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Complexation of polyhydroxy-nitroso dyes with Co^{2+} , Ni^{2+} , and Cr^{3+} : characteristics, chemisorption behavior, and application in electroplating wastewater treatment

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Abstract

Polyhydroxy–nitroso dyes are multifunctional compounds with strong chemisorption capabilities for heavy metal ions, making them promising candidates for wastewater treatment. In this study, the complexation behavior of two phloroglucinol-based polyhydroxy–nitroso dyes with Co^{2+} , Ni^{2+} , and Cr^{3+} was systematically investigated using UV–Vis, FT-IR, EDX, and EPR spectroscopy. The equilibria of the complexation reactions were examined by spectrophotometric titration, and the stoichiometry and stability constants of the resulting complexes in solution were subsequently determined. The chemisorption performance and potential application of these dyes for treating electroplating wastewater were further evaluated under various pH conditions. The results demonstrated that both polyhydroxy–nitroso dyes form stable complexes with metal cations, primarily of ML and ML_2 types. The synthesized compounds efficiently precipitated selected metal ions from acidic solutions, indicating their suitability as metal-adsorbent materials. When applied to electroplating wastewater, the dyes reduced the concentrations of Co^{2+} , Ni^{2+} , and Cr^{3+} by more than 85%.

Keywords: polyhydroxy-nitroso dyes, electroplating wastewater, complexation, chemisorption behavior

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1. Introduction

Phloroglucinol and its derivatives, characterized by the presence of three hydroxyl groups (-OH), readily undergo electrophilic substitution at vacant positions of the benzene ring. The introduction of additional electron-donating functional groups, such as azo or nitroso moieties, leads to the formation of multifunctional dyes that can coordinate metal ions to yield stable chelate complexes [1], [2]. Nitroso dyes, a class of organic compounds containing aromatic rings with a nitroso group (-N=O) directly bonded to a carbon or nitrogen atom, exhibit particularly interesting properties. When nitroso and hydroxyl groups occupy ortho positions, these compounds often undergo isomerization, existing as an equilibrium mixture of nitrosohydroxy and quinonoxime isomers [3]. This tautomerism enhances their ability to form intensely colored complexes with metal ions, making them valuable as biological dyes, particularly in staining animal cells [4]. Furthermore, the presence of nitroso and hydroxyl functionalities imparts additional bioactive properties, including antibacterial, antifungal, and metal-precipitating activities. Metal complexes of hydroxy-nitroso dyes represent a promising class of materials for technological applications, particularly in optical devices, owing to their high thermal stability and strong near-infrared absorption [4], [5], [6].

Electroplating wastewater is a major source of heavy metal contamination, typically containing ions such as Cr^{6+} , Ni^{2+} , Cu^{2+} , Co^{2+} , and Zn^{2+} [7]. Conventional treatment methods—including chemical precipitation, ion exchange, and electrochemical processes—are widely employed for the removal of heavy metals from inorganic effluents [8]. However, these approaches suffer from notable limitations, including incomplete removal, high energy consumption, and the generation of toxic sludge [9], [10]. Recent years have seen a global surge in the development of organic chelating agents for environmental remediation. Internationally, research has focused heavily on the synthesis of multifunctional ligands, such as nitroso-R salts and azo-derivatives, for the preconcentration and removal of transition metals like Fe^{3+} , Co^{2+} , and Cu^{2+} [11]. These studies emphasize the high thermal stability and strong coordination affinity of the oxime/nitroso donor sets. Specifically, the shift toward using these dyes as "green" alternatives to traditional chemical precipitation is a growing international trend, as they offer higher selectivity and lower sludge production [12]. In Vietnam, the remediation of industrial effluents, particularly from the rapidly expanding electroplating and electronics sectors, remains a critical environmental challenge. Domestic research has increasingly prioritized the exploration of modified organic frameworks capable of addressing heavy metal contamination under the highly acidic conditions typical of local industrial discharge [13]. Recently, we reported that two novel polyhydroxy-nitroso dyes are capable of forming insoluble complexes with heavy metal ions, even under acidic conditions [1], [2], [14]. These ligands therefore represent a promising, environmentally friendly alternative for chemical precipitation, offering effective removal of metal ions in acidic as well as neutral media. In the present study, the complexation behavior of two polyhydroxy-nitroso dyes with Co^{2+} , Ni^{2+} , and Cr^{3+} ions was systematically investigated.

2. Materials and Methods

2.1. Synthesis and characterization of polyhydroxy-nitroso dyes

The polyhydroxyl-nitroso dyes 2,4,6-trinitrosobenzene-1,3,5-triol (H_3L^1) and 1-(2,4,6-trihydroxy-3,5-dinitrosophenyl)ethanone (H_3L^2) were synthesized and purified following previously reported procedures (Fig. 1) [1]. Briefly, 0.01 mol of phloroglucinol and 2,4,6-trihydroxyacetophenone were separately dissolved in a mixture of 90 mL of 50% aqueous ethanol and 10 mL of 10 M HCl. To each resulting solution, 10 mL of a 4 M aqueous sodium nitrite solution was added dropwise under continuous

stirring, while the reaction temperature was strictly maintained at 0°C. After 90 min, the precipitated products were filtered, thoroughly washed with water and ethanol, and dried under reduced pressure. The purity of the nitroso dyes was confirmed by thin-layer chromatography (TLC) using benzene : methanol : acetic acid (3 : 1 : 1, v/v/v) as the eluent. For H₃L¹, ¹³C-NMR (151 MHz, DMSO-d₆, ppm): 164.04 and 127.47; IR spectrum: O–H (3500–3200 cm⁻¹), C=N (1670–1640 cm⁻¹), N=O (~1550 cm⁻¹), C–O (1200–1000 cm⁻¹); MS: m/z=213.1. For H₃L², ¹H-NMR (600 MHz, DMSO-d₆, ppm): 12.19 (2H); 10.33 (1H); 2.46(3H); ¹³C-NMR (151 MHz, DMSO-d₆, ppm): 202.58; 165.28; 164.83; 135.22; 104.54; 32.89; IR spectrum: O–H (3180.6 cm⁻¹); C=O (1693 cm⁻¹) N=O (~1553 cm⁻¹), C–O (1250–1100 cm⁻¹); MS: m/z=225.7.

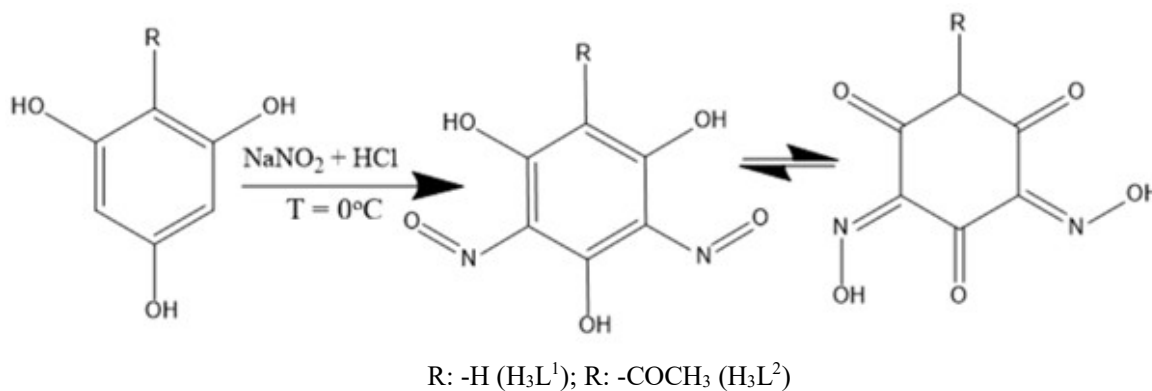


Figure 1. Synthesis of two polyhydroxyl-nitroso dyes based on phloroglucinol.

2.2. Complexation of polyhydroxyl-nitroso dyes with metal cations

Find grammar mistakes and any mistakes when writing in this 2.3. Chemisorption Behavior

Metal ion solutions (100 ppm) were prepared at pH values of 2, 3, 4, 5, 6, and 7. A 20 % stoichiometric excess of the ligands was added. After 60 min of stirring, the precipitates were filtered off and the remaining concentrations of the metal cations were determined by atomic absorption spectroscopy (AAS).

2.3. Electroplating wastewater treatment

Electroplating wastewater was collected in April 2025 from Hiep Phuoc Thanh Production Co., Ltd. (pH 2.3). The sample was first filtered to remove insoluble materials, after which an appropriate amount of solid Na₂SO₃ was added to completely reduce Cr(VI) to Cr(III). An excess of the ligands was then added to the treated solutions. After 60 min of stirring, the precipitates were filtered off, and the residual concentrations of the metal cations were determined by atomic absorption spectroscopy (AAS).

2.4. Analytical method

EPR spectra were recorded at Q-band (300 K) using a Bruker ELEXSYS E580 spectrometer and at X-band over the temperature range of 4–300 K using a Bruker EMX/plus spectrometer. Infrared (IR) spectra (400–4000 cm⁻¹) were obtained in KBr pellets with a Shimadzu IR Prestige FT-IR spectrometer at a resolution of 4 cm⁻¹. UV–Vis spectra (200–700 nm) were measured in ethanol using a Varian Cary-50 spectrophotometer. Metal contents were quantified by atomic absorption spectroscopy (AAS) on a PerkinElmer AAnalyst 400 instrument employing flame atomization. Energy-dispersive X-ray (EDX) analysis was performed using a Hitachi SU-8010 scanning electron microscope equipped with an EDX detector, operating at an accelerating voltage of 15–20 kV and a current of 10–15 μA.

3. Results and Discussion

3.1. Complexation of polyhydroxy-nitroso dye with metal cation

The complexation behavior of the two synthesized polyhydroxy-nitroso dyes in aqueous ethanol was investigated by spectrophotometric titration (at pH = 4.5), and the corresponding results are presented in Figure 2.

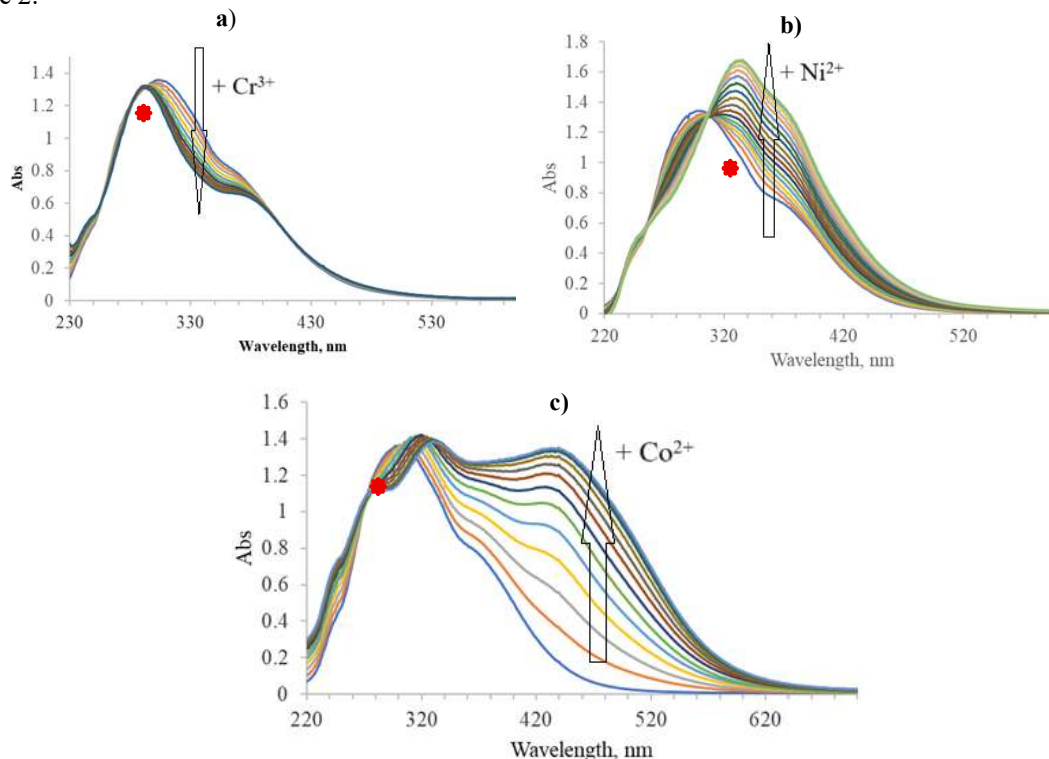


Figure 2. Spectrophotometric titration of H₃L¹ (1.0 × 10⁻⁵ M) in aqueous ethanol upon the stepwise addition 5 – 100 μL of 1.0 × 10⁻³ M the solution of salts: a) CrCl₃, b) NiCl₂, and c) CoCl₂. Arrows indicate the spectral response to increasing volumes of the respective metal salt solutions. Arrows indicate the spectral response to increasing metal ion concentrations, while the red markers designate the isosbestic points.

As shown in Figures 2 and 3, the initial UV–Vis spectrum of the ligand (H₂L¹)⁻ (monoanionic form) in aqueous solution exhibits a strong absorption band at 292 nm in the UV region (250–400 nm), which can be attributed to $\pi \rightarrow \pi^*$ electronic transitions [16]. These high-energy transitions arise from the excitation of electrons in π -bonding orbitals of the aromatic ring system and conjugated substituents (e.g., C=O, N=O) to anti-bonding π^* orbitals [1]. In addition, a broader and more intense absorption band is observed in the 335–400 nm region, corresponding to $n \rightarrow \pi^*$ transitions, which involve the excitation of non-bonding electrons from heteroatoms such as oxygen and nitrogen into anti-bonding π^* orbitals [17]. A similar spectral profile was obtained for the ligand (H₂L²)⁻. Upon titration of the ligands with metal ions, significant changes in the position and intensity of the absorption bands were observed, confirming complex formation via coordination bonds. The establishment of these bonds alters the electron density distribution within the dye molecules, leading to the observed spectral shifts and intensity variations [18].

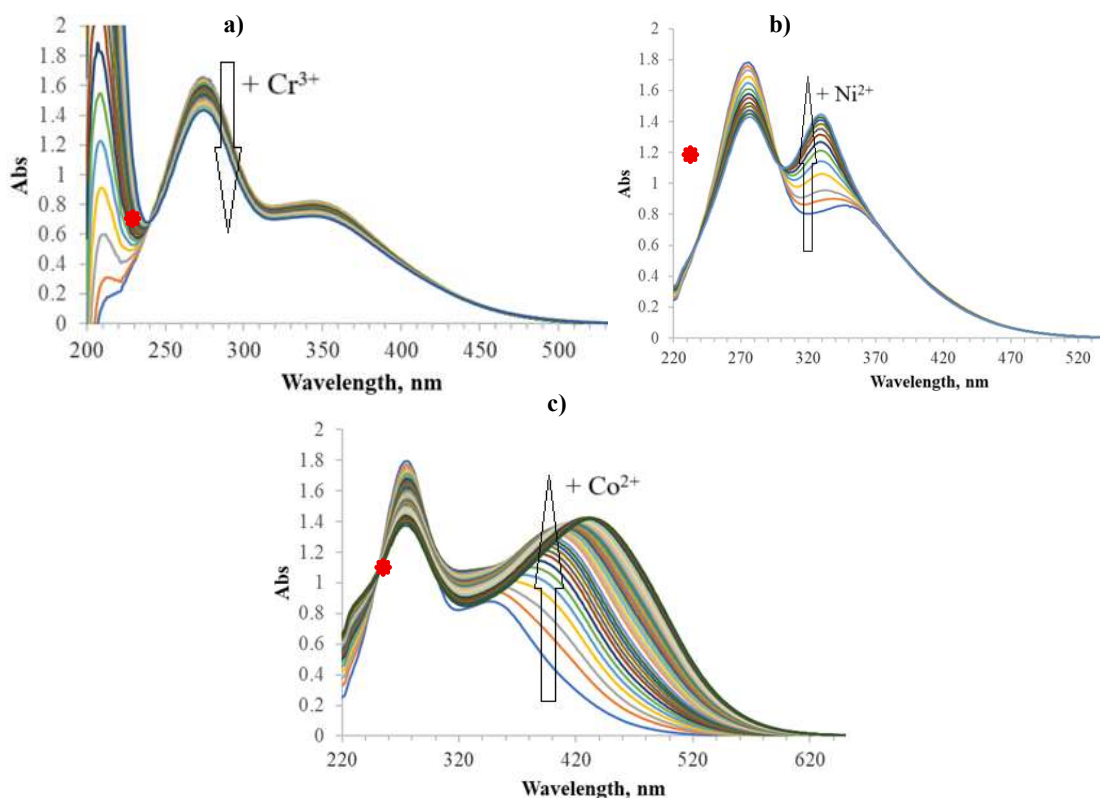


Figure 3. Spectrophotometric titration of H_3L^2 (1.0×10^{-5} M) in aqueous ethanol upon the stepwise addition 5 – 100 μ L of 1.0×10^{-3} M the solution of salts: a) $CrCl_3$, b) $NiCl_2$, and c) $CoCl_2$. Arrows indicate the spectral response to increasing metal ion concentrations, while the red markers designate the isosbestic points.

For the Cr^{3+} complexes, a hypsochromic shift accompanied by a decrease in absorption intensity was observed for both ligands in the 240–270 nm region. Distinct isosbestic points appeared near 255 nm (H_3L^1) and 240 nm (H_3L^2), confirming the establishment of a complexation equilibrium in solution [19]. In contrast, for the Ni^{2+} and Co^{2+} complexes, bathochromic shifts were detected for both ligands. The presence of isosbestic points during titration further indicated equilibrium between free ligands and their corresponding metal complexes. These spectral changes arise from the coordination of Ni^{2+} and Co^{2+} ions to the ligands via oxygen or nitrogen donor atoms of the hydroxyl or oxime groups (present in the keto–oxime tautomeric form). Such binding extends the π -conjugated system and enhances d–d transitions within the ligand field, thereby decreasing the orbital energy gap and resulting in red-shifted absorptions with increased intensity [20]. Notably, these observations are consistent with previously reported spectral features of hydroxy-nitroso and azo-type complexes with transition metals, where ligand-to-metal charge transfer and extended conjugation similarly contribute to bathochromic shifts and intensity enhancement, thereby supporting the proposed complexation mechanism [2].

The compositions of the metal–ligand complexes formed in aqueous ethanol, along with their corresponding formation (stability) constants determined from spectrophotometric titration, are summarized in Table 1.

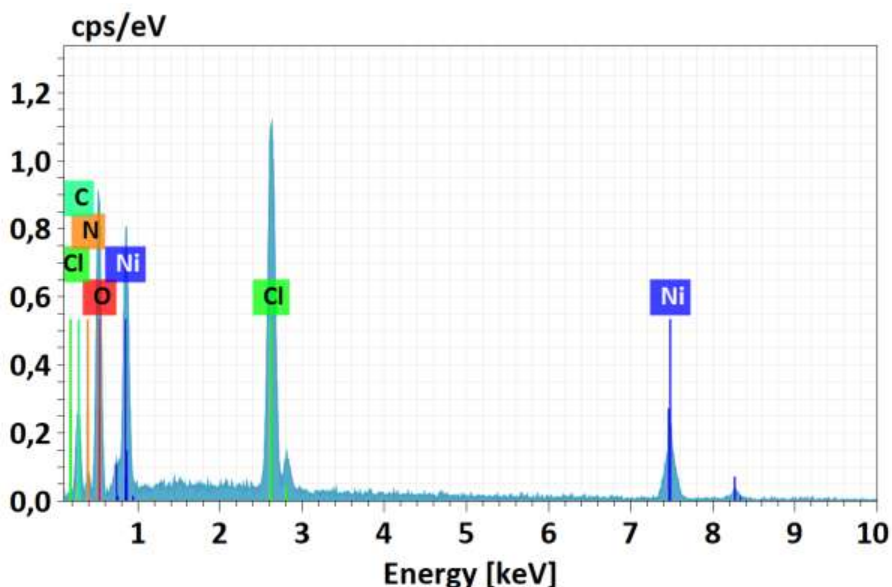
Table 1. Composition of some metal complexes in ethanol solutions and their formation constants according to spectrophotometric titration.

Ligands	M ⁿ⁺	λ_{\max} , nm	$\Delta\lambda$, nm*	log ϵ	log β	n(L:M)**
H ₃ L ¹	-	292	-	-	-	-
	Cr ³⁺	284	-8	4.12	9.74	2
	Ni ²⁺	333	41	3.87	7.62	1
	Co ²⁺	344	52	4.44	7.00	1
H ₃ L ²	-	276	-	-	-	-
	Cr ³⁺	274	-2	4.09	11.85	2
	Ni ²⁺	325	49	3.59	10.26	1
	Co ²⁺	429	153	3.88	8.25	1

* $\Delta\lambda = \lambda_{\max}(\text{complex}) - \lambda_{\max}(\text{ligand})$; ** determine at $\lambda_{\max}(\text{complex})$

The calculated complex formation constants indicate that the synthesized complexes exhibit relatively high stability in solution (Table 1). Chromium(III) was found to form complexes of the ML₂ type, whereas nickel(II) and cobalt(II) formed ML-type complexes.

The structural characteristics of the solid-state complexes were further investigated by IR, EDX, and EPR spectroscopy. A representative EDX spectrum of the Ni²⁺-H₃L² complex is shown in Figure 4.

**Figure 4.** EDX spectrum of Ni(H₂L₂)Cl.3H₂O complex.

As shown in Figure 4, the EDX spectrum of the Ni-ligand complex confirms the presence of the principal constituent elements C, N, and O, originating from the organic framework. Strong Ni signals (at ~0.85 and 7.5–8.3 keV) provide clear evidence of nickel incorporation into the complex. In addition, distinct Cl peaks were detected, indicating the retention of chloride, most likely as a coordinated ligand. The absence of extraneous elements suggests that the product possesses high purity. These findings confirm the successful formation of the nickel complex with the designed ligand framework, and the elemental composition is consistent with the proposed coordination environment. Based on the EDX analysis, the molecular formulas of six complexes were predicted and are summarized in Table 2.

Table 2. Characteristic data of the synthesized metal–ligand complexes.

No	Compound	Molecular formula	Elemental analysis, % (calc/found)					IR (KBr), cm ⁻¹
			C	N	O	Cl	M	
1	Ni(H ₂ L ¹)Cl.3H ₂ O	C ₆ H ₈ ClN ₃ NiO ₉	20.46/ 21.10	11.93/ 11.12	40.88/ 39.62	10.07/ 10.98	16.66/ 17.18	3273 (O-H); 1634 (C=N); 1424 (N-O); 515/435 (Ni-O/Ni-N)
2	Co(H ₂ L ¹)Cl.4H ₂ O	C ₆ H ₁₀ ClN ₃ CoO ₁₀	19.56/ 18.20	11.40/ 12.34	43.42/ 44.90	9.62/ 10.35	15.99/ 14.21	3280 (O-H); 1634 (C=O); 1515 (N-O); 528 (br) (Co-O/Co-N)
3	Cr(H ₂ L ¹) ₂ Cl.2H ₂ O	C ₁₂ H ₈ ClN ₆ CrO ₁₄	26.71/ 27.67	15.57/ 15.12	41.51/ 39.57	6.57/ 7.31	9.64/ 10.33	3143 (O-H); 1679/1626 (C=O); 1419 (N-O); 529 (br) (Cr-O/Cr-N)
4	Ni(H ₂ L ²)Cl.3H ₂ O	C ₈ H ₁₁ ClN ₂ NiO ₉	26.53/ 26.12	7.73/ 8.44	39.75/ 39.81	9.79/ 10.34	16.20/ 15.29	3300 (O-H); 2889 (C-H); 1645 (C=O); 1430 (N-O); 515/433 (Ni-O/Ni-N)
5	Co(H ₂ L ²)Cl.3H ₂ O	C ₈ H ₁₁ ClN ₂ CoO ₉	26.51/ 25.41	7.73/ 8.44	39.72/ 40.42	9.78/ 8.34	16.26/ 17.39	3392 (O-H); 2891 (C-H); 1616 (C=O); 1492 (N-O); 545/483 (Co-O/Co-N)
6	Cr(H ₂ L ²) ₂ Cl.2H ₂ O	C ₁₆ H ₁₄ Cl N ₄ CrO ₁₄	34.34/ 33.12	10.01/ 11.67	40.02/ 38.05	6.33/ 6.22	9.26/ 10.94	3373 (O-H); 2989 (C-H); 1691/1652 (C=O); 1437 (N-O); 521/453 (Cr-O/Cr-N)

The coordination of the carbonyl and nitroso groups of H3L1 and H3L2 with metal cations was confirmed by the low-frequency shifts of the C=O and N=O stretching vibrations in the IR spectra of the complexes compared with those of the free ligands. The displacement of the $\nu_{C=O}$ band indicates an increased degree of covalency in the M–O bond. Furthermore, the coordination of both C=O and N=O groups was supported by the appearance of new absorption bands in the ranges 430–470 cm⁻¹ (ν_{M-N}) and 496–517 cm⁻¹ (ν_{M-O}), which are characteristic of metal–ligand bond formation [21].

The EPR measurements were performed on the polycrystalline Co, Ni, and Cr complex samples to determine the multiplicity of the central ion and the type of their coordination polyhedra. No signals were observed in the EPR spectra of Ni(H₂L₂)Cl.3H₂O. This is apparently due to the low-spin state ($S = 0$) of Ni(II) ions [2]. The powdered Co(H₂L₂)Cl.3H₂O complex exhibits a single, intense derivative signal centered at $H \approx (3.1-3.3) \times 10^3$ Oe, corresponding to $g_{eff} \approx 2.1$ ($g = h\nu/\mu_{BH}$). The line is fairly broad with only poorly resolved ⁵⁹Co ($I = 7/2$) hyperfine structure, consistent with fast spin–lattice relaxation and significant spin–orbit coupling typical for high-spin Co(II) ($S = 3/2$) in an approximately axial field. The absence of signals at $g \gg 4$ and the dominance of the $g \approx 2$ region indicate an octahedral-like environment [22], [23]. Overall, the spectrum supports a high-spin Co(II) center in a near-octahedral coordination sphere provided by the oxime/oxo donor set of the ligand.

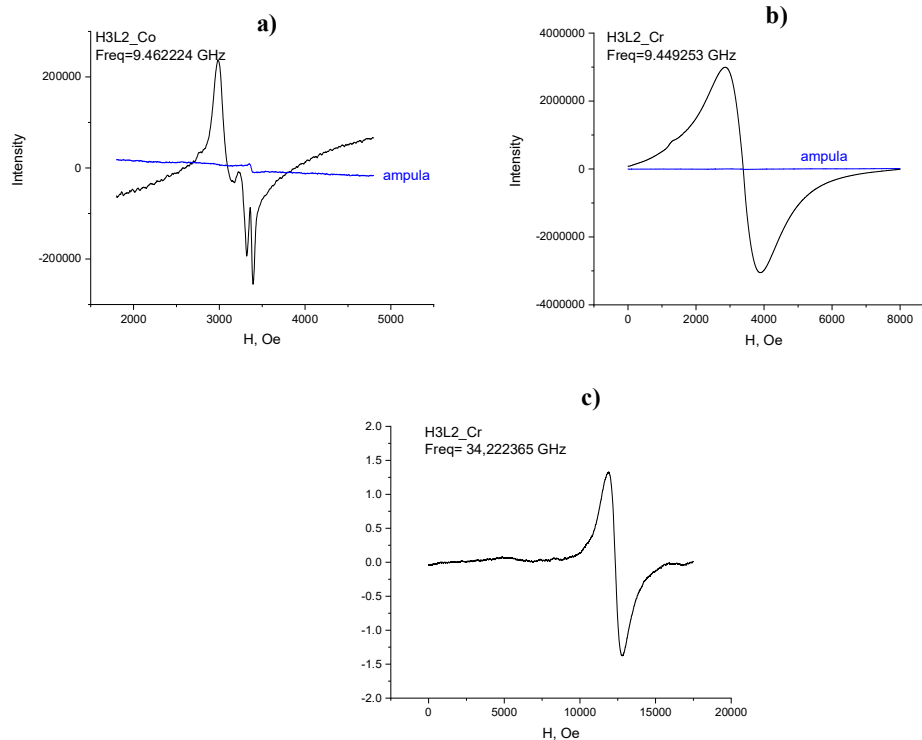


Figure 4. Q band EPR spectrum of the crystals: a) $\text{Co}(\text{H}_2\text{L}^2)\text{Cl}\cdot 3\text{H}_2\text{O}$ at 9.46 GHz, b) $\text{Cr}(\text{H}_2\text{L}^2)_2\text{Cl}\cdot 2\text{H}_2\text{O}$ at 9.45 GHz and c) $\text{Cr}(\text{H}_2\text{L}^2)_2\text{Cl}\cdot 2\text{H}_2\text{O}$ at 34.22 GHz at a room temperature.

EPR spectra of the chromium complex (powder) recorded at X-band ($\nu = 9.449$ GHz) and Q-band ($\nu = 34.223$ GHz) show a single intense resonance at $g \approx 2.0g$ (X-band $g_{\text{eff}} = 2.05 \pm 0.05$; Q-band $g_{\text{eff}} = 2.00 \pm 0.05$). The broad line and the absence of resolved Cr hyperfine structure are characteristic of high-spin Cr(III) ($S=3/2$) in an approximately axial octahedral ligand field (${}^4\text{A}_2$ ground state)[24]. Signals at $g \gg 4$ are not observed, supporting a single Cr(III) species as the dominant paramagnet and are fully consistent with an octahedral Cr(III) center chelated by the oxime/oxo donor set of the ligand. These IR, EDX and EPR spectral features are consistent with the stoichiometries determined from spectrophotometric studies, where Cr^{3+} forms ML_2 -type complexes while Ni^{2+} and Co^{2+} form ML -type complexes, confirming bidentate coordination through oxygen and nitrogen donor sites.

3.2. Chemisorbent for removing heavy metal cations

In previous studies, the two synthesized ligands demonstrated excellent chemisorption behavior toward several heavy metal ions, including Cu^{2+} , Cd^{2+} , and Zn^{2+} [1]. In the present work, their chemisorptive performance was further evaluated with respect to the removal of Co^{2+} , Ni^{2+} , and Cr^{3+} ions from electroplating wastewater. Since industrial effluents are typically acidic, the development of dye-based sorbents capable of operating efficiently under low-pH conditions is essential to minimize treatment costs and environmental impact. Therefore, this study investigated the chemisorptive behavior of both synthesized ligands toward metal ions over a range of pH conditions. For this purpose, a series of aqueous solutions (100 ppm) of Co^{2+} , Ni^{2+} , and Cr^{3+} ions were prepared by diluting concentrated salt solutions. A 20% excess of the stoichiometric amount of the organic ligand was then added, and the pH of each solution was adjusted within the range of 2–7. After 60 minutes of stirring, the resulting precipitates were filtered,

and the residual metal ion concentrations in the filtrates were determined using atomic absorption spectroscopy (AAS). The results are summarized in Table 3.

Table 3. Concentrations of some metal cations before and after treatment of aqueous solutions of their salts with H₃L¹ and H₃L² under static conditions.

Ion	pH	Initial concentration (ppm)	H ₃ L ¹		H ₃ L ²	
			Final concentration of metal (ppm)	Removal degree of metal (%)	Final concentration of metal (ppm)	Removal degree of metal (%)
Cr ³⁺	2	100	18.45	81.55	12.44	87.56
	3	100	13.68	86.32	9.35	90.65
	4	100	10.93	89.07	6.45	93.55
	5	100	7.45	92.55	3.91	96.09
	6	100	3.22	96.78	1.79	98.21
	7	100	1.12	98.88	0.652	99.35
	2.3*	154.1	8.50	94.48	3.98	97.42
Ni ²⁺	2	100	21.16	78.84	19.22	80.78
	3	100	18.23	81.77	16.82	83.18
	4	100	11.23	88.77	14.34	85.66
	5	100	7.45	92.55	10.23	89.77
	6	100	4.33	95.67	6.54	93.46
	7	100	2.33	97.67	2.12	97.88
	2.3*	73.2	13.40	81.69	7.50	89.75
Co ²⁺	2	100	20.22	79.78	17.45	82.55
	3	100	19.33	80.67	13.2	86.80
	4	100	15.39	84.61	10.11	89.89
	5	100	12.34	87.66	19.22	80.78
	6	100	8.44	91.56	16.82	83.18
	7	100	6.42	93.58	14.34	85.66
	2.3*	88.4	11.50	86.99	13.2	85.06

* Electroplating wastewater sample

As shown in Table 3, the efficiency of metal ion removal increases from H₃L¹ to H₃L² and follows the order Cr³⁺ > Ni²⁺ > Co²⁺. An increase in pH also enhances the removal rate, with maximum efficiency observed for Cr³⁺ ions at pH 5–7, achieving up to 96% removal. These findings correlate well with the relative stability constants determined from spectrophotometric studies, confirming that complex stability plays a crucial role in metal ion removal efficiency. Based on these results, the potential of the synthesized ligands for treating real electroplating wastewater was evaluated. Electroplating wastewater was collected in April 2025 from Hiep Phuoc Thanh Production Co., Ltd. The initial pH was 2.3 and was not adjusted prior to treatment with the studied ligands. The sample was pre-filtered to remove suspended solids, and Cr(VI) was completely reduced to Cr(III) using Na₂SO₃ before treatment with the ligands. The analysis of the raw wastewater revealed high concentrations of heavy metals, with Cr³⁺ being predominant (154.1 ppm), followed by Co²⁺ (88.4 ppm) and Ni²⁺ (73.2 ppm). Treatment with the H₃L² ligand demonstrated excellent performance, achieving almost complete removal of Cr³⁺ (97.42%, from 154.1 ppm to 3.98 ppm), along with high efficiencies for Co²⁺ (85.06%), and Ni²⁺ (89.75%). The H₃L¹ ligand also exhibited good removal efficiency, though slightly lower than H₃L². For Cr³⁺, the removal reached 94.48%, while Co²⁺ and Ni²⁺, showed efficiencies of 86.99% and 81.69%, respectively. Notably, for both ligands, the removal of Cr³⁺, Co²⁺, and Ni²⁺ from electroplating wastewater was substantially higher than under simulated single-metal conditions (pH 2–3). This enhancement is attributed to matrix effects in the real effluent: coexisting cations and anions promote mixed-metal/mixed-ligand complexation and co-precipitation, yielding species of lower solubility and thus reducing the dissolved metal concentrations in

the filtrate. The higher ionic strength and suspended solids in wastewater may further compress electrical double layers and facilitate aggregation, improving separation during filtration.

These results demonstrate that both ligands, particularly H_3L^2 , are highly effective for the removal of heavy metals from acidic electroplating wastewater, confirming their strong potential as environmentally friendly chelating agents for wastewater treatment.

4. Conclusion

This study systematically investigated the complexation behavior and chemisorption properties of two synthesized polyhydroxy-nitroso dyes, 2,4,6-trinitrosobenzene-1,3,5-triol (H_3L^1) and 1-(2,4,6-trihydroxy-3,5-dinitrosophenyl) ethanone (H_3L^2), toward Co^{2+} , Ni^{2+} , and Cr^{3+} ions. Spectrophotometric titration, IR, EPR, and EDX analyses confirmed the formation of stable ML and ML_2 complexes through coordination of metal ions with the carbonyl and nitroso groups of the ligands. The observed shifts in electronic and vibrational spectra, together with the determined stability constants, demonstrated the strong affinity of these ligands for transition metal ions and supported a bidentate coordination mode via oxygen and nitrogen donor atoms. Chemisorption experiments revealed that both ligands efficiently removed metal ions from aqueous solutions, with removal efficiencies increasing with pH. H_3L^2 exhibited superior sorption performance, achieving nearly complete removal of Cr^{3+} (97.4%) and high efficiencies for Co^{2+} (85.06%) and Ni^{2+} (89.8%). The removal trend ($Cr^{3+} > Ni^{2+} > Co^{2+}$) correlated well with the relative stability constants, confirming that stronger complex formation enhances sorption performance. Application to real electroplating wastewater further validated the practical utility of these ligands under acidic conditions (pH 2.3), where conventional adsorbents typically perform poorly. The nearly quantitative removal of Cr^{3+} and other heavy metals highlights their potential as cost-effective, environmentally friendly agents for wastewater purification. Overall, the findings demonstrate that polyhydroxy-nitroso dyes are promising multifunctional ligands combining high complexation ability, acid stability, and strong chemisorptive performance, making them suitable candidates for sustainable heavy metal removal technologies.

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