Synthesis and spectral characterizations of vanadyl(II) and chromium(III) mixed ligand complexes containing metformin drug and glycine amino acid

Abstract: Metformin is one of the most effective drugs for the treatment of type II diabetes. Two new mixed ligand complexes of vanadyl(II) and chromium(III) ions with the general formula [VO(L2)]SO4 and [CrL1L2(Cl)2]Cl, respectively, where L1 is the metformin and L2 is the glycine amino acid, have been synthesized in MeOH solvent with 1:1:1 stoichiometry and characterized by several spectroscopic techniques. The spectroscopic data suggested that the [VO(L2)]SO4 complex possesses a square pyramidal geometry, whereas the [CrL1L2(Cl)2]Cl complex possesses an octahedral geometry. The L1 ligand coordinated to the VO(II) and Cr(III) ions via the O atom of the amino group (C==NH) groups, while the L2 ligand coordinated via the O atom of the carboxylate group (COO) and the N atom of the amino group (NH2). The interaction of ligands L1 and L2 with the metal ions leads to complexes that have organized nanoscale structures with a main diameter of ~14 nm for the [CrL1L2(Cl)2]Cl complex and ~40 nm for the [VO(L2)]SO4 complex.

Keywords: metformin, glycine, mixed ligand complex, VO(II) ion, Cr(III) ion

1 Introduction

Metal complexes are an important class of compounds with applications in various fields such as medicine, material sciences, biology, and catalysis [1,2]. These class of compounds may have different geometries, which make them potentially biologically active and used as anticancer, antifungal, and antibacterial agents. For example, carboplatin, oxaliplatin, and cisplatin, which are platinum-based metallodrugs, are considered anticancer drugs for treating several solid tumors such as ovarian, bladder, and testicular cancers. Platinum-based metallodrugs kill tumor cells by damaging DNA, which inhibit tumor cell division [3–8]. Nevertheless, the adverse side effects and acquired resistance associated with several metallodrugs prevent their effectiveness and widespread applications [9–12]. Because of that, significant attempts have been made to replace metallodrugs by developing innovative drugs with negligible side effects, enhanced efficiency, and decreased drug resistance and toxicity profiles. One of these attempts involves the design of new metal-based drugs by coordinating metal ions with biologically active ligands. Ions of transition metals play an important role in the fields of biochemistry and medicine, and their complexes are extensively used as therapeutic agents and drugs for the treatment of various human diseases, including neurological disorders, diabetes, inflammation, infection control, lymphomas, and carcinomas. Two interesting properties of transition metals enabling the design of metallodrugs with promising biological benefits exhibited: (i) different oxidation states and (ii) the ability to interact with several metal-binding sites [13–15].

Metformin (C6H11N5O) is a well-known AMP-activated protein kinase (AMPK) activator and well-known oral hypoglycemic drug, which has been in clinical use for over half a century, particularly in obese and overweight people. It is the most widely prescribed antidiabetic drug worldwide and the first-line therapy for non-insulin-dependent diabetes and metabolic syndrome. Besides its use in oral hypoglycemic medication for type II diabetes, metformin confers protection against a series of diseases through the activation of AMPK. This drug has antihyperglycemic and anticancer properties, and it strongly
enhances insulin sensitivity in the body, increases the glucose uptake by peripheral tissues through stimulation of intracellular AMPK, and inhibits gluconeogenesis in the liver. This drug has multiple beneficial effects, such as the following:
(i) Does not increase the risk for hypoglycemia
(ii) Reduces weight gain
(iii) Lowers blood lipid levels
(iv) Lowers blood glucose levels.

In vitro and in vivo studies indicated that metformin inhibits the growth of several types of tumors, such as glioma, prostate cancer, and breast cancer [16–23]. Metformin has two imine groups that act as a chelating agent coordinating with many metal and non-metal ions. The interactions of metformin with several lanthanide and transitional metal ions, such as Y(III), Sm(III), Ce(III), La(III), Cd(II), Fe(III), Au(III), Re(V), Tc(V), Pt(II), Co(II), V(IV), Rh(V), Cu(II), Ni(II), Cr(III), Zn(II), Te(V), Pd(II), Os (III), Os(II), Ir(III), and Rh(III), have been investigated and reported in the literature [24–38].

Further research on the complexation of metformin with metal ions, especially in mixed ligand complexes, is still important for establishing good knowledge and a better understanding of the binding modes of metformin in this type of complex as a key point for developing new metformin-based metallo drugs. Therefore, this study was done to present the synthesis and speculated formula of two mixed ligand complexes of vanadyl(IV) and chromium(III) ions with the general formula [VOL1L2]SO4 and [CrL1L2(Cl)2]Cl, respectively, where L1 is the metformin and L2 is the glycine amino acid (Figure 1) and to observe the X-ray diffraction patterns, phase purity, surface morphologies, and particle shapes of the synthesized mixed ligand complexes.

2 Experimental

2.1 Instruments and chemicals

The spectrometers such as Perkin-ElmerLambda 25 UV/Vis spectrophotometer, Shimadzu FT-IR spectrophotometer, and Jeol JES-FE2XG electron spin resonance spectrometer were used to scan the UV-visible, IR, and ESR spectra at the room temperature, respectively. The microscopes such as JEOL JEM-1200 EX II transmission electron microscope (TEM) and Quanta FEG 250 scanning electron microscope (SEM) were applied to picture the TEM and SEM images, respectively. Perkin-Elmer 2400CHN elemental analyzer was applied to collect the elemental data. X’Pert Philips X-ray powder diffractometer was applied to collect the XRD spectra of the complexes, where HACH digital conductivity meter and magnetic susceptibility balance were applied for the molar conductivity and magnetic measurements, respectively. Solvents and chemicals were purchased from Merck KGaA company (Darmstadt, Germany) in analytical grade and used without further modification: metformin hydrochloride (C4H11N5·HCl ≥97%), glycine (NH2CH2COOH ≥99%), VOSO4·xH2O 97%, and CrCl3·6H2O ≥98%.

2.2 Syntheses

Mixed ligand complexes [VOL1L2]SO4 and [CrL1L2(Cl)2]Cl were synthesized as follows: To a methanolic solution of L1 (metformin) (1 mmol in 10 mL), 1 mmol of L2 (glycine) dissolved in MeOH solvent (10 mL) was added. The solution was stirred well for 10 min. Then, 1 mmol of VOSO4·H2O dissolved in MeOH solvent (10 mL) was added to prepare the VOL1L2 complex, and the pH of the mixture was adjusted to ~8 with the ammonia solution (5%). The resultant homogenous greenish-blue solution was refluxed with stirring for 30 min at 65°C. On cooling the reactant media, the greenish-blue-colored precipitate was separated, which was recrystallized from the MeOH solvent. The final product was filtered, washed with MeOH and CH3OCH3, and then dried in an oven at 70°C. The [CrL1L2(Cl)2]Cl complex was similarly synthesized as described for the VOL1L2 complex using 1 mmol of CrCl3·6H2O resulting in a dark green-colored product. The products were next characterized by analytical, thermal, and different spectral methods.
[VOL₁L₂]SO₄ complex:
Gross formula, C₆H₁₆N₆O₇SV; general formula, [VOL₁L₂]SO₄; molecular weight, 367.23 g mol⁻¹; elemental results: calc. (found) for C, 21.62% (21.52); H, 4.39% (4.55); N, 22.89% (22.67); and metal, 13.87% (14.13).

[CrL₁L₂(Cl)₂]Cl complex:
Gross formula, C₆H₁₆N₆O₇SV; general formula, [CrL₁L₂Cl]₂Cl; molecular weight, 362.58 g mol⁻¹; elemental results: calc.(found) for C, 19.88% (19.75); H, 4.45% (4.34); N, 23.18% (23.06); and metal, 14.34% (14.21).

Ethical approval: The study was conducted and approved by the Ethical Committee of Taif University (Fast–track Research Funding program).

### 3 Results and discussion

#### 3.1 Analytical, conductance, and UV-visible spectral results

In this present research, the reaction of L₁ and L₂ with VO(II) ions in MeOH solvent at (pH ~ 8; 65°C) gave a greenish-blue-colored complex with the general formula [VOL₁L₂]SO₄. When L₁ and L₂ reacted with Cr(III) ions at the same condition, a dark green-colored complex was formed with the general formula [CrL₁L₂]Cl. Elemental data of the two complexes are presented in the experimental section. The data indicate that the reaction stoichiometry is 1:1:1 (L₁;L₂;Metal ion), which suggested that the general composition of the complexes obtained with VO(II) and Cr(III) ions are [VOL₁L₂]SO₄ and [CrL₁L₂(Cl)₂]Cl, respectively.

The molar conductivity of the [VOL₁L₂]SO₄ and [CrL₁L₂(Cl)₂]Cl complexes in DMSO (10⁻³ M) at 25°C is proportionate with their electrolytic nature [25–28] with 54 and 61 Ω⁻¹ cm⁻¹ mol⁻¹ values, respectively. The corresponding gross formulas are C₆H₁₆N₆O₇SV and C₆H₁₆N₆O₂Cl₃Cr, respectively. The [VOL₁L₂]SO₄ complex has an effective magnetic moment (μ eff) of 1.71 B.M. at the room temperature [39]. The [CrL₁L₂(Cl)₂]Cl complex has an effective magnetic moment (μ eff) of 3.14 B.M. at the room temperature, which revealed that Cr(III) complex possesses an octahedral geometry [40]. The UV-visible spectra of [VOL₁L₂]SO₄ and [CrL₁L₂(Cl)₂]Cl complexes were scanned over the 200–1,000 nm wavelength range at the room temperature in DMSO solvent and presented in Figure 2. The spectrum of [CrL₁L₂(Cl)₂]Cl complex showed three bands at 37,736, 23,529, and 16,667 cm⁻¹, where that of the [VOL₁L₂]SO₄ complex exhibited four bands at 36,364, 22,894, 22,155, and 18,642 cm⁻¹ at the room temperature, which revealed that Cr(III) complex possesses an octahedral geometry [40]. The UV-visible spectra of [VOL₁L₂]SO₄ and [CrL₁L₂(Cl)₂]Cl complexes were scanned over the 200–1,000 nm wavelength range at the room temperature in DMSO solvent and presented in Figure 2. The spectrum of [CrL₁L₂(Cl)₂]Cl complex showed three bands at 37,736, 23,529, and 16,667 cm⁻¹, where that of the [VOL₁L₂]SO₄ complex exhibited four bands at 36,364, 22,894, 22,155, and 18,642 cm⁻¹. Among these bands, the bands observed at 37,736 and 36,364 cm⁻¹ were very strong. The band at 36,364 nm appeared in the spectrum of [VOL₁L₂]SO₄

#### Table 1: Characteristic IR bands (cm⁻¹) for L₁, L₂, and the mixed ligand complexes

<table>
<thead>
<tr>
<th>Free L₁</th>
<th>Free L₂</th>
<th>[VOL₁L₂]SO₄</th>
<th>[CrL₁L₂(Cl)₂]Cl</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,369</td>
<td>—</td>
<td>3,394</td>
<td>3,600–2,560</td>
<td>v(N=H), C=NH</td>
</tr>
<tr>
<td>3,295</td>
<td>3,244</td>
<td>—</td>
<td>—</td>
<td>v(0–H)</td>
</tr>
<tr>
<td>3,153</td>
<td>3,170</td>
<td>3,173</td>
<td>1,605</td>
<td>v(N=H); NH₂</td>
</tr>
<tr>
<td>3,088</td>
<td>—</td>
<td>3,020</td>
<td>—</td>
<td>ν₅₅(C=C=H)</td>
</tr>
<tr>
<td>2,815</td>
<td>—</td>
<td>—</td>
<td>1,615</td>
<td>ν₁(C–H)</td>
</tr>
<tr>
<td>2,551</td>
<td>—</td>
<td>—</td>
<td>1,611</td>
<td>ν₁(COO)</td>
</tr>
<tr>
<td>1,643</td>
<td>1,436</td>
<td>1,482</td>
<td>1,440</td>
<td>δ(N=H); in-plane def.</td>
</tr>
<tr>
<td>—</td>
<td>1,414</td>
<td>1,390</td>
<td>1,383</td>
<td>ν₁(COO)</td>
</tr>
<tr>
<td>—</td>
<td>1,326</td>
<td>1,348</td>
<td>1,354</td>
<td>δ(C≡C)</td>
</tr>
<tr>
<td>1,271</td>
<td>1,298</td>
<td>1,306</td>
<td>1,210</td>
<td>ν₅₅(C=N)</td>
</tr>
<tr>
<td>1,168</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>υ₂(C=N)</td>
</tr>
<tr>
<td>1,056</td>
<td>1,098</td>
<td>1,063</td>
<td>—</td>
<td>δ(CH) in-plane bending</td>
</tr>
<tr>
<td>—</td>
<td>1,039</td>
<td>—</td>
<td>1,000</td>
<td>ν₁(C≡N)</td>
</tr>
<tr>
<td>—</td>
<td>973</td>
<td>—</td>
<td>—</td>
<td>ν(ν=O)</td>
</tr>
<tr>
<td>933</td>
<td>929</td>
<td>850</td>
<td>849</td>
<td>δ(C≡C)</td>
</tr>
<tr>
<td>635</td>
<td>—</td>
<td>701</td>
<td>762</td>
<td>δ(CH) out-of-plane bending</td>
</tr>
<tr>
<td>—</td>
<td>596</td>
<td>604</td>
<td>—</td>
<td>ν(M=O); ν₃</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>(M=N)</td>
</tr>
</tbody>
</table>
complex was stronger and broader than the band observed at 37,736 cm\(^{-1}\) in the spectrum of \([\text{CrL}_1\text{L}_2(\text{Cl})_2] \text{Cl}\) complex \([40–42]\). The electronic \([\text{VOL}_1\text{L}_2]\text{SO}_4\) complex spectrum show bands at regions 12,121, 16,667, and 23,529 cm\(^{-1}\). These spectra are similar to those of other five-coordinate oxovanadium(IV) complexes involving nitrogen donor atoms. These spectral bands are interpreted according to an energy level scheme reported by Lever for distorted, five-coordinate square pyramidal oxovanadium(IV) complexes \([40]\). Accordingly, the observed bands can be assigned to \(^2\text{B}_2 \rightarrow ^2\text{E}\), \(^2\text{B}_2 \rightarrow ^2\text{B}_1\), and \(^2\text{B}_2 \rightarrow ^2\text{A}_2\) transitions, respectively. One more band is observed at the region 36,364 cm\(^{-1}\), which may be due to the transition of the metformin linkages \([40]\). For the chromium complex, two peaks at 16,667 and 23,529 cm\(^{-1}\) were assigned to \(^4\text{A}_2\text{g} \rightarrow ^4\text{T}_{2\text{g}}\) and \(^4\text{A}_2\text{g} \rightarrow ^4\text{T}_{1\text{g}}\) (f–d) transitions, respectively. The appearance of these two bands confirms octahedral (Oh) geometry for this complex \([40]\). The other band exhibited at the region 37,736 cm\(^{-1}\) is assigned to the transition of the metformin linkages.

### 3.2 IR spectral results

#### 3.2.1 Free ligands

A free \(L_1\) molecule has three significant vibrational bands \([27,43]\):

(a) The C–H vibrations:

The two aliphatic CH\(_3\) groups give bands at 2,815 and 3,088 cm\(^{-1}\), attributed to the \(v_{\text{as}}(\text{C–H})\) and \(v_{\text{s}}(\text{C–H})\) vibrations. The C–H bending deformation vibrations resonate at 1,463 cm\(^{-1}\), where the \(\delta_{\text{rock}}(\text{C–H})\) vibrations give a sharp band at ~933 cm\(^{-1}\).
Table 1 reports the band assignments for the important IR bands in free ligands and the mixed ligand complexes, where their IR spectra are shown in Figure 3. In the [VOL₁L₂]SO₄ complex, the bands due to the ν(N–H) vibrations of the ligands were located at 3,394 and 3,173 cm⁻¹. The IR spectrum of [CrL₁L₂(Cl)₂]Cl complex showed a very wide absorption band ranged from 3,600 to 2,560 cm⁻¹ due to the overlapping of bands due to the ν(N–H), νas(C–H), and νs(C–H) vibrations. The bands located at 1,608 and 1,605 cm⁻¹ in spectra of [VOL₁L₂]SO₄ and [CrL₁L₂(Cl)₂]Cl complexes were attributed to the νas(COO) vibrations, respectively, that of the νs(COO) vibrations were resonated at 1,390 and 1,383 cm⁻¹, respectively. These bands represent a Δν difference between νas(COO) and νs(COO): [Δν = νas – νs] equal to 218 cm⁻¹ for the [VOL₁L₂]SO₄ complex and 222 cm⁻¹ for the [CrL₁L₂(Cl)₂]Cl complex, suggesting a unidentate coordination mode for the carboxylate group (COO) of L₂ in the mixed ligand [45]. The bands attributed to the ν(C=O) vibrations located at 1,624 cm⁻¹ in free L₁ were shifted to 1,646 cm⁻¹ in the [VOL₁L₂]SO₄ complex and to 1,643 cm⁻¹ in the [CrL₁L₂(Cl)₂]Cl complex and decreased in intensity. The outlined shifts in the C=O band upon complexation suggested that the L₁ ligand was coordinated to the Cr(III) and VO(II) ions via the nitrogen atoms of the imino (C=NH) groups without any displacement of protons. The [VOL₁L₂]SO₄ complex exhibited a medium and broadband at 973 cm⁻¹ due to the νν as(V=O) vibrations [45]. It is worth mentioning that the test against the presence of the sulfate group gave a positive result; this conclusion was supported by detected the two IR active ν₁ and ν₃ frequencies at about 1,098 and 627 cm⁻¹. Based on these observations, the proposed formula of [VOL₁L₂]SO₄ and [CrL₁L₂(Cl)₂]Cl complexes are shown in Figure 4.

### 3.2.2 Mixed ligand complexes

The IR data (cm⁻¹) of free L₂ molecule are as follows: 3,244 ν(NH₃), 2,551 ν(CH₃), 1,661 and 1,512 δ(NH₃), 1,611 νas(COO), 1,436 δdef(CH₂), 1,407 νs(COO), 1,326 δwag(CH₂) and δwag(NH₃), 1,138 δrock(NH₃), 1,039 ν(C–N), and 929 δrock(CH₂) [44].

### 3.3 ESR spectral results

The Jeol JES-CE2XG electron spin resonance spectrometer was used to scan the powder ESR spectrum of the VOL₁L₂ complex, and the obtained spectrum is presented in Figure 5. Electron spin resonance spectrum of vanadyl(II) complex in the polycrystalline state was recorded on

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**Table 2: Values of Hamiltonian and bonding parameters for the [VOL₁L₂]SO₄ complex**

<table>
<thead>
<tr>
<th>[VOL₁L₂]SO₄</th>
<th>ESR data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α²</td>
</tr>
<tr>
<td></td>
<td>0.1648</td>
</tr>
</tbody>
</table>
ESR spectrometer using 2,2-diphenyl-1-picrylhydrazyl DPPH (Figure 5) free radical as “g” marker ($g = 2.0027$) at the room temperature. The Hamiltonian spectral data obtained from this spectrum are presented in Table 2. The powder ESR spectrum and the values of $g$ and $A$ for the [VOL$_2$L$_2$]SO$_4$ complex agree with a square pyramidal geometry [46]. Equations (1) and (2) were used to calculate the values of anisotropic ($A$) and isotropic ($g$).

$$g_0 = \frac{g_i + 2g_e}{3} \quad (1)$$

$$A_0 = \frac{A_i + 2A_e}{3} \quad (2)$$

Equations (3) and (4) were used to calculate the covalency of the $\beta^2$; in plane $n$- and $\alpha^2$; in plane $\sigma$-bonding [47,48]:

$$\beta^2 = \frac{7}{6}(-A_i/P + A_e/P + g_i - 5/14g_e - 9/14g_e) \quad (3)$$

$$\alpha^2 = \frac{(2.0023 - g_i)E}{8A\beta^2} \quad (4)$$

where $E$ is the electronic transition energy, $\lambda = 135$ cm$^{-1}$, and $P = 128 \times 10^{-4}$cm$^{-1}$. It is reported in the literature that a $g_{||}$ value more than 2.3 for a metal-ligand bond with ionic character and less than 2.3 for a covalent character [49]. The $g_{||}$ value for the [VOL$_2$L$_2$]SO$_4$ complex was 1.99, suggesting a covalent character of the ligand-metal bond. The $\alpha^2$ value for the complex was found much smaller than the $\beta^2$ value.

### 3.4 XRD, SEM, and TEM results

To observe the X-ray diffraction patterns, phase purity, surface morphologies, and particle shapes of the [VOL$_2$L$_2$] SO$_4$ and [CrL$_2$L$_2$(Cl)$_2$]Cl complexes, XRD, SEM, and TEM techniques were used. Analyses of the XRD spectra (Figure 6), SEM micrographs (Figure 7), and TEM micrographs (Figure 8) of these complexes provided the following observations:

(i) The [CrL$_2$L$_2$(Cl)$_2$]Cl complex displayed one broad peak ranging from $2\theta$ 20$^\circ$ to 30$^\circ$ in its XRD profile. This broad peak had a maximum at diffraction line $2\theta$ of approximately 26.531$^\circ$.

(ii) The [VOL$_2$L$_2$]SO$_4$ complex displayed a group of intense lines at Bragg’s angle $2\theta$ in the range of 16–33$^\circ$. These lines were observed at $2\theta$ 16.947$^\circ$, 19.374$^\circ$, 20.361$^\circ$, 22.335$^\circ$, 24.310$^\circ$, 28.095$^\circ$, and 30.562$^\circ$.

(iii) The SEM micrographs captured at various levels of magnification (i.e., ×150, ×500, ×1,000, ×2,000) indicated visible microstructural differences between the particles of [VOL$_2$L$_2$]SO$_4$ and [CrL$_2$L$_2$(Cl)$_2$]Cl complexes.

(iv) The SEM micrographs of the [VOL$_2$L$_2$]SO$_4$ complex indicated that it consists of small spherical granules fused together. Several clear holes were observed between these granules, and the surfaces of the completely fused granules had several cracks.
Figure 7: (a) SEM micrographs of [VOL₂SO₄] complex. (b) SEM micrographs of [CrL₂(Cl)₂]Cl complex.
The SEM micrographs of the \([\text{CrL}_1\text{L}_2\text{Cl}_2\text{Cl}]\) complex shows a coral reefs-like shaped morphology. The TEM micrographs revealed that the shape of the \([\text{CrL}_1\text{L}_2\text{Cl}_2\text{Cl}]\) particles was almost spherical, where the shape of the \([\text{VOL}_1\text{L}_2\text{SO}_4]\) particles were mixed spherical and oval-shaped. Most particles of \([\text{VOL}_1\text{L}_2\text{SO}_4]\) and \([\text{CrL}_1\text{L}_2\text{Cl}_2\text{Cl}]\) complexes had diameters is in the range of 7–20 and 20–60 nm, respectively. The average particle size of \([\text{CrL}_1\text{L}_2\text{Cl}_2\text{Cl}]\) complex is ~14 nm, where it is ~40 nm for the \([\text{VOL}_1\text{L}_2\text{SO}_4]\) complex. This indicated that the particles of the \([\text{VOL}_1\text{L}_2\text{SO}_4]\) complex are higher by 2.8 times than the particles of the \([\text{CrL}_1\text{L}_2\text{Cl}_2\text{Cl}]\) complex.

**4 Conclusion**

In this work, we sought to synthesize and characterize two mixed ligand complexes containing drug metformin as \(L_1\) and glycine amino acid as \(L_2\) with the metal ions of \(\text{Cr(III)}\) and \(\text{VO(II)}\). The interaction via a 1:1:1 (\(L_1\):\(L_2\):Metal ion) stoichiometry yielded two complexes: a greenish-blue-colored complex formulated as \([\text{VOL}_1\text{L}_2\text{SO}_4]\) with a square pyramidal geometry and a dark green-colored complex formulated as \([\text{CrL}_1\text{L}_2\text{Cl}_2\text{Cl}]\) with an octahedral structure. Spectroscopic results indicated that \(L_1\) ligand coordinated to the \(\text{VO(II)}\) and \(\text{Cr(III)}\) ions via the \(N\) atoms of the imino (\(-\text{C}=\text{NH}\)) groups, where the \(L_2\) ligand coordinated via the \(O\) atom of the carboxylate group (\(\text{COO}\)) and the \(N\) atom of the amino group (\(\text{NH}_2\)). SEM and TEM results indicated that the complexes had organized nanoscale structures with a main diameter of ~14 nm for the \([\text{CrL}_1\text{L}_2\text{Cl}_2\text{Cl}]\) complex and ~40 nm for the \([\text{VOL}_1\text{L}_2\text{SO}_4]\) complex.

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**Conflict of interest:** The authors declare that they have no conflicts of interest.

**Data availability statement:** The data used to support the findings of this study are included within the article.

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