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Mn(II), Co(II) and Ni(II) complexes of 4-(2-thiazolylazo)resorcinol: Syntheses, characterization, catalase-like activity, thermal and electrochemical behaviour

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ABSTRACT

Manganese(II), cobalt(II) and nickel(II) acetates react with the ligand, 4-(2-thiazolylazo)resorcinol, to form complexes of general formula [ML_2] for M=Co(II), Ni(II) and [ML_2]$\cdot$2H_2O for M=Mn(II). Each of the azo complexes was characterized using elemental analysis, electrolytic conductance, UV–visible spectroscopy and magnetic susceptibility. An octahedral structure is proposed for all complexes prepared, which molar conductance data revealed to be non-electrolytes. IR spectra reveal that the ligand is coordinated to the metal ions in a tridentate manner via the resorcinol OH, azo N and thiazole N groups as donor sites. The electrochemical behaviour of the ligand and its complexes were obtained by cyclic voltammetry. Thermal decomposition studies were undertaken to secure additional information on the structure of the investigated compounds. The manganese(II) complex catalysed the disproportionation of hydrogen peroxide in the presence of imidazole.

1. Introduction

Azo compounds and their complexes with transition metals have attracted much attention, in part because of their physicochemical properties and applications in many important areas. They are highly colored and have been studied widely because of their excellent thermal and optical properties in applications such as optical data storage, photoswitching, non-linear optics and photochromic materials, dyes, chemical analysis and pharmaceuticals [1–8]. Furthermore, azo compounds are known to be involved in a number of biological reactions such as inhibition of DNA, RNA, and protein synthesis, carcinogenesis, and biological activity against bacteria and fungi [9,10].

Heterocyclic azo compounds such as 4-(2-thiazolylazo)-resorcinol 1, are popular as metal complexing ligands in spectrophotometry, chromatography and electrophoresis since they can advantageously form highly sensitive metal complexes, and are very easily synthesized and purified [11–14].

The azo dyes produced by diazotization of aromatic amines, which contain at least one azo group (–N=N–), which is attached to at least one aromatic moiety, are the most widely used dyes in the textile, printing, leather, papermaking, drug and food industries [15]. Metal-complex dyes are very versatile in terms of applications. Virtually all substrates, apart from a few synthetic fibers, can be dyed and printed with this class of dyes. In commercial terms the most important chelated metals are chromium, cobalt, copper, iron, and nickel [16]. We have previously reported the synthesis of some transition metal complexes of 4-(2-pyridylazo)resorcinol [17]. This paper describes the synthesis, spectroscopic characterization, thermal decomposition and catalytic activity of a series of 4-(2-thiazolylazo)resorcinol complexes. Furthermore, the paper describes the electrochemical behaviour of 4-(2-thiazolylazo)-resorcinol and its complexes in organic media.

Catalases are enzymes that disproportionate hydrogen peroxide into H_2O and O_2, and thereby protect living organisms from reactive oxygen species (ROS) that are responsible for “oxidative stress” reactions in the cell leading *e.g.* to aging [18,19]. In previous studies, we reported that the catalytic activity of the heterodinuclear copper(II)–manganese(II) Schiff base complexes were investigated for the disproportionation of hydrogen peroxide [20]. In this study, we also investigate the catalytic activity of the Mn(II) complex 2 of 4-(2-thiazolylazo)resorcinol.

2. Experimental

2.1. Materials and physical measurements

All the chemicals and solvents used for the synthesis and the measurements were of analytical reagent grade. Metal salts were purchased from Acros and Merck and 4-(2-thiazolylazo)resorcinol 1 was obtained from Fluka.

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Elemental analyses (carbon, hydrogen, nitrogen and sulfur) were performed on a LECO 932 CHNS analyser. Mn, Co and Ni were determined by atomic absorption spectroscopy using a Perkin Elmer 800 AA Spectrometer. The Fourier transform infrared spectra were recorded on a Jasco FT/IR-5300 spectrophotometer in the range 400–4000 cm^{-1} with a KBr disc and electronic spectra were recorded using a Perkin Elmer λ 20 UV/Vis. spectrophotometer in ethanol at 300 K in 1 cm quartz cuvettes. Room temperature magnetic susceptibility measurements were carried out on powdered samples using a Sherwood Scientific MX1 Model Gouy Magnetic Susceptibility Balance. The conductance measurements of all the complexes were carried out at room temperature using an Optic Ivymen System conductivity meter. A Perkin Elmer Pyris 1 TGA thermal analyzer was used to record simultaneously TG and DTG curves in the Central Laboratory at METU. The TG, DTG experiments were carried out in dynamic nitrogen atmosphere (20 $cm^3\,min^{-1}$) with a heating rate of 10 $^\circ C\,min^{-1}$ in temperature range 20–1000 °C.

2.2. Cyclic voltammetry measurements

Electrochemical measurements were performed with Autolab PGSTAT 302N Potentiostat/Galvanostat controlled by GPES 4.9 version software (Ecochemic, The Netherlands). The three-electrode system was used for all measurements; a platinum (Pt) electrode of 2 mm diameters as a working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode. Cyclic voltammetry studies were carried out in DMF containing 0.1 M TBAP as supporting electrolyte.

Cyclic voltammograms were performed in a potential range of 0.0 to +1.0 V at scan rate of 50 $mV\,s^{-1}$. All solutions were purged with nitrogen steam for 30 min before measurement and the working electrode was polished before each experiment. The procedure was performed at room temperature and a nitrogen atmosphere was maintained over the solution during the measurements.

2.3. Catalase-like activity studies

Volumetric measurements of evolved dioxygen during the reactions of the Mn(II) complexes with H_2O_2 were carried out as follows: a 50 cm^3 three-necked round-bottom flask containing a solution of the complex (0.005 mmol solid sample) in DMF (10 cm^3) was placed in a water bath (25 °C). One of the necks was connected to a burette and the others were stoppered by a rubber septum. While the solution was stirring, H_2O_2 (1.33 mmol, 0.150 cm^3) was injected into it through the rubber septum with a syringe. Volumes of evolved dioxygen were measured at 1 min time intervals by volumometry. In cases where imidazole (50 mg) was added this was introduced into the reaction vessel before the addition of H_2O_2 (in the absence of the imidazole the complexes were either inactive or very weak catalysts for this reaction). Observed initial rates were expressed as mol Ms^{-1} by taking the volume of the solution (15 cm^3) into account and calculated from the maximum slope of curve describing evolution of O_2 versus time.

2.4. Syntheses

The metal(II) salts; 0.5 mmol each (0.1225 g of $Mn(CH_3COO)_2.4H_2O$, 0.1245 g of $Co(CH_3COO)_2\cdot 4H_2O$ and 0.1244 g of $Ni(CH_3COO)_2\cdot 4H_2O$) were dissolved in about 15 cm^3 distilled water and 1 mmol (0.2257 g) of the ligand, 4-(2-thiazolylazo)resorcinol [caution: irritant] (in three sets) were dissolved in 20 cm^3 of methanol. The ligand solutions (20 cm^3 of 1 solution) were added slowly to the individual metal salt solutions with constant stirring and the pH of the mixture was raised to 7 by the addition of 10% alcoholic ammonia solution. These mixtures were refluxed for about 1 h, in order to complete the reactions. Upon slow evaporation of the solvents lustrous crystals remained which were collected by filtration, washed several times with a 1:1 methanol–water mixture and diethyl ether, and then dried over P_2O_5.

3. Results and discussion

The results of the elemental analyses of 4-(2-thiazolylazo)resorcinol 1 metal complexes are shown in Table 1. In all cases 1:2 (M:L) solid complexes are isolated and found to have the general formula $[ML_2]\cdot nH_2O$ where $n = 0$ in case of M=Co(II) 3, Ni(II) 4 and $n = 2$ in case of Mn(II) 2. The solubility of the complexes (2–4) in DMF permitted determination of the molar conductivity (Λ_m) of 10^{-3} M solution at 25 °C, and by comparison, the type of electrolyte of each complex. The low conductivity values of the all complexes listed in Table 1 indicate that the complexes are non-electrolytes.

4-(2-Thiazolylazo)resorcinol 1 (Fig. 1) is a tridentate ligand with the thiazole nitrogen, azo nitrogen and the ortho hydroxyl oxygen as the coordination sites which usually forms 1:2, metal:ligand, chelates (Fig. 2). All the complexes and the ligand are colored, insoluble in water and common hydrocarbon solvents, partially soluble in chloroform, and soluble in ethanol, methanol and DMF.

3.1. Infrared spectra

The IR spectra of the free ligand and its metal chelates were carried out in the 4000–400 cm^{-1} range (Table 2). IR spectra of the ligand show a broad band at about 3394 cm^{-1} due to the OH groups. In the metal complexes this broad band is still broad due to other OH group of resorcinol, which renders it difficult to attribute to the involvement of phenolic OH group in coordination. The stretching vibration of the thiazolylazo nitrogen ν(C=N) is observed in the form of an intense band at 1630 cm^{-1} in the free ligand. The spectral region at 1600–1400 cm^{-1} is complicated because of the stretching modes of –C=C– and –N=N– which are superimposed in the same region. However, the band appearing at 1587 cm^{-1} can be assigned to ν(N=N) of the azo group of the ligand. The strong band appearing at 1273 cm^{-1} in the free ligand is due to the ν(C–O) vibration [21].

The involvement of the deprotonated phenolic OH group in chelation is confirmed by the blue-shift of the ν(C–O) stretching band, to the extent of 61–84 cm^{-1} (1189–1212 cm^{-1}) in the complexes. This is further supported by the appearance of the band

Table 1
Analytical and physical data of metal complexes of 4-(2-thiazolylazo)resorcinol.

Compound	Color (%yield)	Mp, °C	Conductance $\Omega^{-1}\,cm^2\,mol^{-1}$	μ_{eff} (B.M.)	Contents(found/calcd.) %				
					C	H	N	S	Metal
$[MnL_2]\cdot 2H_2O$ (2) $[C_{18}H_{16}N_6O_6S_2Mn]$	Green (98)	297[a]	28	6.91	40.46 (40.68)	2.78 (3.03)	15.45 (15.81)	11.82 (12.07)	10.71 (10.34)
$[CoL_2]$ (3) $[C_{18}H_{12}N_6O_4S_2Co]$	Dark green (91)	332[a]	22	0.92	42.94 (43.29)	2.40 (2.42)	16.61 (16.83)	12.59 (12.84)	11.54 (11.80)
$[NiL_2]$ (4) $[C_{18}H_{12}N_6O_4S_2Ni]$	Dark green (61)	329[a]	18	3.25	42.99 (43.31)	2.58 (2.42)	16.69 (16.84)	12.56 (12.85)	11.62 (11.76)

[a] Decomposition point.

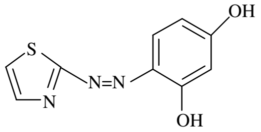

Fig. 1. 4-(2-Thiazolylazo)resorcinol, 1.

Table 2
Selected IR data (4000–400 cm^{-1}) of 4-(2-thiazolylazo)resorcinol and its complexes.

Compound	ν(C=N)	ν(N=N)	ν(C–O)	ν(M–O)	ν(M–N)	ν(M–N)$_{azo}$
1	1630 s	1587 s	1273 s	–	–	–
2	1590 s	1536 m	1189 s	532 m	507 w	424 w
3	1593 m	1492 m	1202 s	580 w	519 w	448 w
4	1609 m	1542 m	1212 s	525 w	445 w	422 w

Table 3
Electronic bands and d–d transitions of TAR and its metal complexes.

Compound	Maximum wavelength (nm)
1	219, 262, 412s, 445
2	219, 261, 412s, 490
3	217, 254, 337, 513
4	217, 241, 320, 426, 516s, 543, 586s

s, Shoulder.

at 525–580 cm^{-1} due to metal-oxygen stretching vibrations in the complexes. The ν(C=N) band is shifted to lower (21–40 cm^{-1}) frequencies in the complexes indicating that it has been affected upon coordination to the metal ions [21,22]. This view is further supported by the appearance of the band corresponding to the metal-nitrogen stretching vibration of thiazole nitrogen at 445–519 cm^{-1} in the complexes. The band at 774 cm^{-1} in the ligand is still in the same position in the complexes indicating the non-involvement of the thiazole S in coordination. Then (N=N) band is shifted to lower (95–45 cm^{-1}) frequencies in the complexes indicating that it has been affected upon coordination to the metal ions. In the far-IR spectra of all complexes, the metal-ligand bands observed at 422–448 cm^{-1} region can be assigned to the ν(M–N) stretching vibrations of the azo nitrogen. Therefore, the IR spectra indicate that 1 behaves as monobasic acid and the coordination sites being ArOH, N=N and the N atom of the thiazole moiety [21–26].

3.2. *UV/Vis spectra*

The electronic spectra for 1 and its complexes recorded in EtOH are given in Table 3. The electronic spectral data of the ligand exhibit four bands in the UV region. The band appearing in 219 nm is attributed to and π–π^* transition of the ligands. The band around 262 nm can be assigned to intra ligand of π–π^* transition. The other two bands observed in the region of 445 and 412 nm (shoulder) are attributed to n–π^* electronic transitions [27–29].

3.2.1. *Electronic absorption spectra of the complexes*

Elemental analysis, IR and molar conductivity data are used to proof the stoichiometry and formulation of the complexes. An octahedral geometry is assumed for all complexes, based on the magnetic data and spectral (UV/Vis) studies.

Electronic absorption spectra of the complexes were recorded in EtOH solutions (Table 3). Mn(II), Co(II) and Ni(II) chelates (2–4) show four bands at 217–219, 241–261, 412–513 and 490–516 nm which are attributed to the π–π^* and n–π^* transitions, respectively, within the ligand. In the electronic spectra of some complexes, there is a band around 267–337 nm (Fig. 3). This band is assigned as a charge transfer (CT) transition [28,29]. Four bands observed in the UV spectrum of Mn(II) complex are due to intraligand transitions. The expected weak d–d transition in the visible region for this complex cannot be detected. The magnetic moment (6.91 B.M.) is an evidence for an octahedral structure [23]. For 3, the magnetic moment (0.92 B.M.) is within the range of low spin octahedral cobalt(II) complexes. The expected weak d–d transitions of an octahedral cobalt(II) complex cannot be observed. The reason for this may be due to the masking of this band by the strong charge transfer band of the ligand. The band at 337 nm refers to the charge transfer transition (L-MCT). The magnetic moment of 4 has been found to be 3.25 B.M., which is within the range of values corresponding to an octahedral geometry. The UV spectra of 4 are consistent with the formation of an octahedral geometry with the appearence of two bands at: $\nu_1 = (543$ nm; $\Sigma = 7.212 \times 10^3$ L mol^{-1} cm^{-1}): ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ν_2: (586 nm; $\Sigma = 3.871 \times 10^3$ L mol^{-1} cm^{-1}): ${}^3A_{2g} \rightarrow {}^3T_{1g}$(F). But ν_3: ${}^3A_{2g} \rightarrow {}^3T_{1g}$(P) was not observed. The band at 320 nm refers to the charge transfer band (L-MCT) [22,23]. Unfortunately, the some expected weak d–d transition in the visible region for some complexes cannot be detected even with concentrated solution. It may be lost in the low energy tail of the charge transfer transition [28,29]. Coordination compounds exhibit strong charge-transfer absorptions, typically in the ultraviolet and/or visible portion of the spectrum. These absorptions may be much more intense than d-d transitions. Many ligands give highly colored complexes that have a series of overlapping absorption bands in the ultraviolet part of the spectrum as well as the visible. In such cases the d–d transitions may be completely overwhelmed and essentially impossible to observe [30].

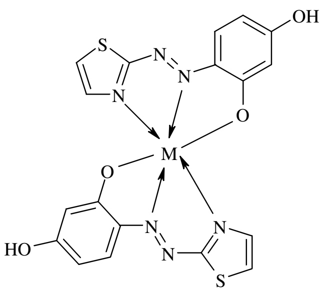

Fig. 2. Suggested structural formula of metal complexes.

3.3. *Cyclic voltammetry*

The electrochemical properties of the ligand 1 and its complexes were investigated using cyclic voltammetry. The cyclic voltammogram (CV) of 1 in DMF strongly shows one anodic wave ($E_{p,a}$) in the

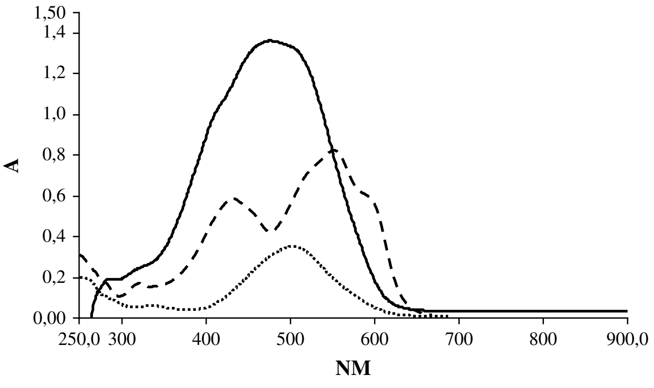

Fig. 3. UV–visible spectra of the complexes (2, —; 3, ·····; 4, --).

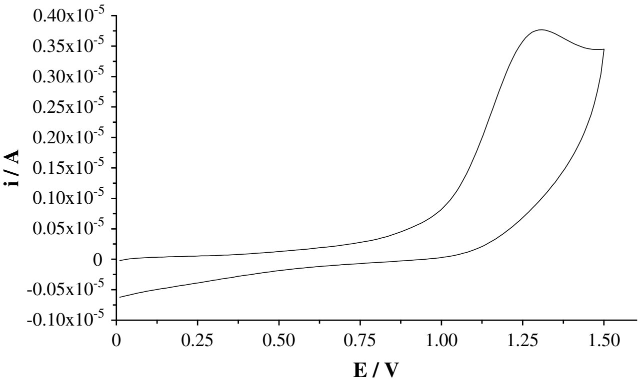

Fig. 4. Cyclic voltammogram of 1.0×10^{-3} M 4-(2-thiazolylazo)resorcinol in DMF solution (0.1 M TBAP) at scan rate of 50 mV s^{-1} versus Ag/Ag$^+$ electrode.

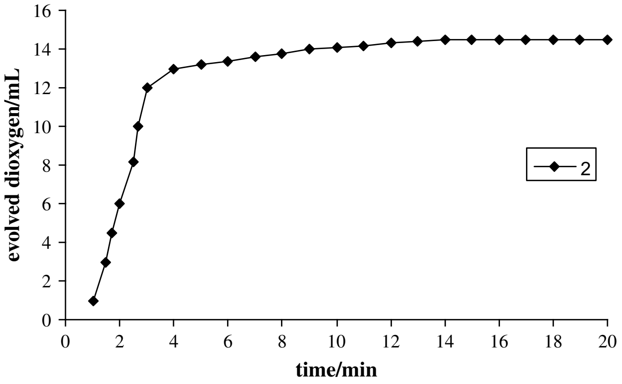

Fig. 6. Time courses of dioxygen evolution in the disproportionation of H_2O_2 by [2] complexes in DMF, [2] = 0.005 mmol, [H_2O_2] = 1.33 mmol, 298 K.

positive range (+1.30 V) which can be attributed to the redox behaviour (Fig. 4) of the groups present in 1. The anodic peak current increases with increasing concentration of the ligand 1. This anodic wave seen in the CVs for all metal complexes are presumed to be ligand based oxidation.

The voltammograms of the metal complexes 2 and 4 showed oxidation peaks, whereas the voltammogram of the 3 did not display any peak under experimental conditions used in this study. The representative voltammograms of 2 and 4 as compared with the CV of 1 are shown in Fig. 5a and b in a potential range between 0.0 and +1.0 V at 50 mV s^{-1}, respectively.

In Fig. 5a, in addition to the ligand peak, the obtained oxidation peak of 2 at the positive potential side indicated that the processes take place on the metal center of the complex ($E = +0.70$ V). This peak describes a one-electron oxidation of Mn(II)/Mn(III).

As can be shown in the Fig. 5b, in the CV measurement upon scanning anodically, 4 display an irreversible one-electron peak assigned to the oxidation of Ni(II)–Ni(III) at +0.40 V. The absence of the cathodic signal is indicative of a fast chemical reaction following the charge transfer step and instability of the electrochemically generated Ni(III) species [31,32].

3.4. Thermogravimetric (TGA) analysis

The thermal decomposition behavior of the complexes 2–4 was followed up to 1000 °C in dynamic nitrogen atmosphere. The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formula of the complexes [17,22].

In the case of the Mn(II) complex, a mass loss in the temperature range 35–200 °C corresponds to the loss of two coordinated water molecules (found: 16.00%, calcd.: 15.37%). The TGA profiles over the temperature range 30–250 °C indicate loss of water of moisture, hydration and coordination. The humidity content is lost in the range 30–50 °C. The complex 2 has first decomposition stage in the range 35–200 °C ($TGA_{max} = 115$ °C). This dehydration process probably is due to the loss of hydration water, which may be bound to hydroxyl group of the ligand by hydrogen bonds. The relatively high value of the temperature range for this complex indicates a strong water–ligand interaction. Above 200 °C, 2 decompose in a gradual manner rather than with the observed sharp decomposition, which may be due to fragmentation and thermal degradation of the organic moiety. The continuous loss of weight is observed up to 790 °C. The final solid product of thermal decomposition was identified as MnS (found: 83.14%, calcd. : 83.63%). Above 250 °C the Co(II) and Ni(II) complexes show loss of mass in a gradual manner. The continuous loss of weight is observed up to 740 and 775 °C, respectively; after that the weight of the product of the complexes remains constant. The final weight losses in these cases agree with the formation of the respective metal oxides (found: 84.30%, calcd.: 84.99% for 3 and found: 84.57%, calcd.: 85.02% for 4). The presence of coordinated water molecules in the metal complexes further corroborates the assumption made on the basis of the infrared spectral studies. The final decomposition products were identified by IR spectroscopy with corresponding spectra obtained under the same conditions as the pure oxides and sulfides.

3.5. Catalase-like activity

Many manganese(II) complexes have been found to catalyse the disproportionation of hydrogen peroxide $2H_2O_2 \rightarrow 2H_2O + O_2$ in the presence of added heterocyclic bases (pyridine, imidazole) [19,33–36]. Significantly, heterocyclic bases are known to be present in the vicinity of the active sites of manganoenzymes [19,34].

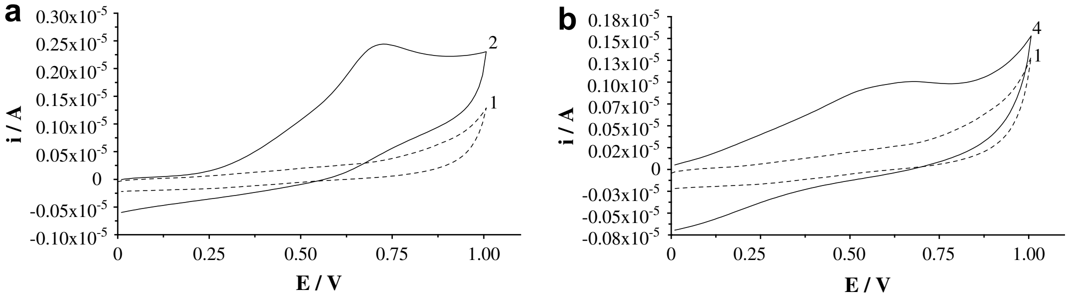

Fig. 5. Cyclic voltammograms 1.0×10^{-3} M of (a) [2] and (b) [4] in DMF (0.1 M TBAP) as compared with the CV of 1 at scan rate of 50 mV s^{-1} versus Ag/Ag$^+$ electrode.

The catalase-like activity of 2 to disproportionate H_2O_2 into H_2O and O_2 was investigated in DMF by volumetric measurements of evolved dioxygen. The time course of the O_2 evolution is shown in Fig. 6. In absence of the imidazole, 2 itself was catalytically almost inactive for this reaction, but the decomposition of H_2O_2 was enhanced in the presence of imidazole. It should be noted that the imidazole base by itself causes only a very slight disproportionation of peroxide, a sluggish reaction which is greatly enhanced when 2 is included in the reaction mixture. This study has demonstrated that 2 in the presence of imidazole is an efficient catalyst for the disproportionation of H_2O_2 in DMF.

4. Conclusions

We have described the synthesis, spectroscopic, magnetic characterization and thermal decomposition of Mn(II), Co(II) and Ni(II) chelates of 4-(2-thiazolylazo)resorcinol. The IR data support that the ligand is coordinated to the metal ions in a tridentate manner and complexation with 4-(2-thiazolylazo)resorcinol through the resorcinol OH, azo N and thiazole N. The molar conductance data reveal that the chelates are non-electrolytes. It was found that these complexes have a metal:ligand ratio of 1:2 and an octahedral structure. The results of elemental analyses and metal analyses with AAS of the complexes are in good agreement with the proposed formula. The thermal analyses data of these chelates shows that 2 have two mole hydrated water molecules. The final decomposition products are found to be the corresponding metal oxides or metal sulfides. The catalase-like activity study has demonstrated that 2 in the presence of imidazole is an efficient catalyst for the disproportionation of H_2O_2 in DMF.

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