Research Article

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

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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 $[\text{VOL}_1\text{L}_2]\text{SO}_4$ and $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$, respectively, where L_1 is the metformin and L_2 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 $[\text{VOL}_1\text{L}_2]\text{SO}_4$ complex possesses a square pyramidal geometry, where the $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complex possesses an octahedral geometry. The L_1 ligand coordinated to the VO(II) and 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 (COO) and the N atom of the amino group (NH_2). The interaction of ligands L_1 and L_2 with the metal ions leads to complexes that have 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.

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 ($\text{C}_4\text{H}_{11}\text{N}_5$) 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

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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 metallodrugs. Therefore, this study was done to present the synthesis and speculated formula of two mixed ligand complexes of vanadyl(II) and chromium(III) ions with the general formula $[\text{VOL}_1\text{L}_2]\text{SO}_4$ and $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$, respectively, where L_1 is the metformin and L_2 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-Elmer Lambda 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 ($\text{C}_4\text{H}_{11}\text{N}_5\text{HCl} \geq 97\%$), glycine ($\text{NH}_2\text{CH}_2\text{COOH} \geq 99\%$), $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ 97%, and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O} \geq 98\%$.

2.2 Syntheses

Mixed ligand complexes $[\text{VOL}_1\text{L}_2]\text{SO}_4$ and $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ were synthesized as follows: To a methanolic solution of L_1 (metformin) (1 mmol in 10 mL), 1 mmol of L_2 (glycine) dissolved in MeOH solvent (10 mL) was added. The solution was stirred well for 10 min. Then, 1 mmol of $\text{VOSO}_4 \cdot \text{H}_2\text{O}$ dissolved in MeOH solvent (10 mL) was added to prepare the VOL_1L_2 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 CH_3OCH_3 , and then dried in an oven at 70°C. The $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complex was similarly synthesized as described for the VOL_1L_2 complex using 1 mmol of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ resulting in a dark green-colored product. The products were next characterized by analytical, thermal, and different spectral methods.

Figure 1: Structures of metformin molecule (L_1) and glycine molecule (L_2).

[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, C₆H₁₆N₆O₂Cl₃Cr; general formula, [CrL₁L₂(Cl)₂]Cl; 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 cm² mol⁻¹ values, respectively. The corresponding gross formulas are C₆H₁₆N₆O₇SV and C₆H₁₆N₆O₂Cl₃Cr, respectively. The [VOL₁L₂]SO₄ complex has an effective molar 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, 23,529, 16,667, and 12,121 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

Figure 2: UV-visible spectra of [VOL₁L₂]SO₄ and [CrL₁L₂(Cl)₂]Cl complexes.

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

Free L ₁	Free L ₂	[VOL ₁ L ₂]SO ₄	[CrL ₁ L ₂ (Cl) ₂]Cl	Assignments
3,369	—	3,394	Very wide band	v(N—H), C=NH
3,295	3,244	—	3,600–2,560	v(O—H)
3,153	3,170	3,173	—	v(N—H)
3,088,	—	3,020	—	v(N—H); NH ₂
2,815	—	—	—	v _{as} (C—H)+
2,551	—	—	—	v _s (C—H)
1,624	—	1,646	1,643	v(CH ₂)
—	1,611	1,608	1,605	v(C=N)
1,556	—	—	—	v _{as} (COO)
1,463	1,436	1,482	1,440	δ(N—H); in-plane def.
—	1,414	1,390	1,383	δ(C—H)
—	1,326	1,348	1,354	deformation
1,271	—	1,298	1,306	v _s (COO)
1,168	—	—	1,210	v _{wag} (CH ₂)
1,056	—	1,098	1,063	δ _{as} (C—N)
—	1,039	—	1,000	v _s (C—N)
—	—	973	—	δ(CH) in-plane bending
933	929	850	849	v(SO ₄); v ₃
635	—	701	762	v(C—N)
—	—	627	—	v(V=O)
—	—	596	604	δ _{rock} (C—H)
—	—	—	—	δ(CH) out-of-plane bending
—	—	—	—	v(SO ₄); v ₄
—	—	—	—	v(M—O), v(M—N)

Figure 3: IR spectra of (a) metformin drug (L_1), (b) glycine amino acid (L_2), (c) $[\text{VOL}_1\text{L}_2]\text{SO}_4$, and (d) $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complexes.

Figure 4: The proposed structure of the $[\text{VOL}_1\text{L}_2]\text{SO}_4$ and $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complexes.

complex was stronger and broader than the band observed at $37,736\text{ cm}^{-1}$ 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 $23,529\text{ cm}^{-1}$. 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 $36,364\text{ cm}^{-1}$, which may be due to the transition of the metformin linkages [40]. For the chromium complex, two peaks at 16,667 and $23,529\text{ cm}^{-1}$ were assigned to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ (f) d-d transitions, respectively. The appearance of these two bands confirms octahedral (O_h) geometry for this complex [40]. The other band exhibited at the region $37,736\text{ cm}^{-1}$ 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 $3,088\text{ cm}^{-1}$ attributed to the $\nu_{\text{as}}(\text{C-H})$ and $\nu_{\text{s}}(\text{C-H})$ vibrations. The C–H bending deformation vibrations resonated at $1,463\text{ cm}^{-1}$, where the $\delta_{\text{rock}}(\text{C-H})$ vibrations give a sharp band at $\sim 933\text{ cm}^{-1}$.

Figure 5: ESR spectrum of $[\text{VOL}_1\text{L}_2]\text{SO}_4$ complex in solid state at the room temperature.

(b) The C=N and C–N vibrations:

The $\nu(\text{C}=\text{N})$ vibrations resonated at $1,624\text{ cm}^{-1}$, where the vibrations of C–N band resonated at $1,271\text{ cm}^{-1}$ for asymmetric stretching and at $1,168\text{ cm}^{-1}$ for symmetric stretching.

(c) The N–H vibrations:

The $\nu(\text{N–H})$ vibrations of imino ($-\text{C}=\text{NH}$), secondary ($-\text{NH}$), and primary ($-\text{NH}_2$) groups give strong bands around $3,369\text{--}3,295\text{ cm}^{-1}$ for asymmetric stretching and at $3,153\text{ cm}^{-1}$ for symmetric stretching. The $\delta(\text{N–H})$ vibrations gave a very strong band at $1,556\text{ cm}^{-1}$.

The amino group of L_2 molecule can lose a hydrogen ion and become negatively charged or can accept a hydrogen ion and become positively charged, this is called as the zwitterion structure of L_2 molecule in solution.

The IR data (cm^{-1}) of free L_2 molecule are as follows: $3,244\text{ cm}^{-1}$ $\nu(\text{NH}_3)$, $2,551\text{ cm}^{-1}$ $\nu(\text{CH}_2)$, $1,661$ and $1,512\text{ cm}^{-1}$ $\delta(\text{NH}_3)$, $1,611\text{ cm}^{-1}$ $\nu_{\text{as}}(\text{COO})$, $1,436\text{ cm}^{-1}$ $\delta_{\text{def}}(\text{CH}_2)$, $1,407\text{ cm}^{-1}$ $\nu_{\text{s}}(\text{COO})$, $1,326\text{ cm}^{-1}$ $\delta_{\text{wag}}(\text{CH}_2)$ and $\delta_{\text{wag}}(\text{NH}_3)$, $1,138\text{ cm}^{-1}$ $\delta_{\text{rock}}(\text{NH}_3)$, $1,039\text{ cm}^{-1}$ $\nu(\text{C–N})$, and 929 cm^{-1} $\delta_{\text{rock}}(\text{CH}_2)$ [44].

3.2.2 Mixed ligand complexes

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 $[\text{VOL}_1\text{L}_2]\text{SO}_4$ complex, the bands due to the $\nu(\text{N–H})$ vibrations of the ligands were located at $3,394$ and $3,173\text{ cm}^{-1}$. The IR spectrum of $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complex showed a very wide absorption band ranged from $3,600$ to $2,560\text{ cm}^{-1}$ due to the overlapping of bands due to the $\nu(\text{N–H})$, $\nu_{\text{as}}(\text{C–H})$, and $\nu_{\text{s}}(\text{C–H})$ vibrations. The bands located at $1,608$ and $1,605\text{ cm}^{-1}$ in spectra of $[\text{VOL}_1\text{L}_2]\text{SO}_4$ and $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complexes were attributed to the $\nu_{\text{as}}(\text{COO})$ vibrations, respectively, that of the $\nu_{\text{s}}(\text{COO})$ vibrations were resonated at $1,390$ and $1,383\text{ cm}^{-1}$, respectively. These bands represent a $\Delta\nu$ difference between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$: $[\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}]$ equal to 218 cm^{-1} for the $[\text{VOL}_1\text{L}_2]\text{SO}_4$ complex and 222 cm^{-1} for the $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complex, suggesting a unidentate coordination mode for the carboxylate group (COO) of L_2 in the mixed ligand [45]. The bands attributed to the $\nu(\text{C}=\text{N})$ vibrations located at $1,624\text{ cm}^{-1}$ in free L_1 were shifted to $1,646\text{ cm}^{-1}$ in the $[\text{VOL}_1\text{L}_2]\text{SO}_4$ complex and to $1,643\text{ cm}^{-1}$ in the $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complex and decreased in intensity. The outlined shifts in the C=N band upon complexation suggested that the L_1 ligand was coordinated to the $\text{Cr}(\text{III})$ and $\text{VO}(\text{II})$ ions via the nitrogen atoms of the imino ($-\text{C}=\text{NH}$) groups without any displacement of protons. The $[\text{VOL}_1\text{L}_2]\text{SO}_4$ complex exhibited a medium and broadband at 973 cm^{-1} due to the $\nu_{\text{as}}(\text{V}=\text{O})$ 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 ν_3 and ν_4 frequencies at about $1,098$ and 627 cm^{-1} . Based on these observations, the proposed formula of $[\text{VOL}_1\text{L}_2]\text{SO}_4$ and $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complexes are shown in Figure 4.

3.3 ESR spectral results

The Jeol JES-FE2XG electron spin resonance spectrometer was used to scan the powder ESR spectrum of the $[\text{VOL}_1\text{L}_2]$ 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

Table 2: Values of Hamiltonian and bonding parameters for the $[\text{VOL}_1\text{L}_2]\text{SO}_4$ complex

$[\text{VOL}_1\text{L}_2]\text{SO}_4$	ESR data						
	α^2	β^2	A_0	$A_{\perp} (\text{cm}^{-1})$	$A_{\parallel} (\text{cm}^{-1})$	g_0	$g_{\parallel}$
	0.1648	1.1236	368	348	409	1.7956	1.6968
							1.9931

Figure 6: XRD spectra of L_1 , $[VOL_1L_2]SO_4$, and $[CrL_1L_2(Cl)_2]Cl$ complexes.

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 $[VOL_1L_2]SO_4$ complex agree with a square pyramidal geometry [46]. Equations (1) and (2) were used to calculate the values of anisotropic (A) and isotropic (g).

$$g_0 = (g_{\parallel} + 2g_{\perp})/3 \quad (1)$$

$$A_0 = (A_{\parallel} + 2A_{\perp})/3 \quad (2)$$

Equations (3) and (4) were used to calculate the covalency of the β^2 ; in plane π - and α^2 ; in plane σ -bonding [47,48]:

$$\beta^2 = 7/6(-A_{\parallel}/P + A_{\perp}/P + g_{\parallel} - 5/14g_{\perp} - 9/14g_e) \quad (3)$$

$$\alpha^2 = (2.0023 - g_{\parallel})E/8\lambda\beta^2 \quad (4)$$

where E is the electronic transition energy, $\lambda = 135 \text{ cm}^{-1}$, and $P = 128 \times 10^{-4} \text{ cm}^{-1}$. It is reported in the literature that a $g_{\parallel}$ value more than 2.3 for a metal-ligand bond with ionic character and less than 2.3 for a covalent character [49]. The $g_{\parallel}$ value for the $[VOL_1L_2]SO_4$ complex was 1.99, suggesting a covalent character of the ligand-metal bond. The α^2 value for the complex was found much smaller than the β^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 $[VOL_1L_2]SO_4$ and $[CrL_1L_2(Cl)_2]Cl$ 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 $[CrL_1L_2(Cl)_2]Cl$ complex displayed one broad peak ranging from 2θ 20° to 30° in its XRD profile. This broad peak had a maximum at diffraction line 2θ of approximately 26.531° .
- (ii) The $[VOL_1L_2]SO_4$ complex displayed a group of intense lines at Bragg's angle 2θ in the range of 16 – 33° . These lines were observed at 2θ 16.947° , 19.374° , 20.361° , 22.335° , 24.310° , 28.095° , and 30.562° .
- (iii) The SEM micrographs captured at various levels of magnification (i.e., $\times 150$, $\times 500$, $\times 1,000$, $\times 2,000$) indicated visible microstructural differences between the particles of $[VOL_1L_2]SO_4$ and $[CrL_1L_2(Cl)_2]Cl$ complexes.
- (iv) The SEM micrographs of the $[VOL_1L_2]SO_4$ 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 $[\text{VOL}_1\text{L}_2]\text{SO}_4$ complex. (b) SEM micrographs of $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complex.

Figure 8: TEM micrographs of $[\text{VOL}_1\text{L}_2]\text{SO}_4$ and $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complexes.

- (v) The SEM micrographs of the $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ complex shows a coral reefs-like-shaped morphology.
- (vi) 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 $[\text{CrL}_1\text{L}_2(\text{Cl})_2]\text{Cl}$ particles were mixed spherical and oval-shaped.
- (vii) 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 in the range of 7–20 and 20–60 nm, respectively.
- (viii) 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 $\text{Cr}(\text{III})$ and $\text{VO}(\text{II})$. The interaction via a 1:1:1 ($\text{L}_1:\text{L}_2:\text{Metal ion}$) 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 $\text{VO}(\text{II})$ and $\text{Cr}(\text{III})$ 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 (COO) and the N atom of the amino group (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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