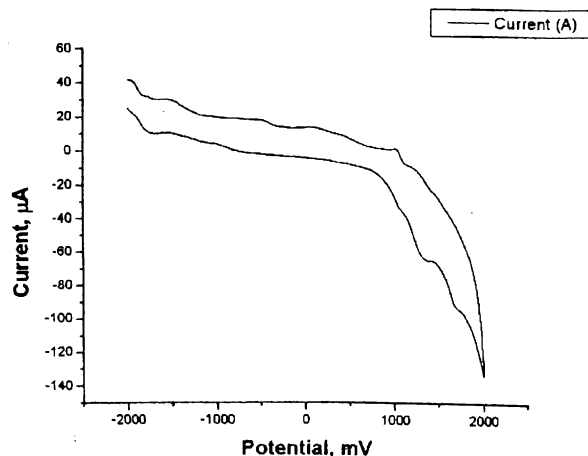


Fig. 2. Cyclic voltammogram of  $[\text{Ni}(\text{CPAAPH})\text{ClO}_4]\text{ClO}_4$ .

singlets at  $\delta$  2.7 and 3.27. The latter may be that due to the  $N$ -methyl group protons. The signal due to five aromatic protons of the antipyrine phenyl ring appeared as a multiplet between  $\delta$  7.46 and 7.55 and that due to 3 protons of phenol ring appear as a multiplet between  $\delta$  6.8–7.3. The phenolic proton signal is observed as a singlet at  $\delta$  5.29.

The cyclic voltammetric study of the complex  $[\text{Ni}(\text{CPAAPH})_2\text{ClO}_4]\text{ClO}_4$  was carried out in deaerated acetonitrile in the potential range  $-2000$  mV to  $+2000$  mV at a scan rate of 100 mV/s. The CV profile given in Fig. 2 shows quasi reversible peaks, indicating the covalent nature of metal ligand linkage<sup>21</sup>.

The ligand CPAAPH and one of its complexes  $[\text{Ni}(\text{CPAAPH})_2(\text{NCS})\text{Cl}]\text{Cl}$  were screened for their possible antibacterial activity against the gram positive bacteria *Staphylococcus aureus* ATCC 25923 and the gram negative bacteria *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 27853 and *Klebsiella pneumoniae* (clinical isolate) by agar diffusion method<sup>22</sup>. All the four bacteria were found to be tolerant to the ligand and the complex at concentrations 100  $\mu\text{g}/\text{ml}$ , 150  $\mu\text{g}/\text{ml}$  and 200  $\mu\text{g}/\text{ml}$  of the samples. Here the positive control was Gentamicin disc and the negative control was Whatmann no. 1 filter paper disc impregnated with 100  $\mu\text{l}$  of absolute methanol.

Thermal behaviour of  $[\text{NiL}(\text{Ac})_2]$  where  $\text{L} = \text{CAAPH}/\text{CPAAPH}$  was studied by TGA in air at a heating rate of  $10^\circ\text{C}/\text{min}$  in conjunction with DTG<sup>23–25</sup>.

TG curve of  $[\text{Ni}(\text{CAAPH})(\text{Ac})_2]$  (Fig. 3) indicates the absence of any water molecule. The complex is stable from ambient temperature up to 533 K as there is no detectable change in TG curve up to nearly 540 K. The decomposition of the complex occurs in two stages. There is no plateau in the TG curve between two stages of decomposition showing that the intermediate product after the first stage of decomposition could not be isolated. The final mass loss observed agrees with the values calculated for the conversion of the complex to its oxide (NiO). The percentage of Ni found from the TG data (12.18) is found to be in good agreement with the experimental (11.63) and theoretical value (11.76). The order parameters for the first and second stages of decomposition are 1.1 and 1.5 respectively<sup>26</sup>. The energy of activation for the first stage of decomposition is found to be  $95.32 \text{ kJ mol}^{-1}$  and that for the second stage of decomposition is  $271.48 \text{ kJ mol}^{-1}$ . The value of  $\Delta S$  for both stages of decomposition is found to be negative<sup>27</sup>.

The TG and DTG curves of  $[\text{Ni}(\text{CPAAPH})(\text{Ac})_2]$  show a plateau up to 503 K indicating the stability of the complex up to this temperature. The complex then decomposes in two stages with the order parameters being 1.2 and 2 with a small plateau between them. The two stages of decomposition are denoted by DTG peaks at 558 K and 658 K. The final plateau occurs above 720 K after which there is no mass loss in TG curve. The final mass loss agrees with the values calculated for conversion of complex to its oxide. The percentage of Ni obtained from TG data (11.13) is found to be in good agreement with experimental (10.96) and theoretical values (11.36). The

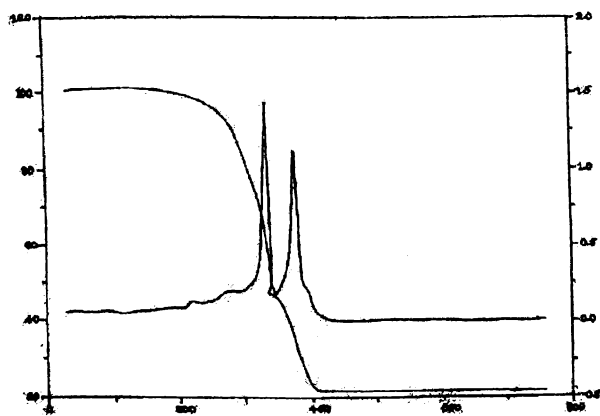
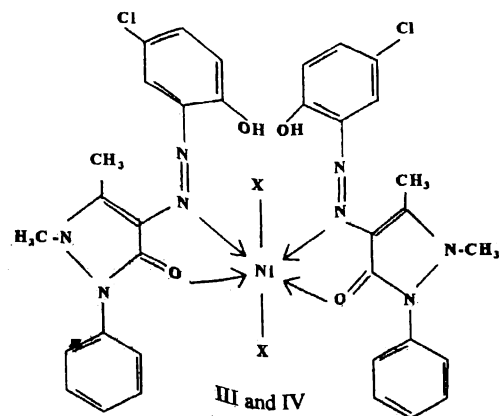
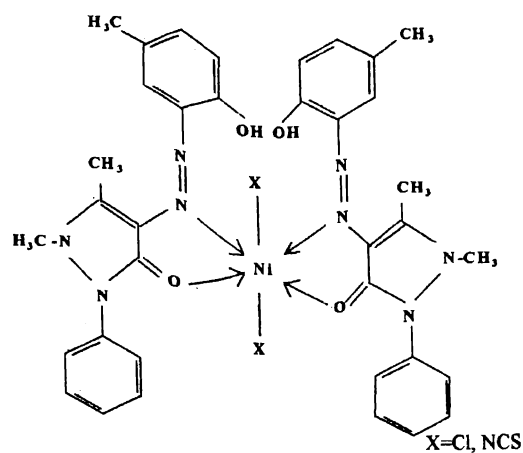
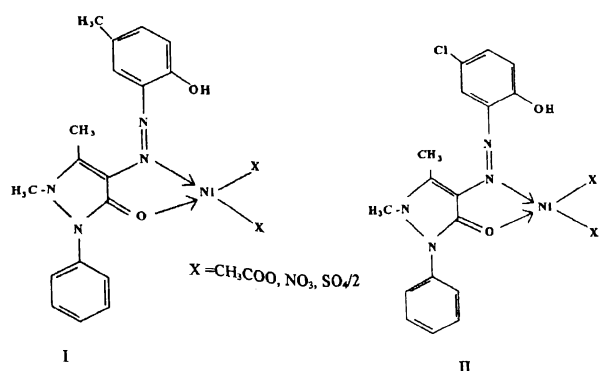


Fig. 3. TG and DTG curves of  $[\text{Ni}(\text{CAAPH})(\text{Ac})_2]$ .

value of  $\Delta S$  is found to be negative for both the stages and the value of energy of activation for stages are found to be  $75.86 \text{ kJ mol}^{-1}$  and  $234.28 \text{ kJ mol}^{-1}$  respectively.

On the basis of the above evidences, the acetate, nitrate and the sulphate complexes of both the ligands are assigned a square planar geometry. An octahedral geometry is suggested for the remaining complexes (Fig. 4).



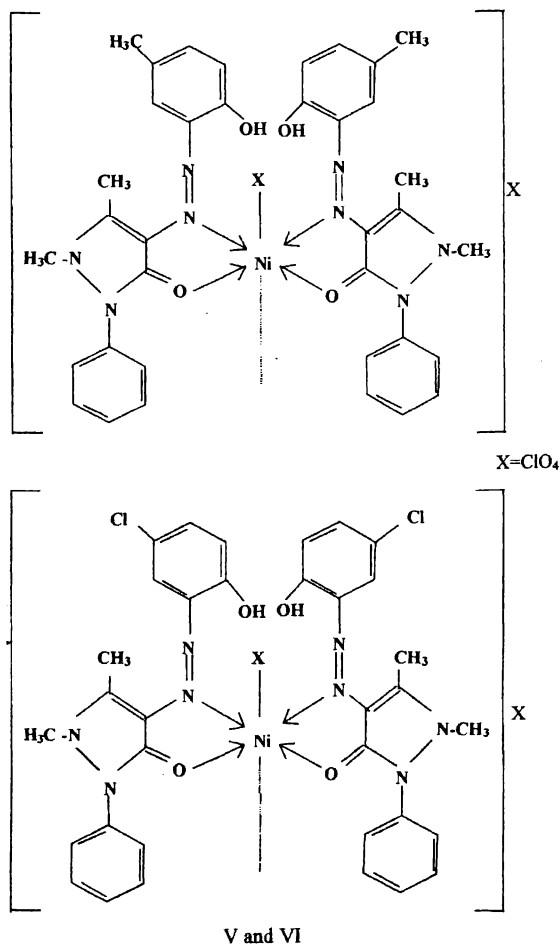


Fig. 4

In the case of the perchlorate complex, hexa-coordination can be achieved by interaction with electron rich centres of the adjacent molecules.

### Experimental

All the chemicals and solvents used were of A.R. grade. 4-Amino antipyrine (Fluka, Switzerland), *p*-cresol (Loba, Mumbai), *p*-chlorophenol (Loba, Mumbai) were used as supplied. Perchlorates and acetates of Ni<sup>II</sup> were prepared from Ni<sup>II</sup> carbonate salt with perchloric acid and glacial acetic acid respectively.

Metal, halide and sulphur in the complexes were estimated by standard methods<sup>5</sup>. Perchlorate was estimated by Kurz's method<sup>6</sup>. Elemental analysis (C, H and N) of the complexes were carried out at the RSIC, CDRI, Lucknow. The IR spectra of ligand and complexes were recorded in the region 4000–400 cm<sup>-1</sup> on a JASCO FTIR 430 spectrophotometer using KBr pellets. The electronic

spectra of the ligands and complexes in solution (CH<sub>3</sub>OH) were recorded on JASCO V-550 UV-VIS spectrophotometer. <sup>1</sup>H NMR spectra of the ligands were recorded in CDCl<sub>3</sub> on a 300 MHz (Broker Advance dpx-300) FTNMR instrument, using TMS as reference. Cyclic voltammetric profile of the complexes were run on a BAS-CV-50W-voltammetric analyser using glassy carbon as the working electrode. Antibacterial nature of the ligand and the complexes were tested by agar diffusion method. The conductances of the complexes in CH<sub>3</sub>OH, CH<sub>3</sub>CN and C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (ca. 10<sup>-3</sup> M) were measured at 300 ± 2 K using an Elico conductivity bridge CM 82T with a dip type cell (ec-03) fitted with platinum electrodes (cell constant 0.94 cm<sup>-1</sup>). The magnetic susceptibilities at room temperature (300 ± 2 K) were measured on a Gouy balance using Hg[Co(NCS)<sub>4</sub>] as the calibrant. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants.

### Synthesis of ligands :

The ligands CAAPH and CPAAPH were synthesised from 4-aminoantipyrine and *p*-cresol/*p*-chlorophenol as the case may be by diazotization and coupling as described in the literature<sup>1-10</sup>.

### Synthesis of complexes :

Metal salts (2.5 mmol) dissolved in methanol slowly added to a hot methanolic solution of the CAAPH/CPAAPH (2.5 mmol) with stirring were heated and refluxed for 5–6 h on a water bath. The complexes obtained by volume reduction were washed with aqueous methanol, benzene and finally with ether and then dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. The thiocyanate complex was prepared by adding ~0.5 g of NH<sub>4</sub>CNS to methanolic solution of metal chloride, stirred, filtered and the clear solution heated and refluxed with the ligands and the complex isolated as described above.

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