

Polymer Complexes, XXIII: Synthesis and Physico-Chemical Studies on Transition Metal Complexes of Symmetric Novel Poly(N,N'-*o*-phenylenediamine)-bis(cinnamaldehyde)

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Summary. New complexes derived from polymeric N,N'-*o*-phenylenediamine bis(cinnamaldehyde) (*L*) with Cu^{II}, Co^{II}, Ni^{II}, Zn^{II}, UO₂^{II} and Pd^{II} were prepared and characterized by elemental analysis, magnetic susceptibilities and spectroscopic (IR, far-IR, ¹H-NMR, ¹³C-NMR and EPR) studies. A bidentate methine nitrogen atoms coordination of the ligand is assigned in the isolated complexes. The stereochemistries of the polymer complexes have been studied with using magnetic and spectroscopic measurements. Analytical data show 2:1 or 1:1 (ligand:metal) stoichiometry with water molecules coordinated to the Zn^{II} ion, as evidenced from IR and thermal analysis (DTA). The ligand was tested as a corrosion inhibitor for copper; the limiting concentration of the ligand to give maximum efficiency (60%) is 10⁻³ mol dm⁻³ at 25 °C.

Keywords. Poly(N,N'-*o*-phenylenediamine)bis(cinnamaldehyde); Polymer complexes; Thermal analysis; Electron paramagnetic resonance; Corrosion inhibition.

Polymere Komplexe, XXIII: Synthese und physikalisch-chemische Untersuchungen an Übergangsmetallkomplexen von symmetrischem Poly(N,N'-*o*-phenylendiamin)bis(zimtaldehyd)

Zusammenfassung. Es wurden neue Komplexe von polymerem Poly(N,N'-*o*-phenylendiamin)bis(zimtaldehyd) mit Cu(II), Co(II), Ni(II), Zn(II), UO₂(II) und Pd(II) hergestellt und mittels Elementaranalyse, magnetischen Suszeptibilitätsmessungen und spektroskopischen Methoden (IR, far-IR, ¹H-NMR, ¹³C-NMR und EPR) charakterisiert. Es wurde eine zweizählige Methin-Stickstoff-Koordination in den Komplexen festgestellt. Die Stereochemie der Polymerkomplexe wurde mittels magnetischer und spektroskopischer Messungen untersucht. Aus den analytischen Daten, mit zusätzlichen Argumenten aus IR und thermischer Analyse (DTA), ergab sich eine 2:1 oder 1:1 (Ligand:Metall)-Stöchiometrie mit an Zn(II) koordinierten Wassermolekülen. Der Ligand wurde als Korrosionsinhibitor für Kupfer getestet; die Grenzkonzentration des Liganden zur maximalen Effizienz (60%) ist 10⁻³ mol dm⁻³ bei 25 °C.

Introduction

In recent years, considerable interest has been focussed on Schiff base homopolymers as ligands. They show a marked action in biological systems [1] and are also of interest in industry [1, 2]. El-Sonbati [2–4] and Diab et al. [5–7] have studied the polymerization of monomers in presence of some transition metal salts. Transition metal complexes of bidentate Schiff base ligand were always of interest [3, 8, 9] since they exhibit a marked tendency to oligomerize, leading to novel structural types and they display a wide variety of magnetic properties. We have previously [10] investigated the complexes of poly(bis(2,6-diaminopyridine)sulphoxide), poly(cinnamaldehyde)anthranilic acid and discussed their different modes of coordination. To the best of our knowledge no work has been reported on Poly(N,N'-*o*-phenylenediamine)bis(cinnamaldehyde) as ligand. In this paper we report on the preparation and characterization of a number of complexes with this type of ligand.

Results and Discussion

Conductance, Magnetic, and Electronic Spectral Data

The molar conductivity of the complexes as $10^{-3} M$ solutions in nitrobenzene at room temperature showed that they are non-electrolytes. On repeating the measurements in dimethylformamide solvent under the same conditions, values are still less than these characteristic of 1:2 electrolytes in this solvent [8, 9]. This could be attributed to a partial dissociation and/or partial replacement of the anion by the solvent molecules. The room temperature magnetic moments of the cooper(II) complexes under investigation (Table 1) are characteristic of one unpaired electron. The μ_{eff} values of cobalt(II) and nickel(II) complexes are normal and indicate an octahedral stereochemistry around the metal ion [3, 11, 12], the moments for the cobalt and nickel complexes are in a range expected for six-coordinate metal ions, with much orbital contribution.

Cobalt(II) Complexes

The hexa-coordinated complexes of cobalt(II) ion (d^7) would be high-spin at the weak field limit and low-spin at the strong ligand field, while these states are expected to have comparable stable states somewhere between the two extremes within a comparatively small range of field strength [13].

The electronic spectra of the complexes are summarized in Table 1, together with the proposed assignments, ligand field parameters, and suggested geometries. The results obtained are in good agreement with other spectra and the literature.

The electronic spectra of complexes (1) and (2) (Table 1) shows three bands ($8050, 8300 \text{ cm}^{-1}$) (ν_1), ($17350, 16600 \text{ cm}^{-1}$) (ν_2) and ($19000, 18700 \text{ cm}^{-1}$) (ν_3). These bands are typical of octahedral cobalt complexes. The ligand field parameters Dq , B and β were calculated using the equations reported for d^7 systems [9], and are given in Table 1. The calculated values of ν_2 are also in proximity of the observed value of this band (Table 1). The Dq values show the trend Cl–Br in agreement with the respective positions of these anions in the spectrochemical series.

Table 1. Electronic spectral bands, assignments, ligand field parameters and proposed geometries for the polymer complexes (1)–(11) (for the structures see Table 2)

Species	Band position (cm^{-1})	Assignment	Geometry
(1) ^a	8300	${}^4T_{1g} \longrightarrow {}^4T_{2g}(F)(\nu_1)$	octahedral
	17350	${}^4T_{1g} \longrightarrow {}^4A_{2g}(F)(\nu_2)$	
	19000	${}^4T_{1g} \longrightarrow {}^4T_{1g}(P)(\nu_3)$	
	23450 ^b		
(2) ^c	8050	${}^4T_{1g} \longrightarrow {}^4T_{2g}(F)(\nu_1)$	octahedral
	16600	${}^4T_{1g} \longrightarrow {}^4A_{2g}(F)(\nu_2)$	
	18700	${}^4T_{1g} \longrightarrow {}^4T_{1g}(P)(\nu_3)$	
	23500 ^b		
(3) ^d	10206	${}^3A_{1g} \longrightarrow {}^3T_{2g}(F)$	octahedral
	15270	${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$	
	22222	${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$	
(4) ^e	10000	${}^3A_{1g} \longrightarrow {}^3T_{2g}(F)$	octahedral
	15625	${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$	
	24800	${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$	
(5) + (6)	13900–16900 ^f	${}^2E_g \longrightarrow {}^2T_{2g}$	octahedral
(7)–(9)	22200–24200 ^g	${}^1A_{1g} \longrightarrow {}^1B_{1g}$	square planar
	29000–31000 ^h		
(11)	21730 ^k	$E^{*1} \longrightarrow {}^3\pi_4$	octahedral

^a $10Dq = 9500 \text{ cm}^{-1}$, $B = 784 \text{ cm}^{-1}$, $\beta = 0.805$, $\nu_2/\nu_1 = 2.1$ and calculated $(\nu_2) = 16740 \text{ cm}^{-1}$

^b The presence of highest energy bands may therefore be taken due to tetragonal distortion along the X-axis

^c $10Dq = 9005 \text{ cm}^{-1}$, $B = 772 \text{ cm}^{-1}$, $\beta = 0.80$, $\nu_2/\nu_1 = 2.1$ and calculated $(\nu_2) = 17560 \text{ cm}^{-1}$

^d $10Dq = 10204 \text{ cm}^{-1}$, $B = 551.5 \text{ cm}^{-1}$, $\beta = 0.53$, $\nu_3/\nu_1 = 2.2$, $\nu_3/\nu_2 = 1.5$, $\nu_2/\nu_1 = 1.5$ and calculated $(\nu_2) = 18367 \text{ cm}^{-1}$

^e $10Dq = 9456 \text{ cm}^{-1}$, $B = 900.5 \text{ cm}^{-1}$, $\beta = 0.93$, $\nu_3/\nu_1 = 2.5$, $\nu_3/\nu_2 = 1.6$, $\nu_2/\nu_1 = 1.6$

^f The broadness of the band is due to the Jahn-Teller distortion operative for the d^9 configuration; a distorted octahedral geometry has been tentatively assigned

^g Δ_1 for compound (7) = 24300 cm^{-1} , Δ_1 for compound (8) = 25800 cm^{-1} and Δ_1 for compound (9) = 25800 cm^{-1}

^h Charge-transfer

^k Similar to the O–U–O symmetric stretching frequency for the first excited state

Nickel(II) Complexes

Nickel(II) has electronic configuration $3d^8$ and should show three bands in consistency with octahedral geometry. The interelectronic repulsion parameter B has been obtained [3]. The β values show a trend of covalent bonding and the calculated and observed data are in good agreement indicating a small orbital contribution from spin-orbit coupling between the first excited state ${}^3T_{2g}$ and the ground state.

Copper(II) Complexes

The observed room temperature magnetic moment of copper(II) complexes

(Table 1) are magnetically dilute which is well within the range of octahedral complexes [3]. Its electronic spectra show a broad band at 13900–16900 cm^{-1} suggesting a distorted octahedral geometry for the complexes [3] (Table 1).

Palladium(II) Complexes

The palladium(II) complexes are diamagnetic as expected for square-planar d^8 metal ion complexes. The electronic spectra of square-planar Pd(II) complexes are expected to show three d-d bands due to the transition [9], $^1A_{1g} \rightarrow ^1A_{2g} \rightarrow ^1B_{1g}$ and $\rightarrow ^1E_g$. The electronic spectra of the complexes under study display bands at 22200–24200 and 29200–31000 cm^{-1} . Assuming a value of $F_2 = 10F_4 = 600$ for Slater-Condon interelectronic repulsion parameters for Pd(II), it is possible to calculate the value of Δ_1 from the first spin allowed d-d transition [14].

IR Spectra

In the $\nu(\text{O-H})$ water region, the spectra of (10) show, respectively, two, one and two strong, sharp bands between 3450 and 3300 cm^{-1} attributed to the presence of coordinated water [8, 9]. Also, in addition to the bands of coordinated water, a broad continuous absorption at 3550 cm^{-1} is due to the presence of crystal water. In the spectrum of (4) and (6) a strong and broad absorption (ca. 3500–3150 cm^{-1}) indicates that lattice water is present [1–6]. In the case of (1)–(3), (5), and (7)–(9) no such band is observed indicating the absence of coordinated and/or lattice water.

The IR spectrum of the ligand was characterized by one or two medium to strong bands at 1635 cm^{-1} assigned to the C=N stretching vibration of the Schiff base linkage [9, 15]. Due to the phenyl group in the Schiff base linkage, there is an increase in the C=N frequency. This trend has been attributed to a conjugation effect [9, 15].

A significant change in the ligand band upon complexing is the increase in $\nu(\text{C=N})$. This shift to higher frequencies in the spectra of the complexes suggests coordination through both nitrogen of the methine groups [9, 16, 17]. Recent studies [17] have shown that the s character of the nitrogen lone pair in the C=N bond increases upon coordination; this change in hybridization produces the shorter C=N bond length and greater C=N stretching force constant, relative to the free neutral Schiff base. The variable magnitude of the shift reflects the variable Lewis acidity of the metal ions in the complexes under study.

The far-IR data of the complexes give an insight into the structure and bonding in the solid state. A medium to very strong metal- and X-sensitive band at a frequency lower than 316 cm^{-1} in the spectra of (3)–(6) arises from the $\nu(\text{M-X})$, vibration in a monomeric octahedral geometry [18]. The absence of $\nu(\text{M-X})$, a band in the appropriate region and the appearance of a new weak to medium band at 410–395 cm^{-1} , assigned to $\nu(\text{M-O}_{\text{water}})$ [2–9], in the spectra of (10) precludes an axial halide in coordinate and is consistent with these complexes containing apical aquo ligands. The $\nu(\text{Pd-Cl})$ mode is assigned to a strong band at 345 cm^{-1} for complex (7). The compound (9) involves Pd-Cl-Pd bridges as supported by the IR spectrum by showing two medium bands at 335 and 260 cm^{-1} assigned to terminal and bridging Pd-Cl, respectively.

The complex (11) exhibits three bands at 930, 840, and 265 cm^{-1} assigned to ν_3 , ν_1 , ν_4 , respectively, of the dioxouranium ion [16]. The force constant (F) for bonding sites of the U=O vibration was calculated by the method of McGlynn

et al. [19] as $7.13 \text{ mdyne } \text{\AA}^{-1}$. The absence of a band in the $1350\text{--}1400 \text{ cm}^{-1}$ region in the spectra of complex (**11**) confirm that ionic nitrates are absent [16]. The values of the frequencies assigned as vibrational modes of the nitrate group are strongly indicative of the presence of coordination monodentate nitrate [20]. The separation of the two highest frequency band is ca. 150 cm^{-1} ; for bidentate nitrates this separation is larger than 185 cm^{-1} . The $\nu_2(A_1)$, $\nu_3(A_1)$ and $\nu_4(B_2)$ modes of the C_{2v} nitrate groups [20, 21] were not assigned, because the regions at 1000 and $700\text{--}760 \text{ cm}^{-1}$ are obscured by strong bands of coordinated *L*. The $1700\text{--}1800 \text{ cm}^{-1}$ region is the key to differentiate with certainty between bidentate and unidentate coordination [16, 22]. The separation of the combination bands appearing around 1753 and 1730 cm^{-1} is about 20 cm^{-1} and this fact indicates a monodentate nitrate group [16]. The region of the free ligand spectrum between 355 and 220 cm^{-1} contains only three very weak bands. This would indicate that some of the other bands observed in this region should be assignable to $\nu(M\text{--}N)$ [16, 23] and $\nu(M\text{--}X)$ [16, 20] vibration. A comparison, however, of the far-IR spectra between *L* and its metal complexes fails to give clear-cut assignments.

Thermal Analysis

A different pattern is observed in the DTA curve of compound (10). The endothermic peaks at 109 and 166°C are due to the removal of uncoordinated water and nonionizable chloride ions, while the exothermic peaks at 252 and 364°C are due to the removal of coordinated water. An exothermic peak corresponding to formation of ZnO appears at 590°C .

Electron Paramagnetic Resonance

For further confirmation of our results the polycrystalline EPR spectra of the paramagnetic complexes (**5**)/(**6**) have been recorded. The EPR spectra show parallel, perpendicular, and average *g*-values of $2.123/2.252$, $2.067/2.054$, and $2.086/2.122$, respectively [1]. These values indicate the trend $g_{11} > g_1 > \text{free electron-spin (2.0023)}$ showing that the unpaired electron is in the $d_{x^2-y^2}$ orbital of the Cu(II) ions. The g_{11} and g_1 values depart considerably from the free-spin value indicating a strong axial distortion of the molecule [24]. These values suggest a tetragonally distorted octahedral structure with D_{4h} symmetry.

Proton Magnetic Resonance Spectra

In the $^1\text{H-NMR}$ spectra of the diamagnetic polymer complexes (*DMSO-d*₆) the signals of the C_6H_5 and $=\text{CH}$ hydrogen atoms shift slightly (ca. 0.3 and 0.1 ppm , respectively) downfield compared with those of free ligand, ($7.1\text{--}8.9$ and 9.4 ppm), suggesting that the donor-atom is far removed from the region of these hydrogens. The integration of these groups of peaks is again $14:2$.

$^{13}\text{C-NMR}$ Spectra

The spectra of the ligand and its complex (**8**) were recorded. The chemical shift of the methine carbon of the $-\text{CH}=\text{N}-$ group observed at 143.5 ppm for the ligand is shifted to 136.2 ppm for the complex, confirming coordination of the methine nitrogen in compound (**8**).

Table 2. Elemental analysis and magnetic data of the polymer complexes

No.	Species ^a	Found (Calcd.) %			Cl/Br	Metal	$\mu_{\text{eff.}}$ ^b B.M.
		C	H	N			
(1)	[CoL ₂ Cl ₂] ^c 2X	68.6 (68.7)	5.2 (5.3)	6.8 (6.7)	8.6 (8.5)	7.1 (7.0)	4.31
(2)	[CoL ₂ Br ₂] ^c X	63.4 (63.5)	4.4 (4.3)	6.2 (6.3)	17.6 (17.4)	6.5 (6.3)	4.05
(3)	[NiL ₂ Cl ₂]	71.8 (71.8)	5.1 (5.0)	6.9 (7.0)	9.1 (8.9)	7.1 (7.3)	3.37
(4)	[NiL ₂ Br ₂] ^c X	63.4 (63.4)	4.5 (4.4)	6.0 (6.2)	17.5 (17.6)	6.7 (6.5)	3.21
(5)	[CuL ₂ Cl ₂]	71.4 (71.4)	4.9 (5.0)	7.1 (6.9)	9.0 (8.8)	8.1 (7.9)	1.93
(6)	[CuL ₂ Br ₂] ^c X	63.0 (63.1)	4.5 (4.4)	6.0 (6.1)	17.7 (17.5)	7.2 (7.0)	1.89
(7)	[PdLCl ₂]	56.0 (56.1)	4.0 (3.9)	5.7 (5.5)	14.0 (13.8)	21.0 (20.7)	dia.
(8)	[PdL ₂]Cl ₂	67.9 (67.8)	4.8 (4.7)	6.8 (6.6)	8.6 (8.4)	12.8 (12.5)	dia.
(9)	[PdL][PdCl ₄]	42.0 (41.7)	3.0 (2.9)	4.0 (4.1)	20.8 (20.6)	31.0 (30.8)	dia.
(10)	[ZnL(X) ₂] ^d Cl ₂	56.9 (57.1)	4.6 (4.6)	5.7 (5.9)	14.2 (14.4)	13.2 (13.4)	dia.
(11)	[UO ₂ L ₂ (NO ₃) ₂]	54.3 (54.0)	3.8 (3.9)	5.5 (5.3)	–	22.8 (22.3)	dia.

^a Air-stable, non-hygroscopic, high melting or decomposition temperature, coloured; insoluble in water, but soluble in coordinating solvents such as *DMF* and *DMSO*

^b Per metal ion and measured at room temperature

^{c,d} The stoichiometry of complexes obtained after drying at 110 °C shows the presence of water molecules. On heating the complex (10) at 160 °C, the mass loss corresponded to the loss of water molecules present. The anhydrous residual mass in each case, which was subjected to elemental analysis, corresponded to the stoichiometry ML_2X_2 ($X = \text{Cl}$ or Br), which confirmed that the water molecules were not present in coordinated form but as water of crystallisation; the presence of coordinated water was confirmed by TGA data where the loss in weight corresponding to two water molecule for compound (10); $X = \text{H}_2\text{O}$

Taking into consideration all the above facts, it is proposed that the complexes of the ligand (1)–(6) have an octahedral structure in which the metal is six-coordinated. Also, compounds (7)–(11) have a square-planar structure and are four coordinated.

Corrosion Inhibition

The behaviour of *L* as a corrosion inhibitor was studied for pitting corrosion of copper, caused by NaCl as a pitting corrosion agent in 75% dioxane and 25% aqueous NaCl (0.4M) solution, by the weight loss method. The metal was in the form of a sheet with 0.65 mm thickness, 8.2 cm² area. The sheet was immersed in an

Table 3. Study of corrosion and corrosion inhibition of copper in 75% dioxane and 25% aqueous NaCl (0.4 mol l^{-1}) solution at different homopolymer (*L*) concentrations

Time (days)	0.00 mol l^{-1} Weight loss g/dm ²	$1 \times 10^{-4} \text{ mol l}^{-1}$ Weight loss g/dm ²	$5 \times 10^{-4} \text{ mol l}^{-1}$ Weight loss g/dm ²	$1 \times 10^{-3} \text{ mol l}^{-1}$ Weight loss g/dm ²
3	0.070	0.050	0.030	0.020
4	0.090	0.075	0.050	0.030
5	0.120	0.120	0.065	0.040
6	0.155	0.135	0.075	0.060
7	0.175	0.166	0.110	0.075
8	0.225	0.180(20) ^a	0.135(40) ^a	0.090(60) ^a

^a Efficiency of different concentrations of homopolymer (*L*) after 8 days

open tube containing 40 ml of the compound solution. The weight loss of the copper sheet was determined for one day at room temperature ($25 \pm 0.1 \text{ }^\circ\text{C}$). Inhibition efficiency was calculated as follows: % Inhibition = $100(W_1 - W_2)/W_1$, where W_1 and W_2 are the weight loss in uninhibited and inhibited solutions. The experimental data (Table 3) reveal that the efficiency of ligand increases as its concentrations increases, indicating the applicability of this compound as a corrosion inhibitor. This inhibiting action is attributed to the formation of a sparingly soluble black copper complex in the medium, which forms a thin film on the metal surface.

Concluding Remarks

From the study presented it is concluded that in the complexes (1)–(11) *L* behaves as bidentate chelate ligand bonding through both the methine nitrogen atoms. The strong chelating ability of *L*, which contains two $-\text{N}=\text{C}-$ groupings, is considered to result in part from $d_\pi-p_\pi$ bonding from the metal to the ligand; this π -bonding imparts some aromatic character to the chelate ring [24].

The fact that for a given equatorial ligand μ_{eff} is in the relation $\text{Cl} > \text{Br}$ cannot be so easily explained. The smaller μ_{eff} value of the bromo complexes may be the result of two opposite effects. (1) The greater polarizability of Br^- versus Cl^- . Bromide is a weaker field ligand than chloride because the electron cloud of a bromide ion is more readily deformed than that of a chloride ion [25]. The weaker ligand field of Br^- implies that it is a better π -donor than Cl^- [25]; the $4p\pi$ -orbitals of Br^- are larger than the $3p$ -orbitals of Cl^- . The better π -donor characteristics of bromide relative to chloride, i.e. stronger interaction with the t_{2g} orbitals, greatly contributes to the increased destabilization of the low-spin state for the dibromo-complexes [26]. (2) The steric effect associated with the larger bromide ion hinders a close approach to the equatorial plane. The longer axial bond lengths in the case of the bromide ion favour the low-spin form. The latter effect prevails over the former.

It is evident from these data that for a given metal salt the $\nu(M-\text{N})$ mode shifts to higher frequencies as the organic ligand is changed. This suggests that the strength of the metal-nitrogen equatorial bonds increases.

Finally, we are currently investigating the coordination chemistry of other N_2 Schiff base ligands, which have a phenyl bridge, the equatorial ligand being quite planar and consequently too rigid to enable other ligands to approach closely the apical sites and the resulting axial elongation being expected to favour low-spin forms.

Experimental Part

All chemicals used in this work were of reagent grade and were used without further purification. Poly(N,N' -*o*-phenylenediamine)bis(cinnamaldehyde) homopolymer (*L*) was prepared according to El-Sonbati et al. [1]. In a typical preparation, a solution of homopolymer (0.01 mol) in *DMF* (20 cm³), the metal salts (0.01 mol) in *DMF* (25 cm³), and 0.1 w/v *AIBN* (*AIBN* = 2,2'-azobisisobutyronitrile) as initiator were used. The resulting mixture was heated under reflux for 6 h. The hot solution were precipitated by adding to a large excess of distilled water containing dilute hydrochloric acid to remove the metal salts incorporated into the polymer complexes. The polymer complexes were filtered, washed with water, and dried in a vacuum oven at 40 °C for several days to yield 86% of yellow crystals. The ¹H-NMR (*DMSO*) spectrum of the homopolymer shows complex peaks between 7.1–8.9 ppm downfield from *TMS* due to C₆H₅-protons, a broad peak at 9.4–9.23 ppm and a doublet at 1.76 ppm; the integration of these signals were in the ratio 14:2. The spectrum suggests that the solid is poly(N,N' -*o*-phenylenediamine)bis(cinnamaldehyde) (*L*), the doublet being due to the CH-protons. The IR (Nujol) spectrum shows a very strong and broad band at 1635 cm⁻¹ assigned to $\nu(C=N)$. Anal. found C 85.77, H 6.1, N 8.35%; C₂₄H₂₀N₂ requires C 85.71, H 5.95, N 8.33%.

C and H microanalyses were carried out at Cairo University Analytical Centre, Egypt. Metal contents in the complexes were estimated by standard methods [1–10]. ¹H-NMR spectra were obtained with a Jeol FX 90 Fourier Transform spectrometer with *DMSO-d*₆ as solvent and *TMS* as internal standard. IR spectra were recorded on a Perkin Elmer model 1340 spectrophotometer. UV-VIS spectra were recorded (Nujol mulls) on a Pye Unicam 8800 spectrophotometer. Magnetic measurements were carried out at room temperature by Guoy's method using Hg(Co(SCN)₄) for calibration and were corrected for diamagnetism by applying Pascal's constants. EPR measurements of powdered samples were recorded at room temperature using X-band microwave frequency, as the first derivative, on a Jeol Jes FE 2XG Spectrometer utilizing 100 KHz magnetic field modulation, using diphenyl picryl hydrazyl (*DPPH*) as reference material. Thermogravimetric analysis were made with a Du Pont 950 thermobalance. The sample (10 mg) was heated at 10° min⁻¹ in a dynamic N₂ atmosphere (70 cm³ min⁻¹); the sample holder was boat-shaped (10 mm × 5 mm × 2.5 mm) and the temperature measuring thermocouple was placed within 1 mm of holder. The weight loss for the corrosion inhibition was carried out according to the standard ASTM method [1]. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a KOH–H₂O₂ mixture. The halide content was then determined by titration with a standard Hg(NO₃)₂ solution using diphenyl carbazone indicator [8].

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