Two Mixed-ligand Coordination Polymers: Treatment Activity on Acute Oral Mucositis during Orthodontic Process by Reducing Inflammatory Response

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Abstract: By modulating the metal centers to adjust the coordination surroundings of the products, two mixed-ligand coordination polymers [Cu₂(L)(biz)(OH)]·H₂O (1) and [Zn(HL)(biz)] (2) (H₃L = 5-(4-carboxybenzyloxy)isophthalic acid, biz = benzimidazole), have been produced under mild hydrothermal conditions. To develop new candidates for the acute oral mucositis during orthodontic process, the acute oral mucositis rat model was constructed and the enzyme linked immunosorbent assay (ELISA) was used to find out the release levels of inflammatory cytokines Tumor Necrosis Factor-α (TNF-α) and Interleukin-1β (IL-1β). Next, the activation of the AKT signaling pathway was estimated through judging the relative expression of the inflammatory genes in the oral mucosa cells via reverse transcription-polymerase chain reaction (RT-PCR). After compounds treatment, the expression level of the AKT signaling pathway was evaluated by a western blot. Finally, the quantity of the reactive oxygen species (ROS) in the oral mucosa cells was gauged with ROS detection kit. All the results in this research indicated the much more excellent treatment activity of compound 1 than 2 on the acute oral mucositis.

Key words: coordination polymer, ELISA, RT-PCR, acute oral mucositis

1 Introduction

Oral mucositis is one of the most common and serious complications during orthodontic process. As the pathogenesis of oral mucositis has not been fully explored, effective prevention and treatment measures are currently lacking¹,². This article aimed to develop new candidates for oral mucositis treatment. Revealing the direct and indirect mechanisms and exploring the related causative factors of oral mucositis plays an important role in prevention and treatment of acute oral mucositis³. AKT pathway is an inflammatory signaling pathway, which could lead to the secretion of inflammatory cells, such as TNF-α. The activation of AKT pathway could aggravate oral mucositis.

In recent ten years, coordination polymers (CPs) has been widely used in gas storage, catalysis, nonlinear optics, ion exchange, optics, magnetism and other fields due to its good properties and reasonable structure. It is a new material with very good application prospect⁴-⁹. Generally speaking, the structural characteristics of CPs and the extended coordination framework solids mainly depend on the properties of organic ligands and metal ions¹⁰-¹². Therefore, the research and development of functional groups with bridging metal centers for the design of specific CPs has become a rapidly developing discipline, which involves coordination chemistry, crystal engineering, material science, supramolecular chemistry and many other fields¹³-¹⁵. At the same time, the coordination polymer based on polycarboxylate has multi-directional coordination ability and high sensitivity to acid, which is conducive to the formation of a variety of CPs structures, so it has been widely concerned.

On the other hand, the metal ions usually process different coordination surroundings, which might also result in the structural diversity of the final products¹⁶-¹⁹. With these in mind, by modulating the metal centers to adjust the coordination surroundings of the products, two mixed-ligand coordination polymers [Cu₂(L)(biz)(OH)]·H₂O (1) and [Zn(HL)(biz)] (2) (H₃L = 5-(4-carboxybenzyloxy)isophthalic acid, biz = benzimidazole), have been produced under mild hydrothermal conditions. In order to determine their structures, single-crystal X-ray diffraction analysis, powder X-ray diffraction (PXRD), IR spectra, and thermo-
gravimetric analysis were carried out. The treatment activity of the compounds on acute oral mucositis during orthodontic process was measured. According to the results of ELISA, the secretion of TNF-α and IL-1β was greatly reduced after the compound was used. The results of the RT-PCR indicated that the relative expression of akt and jnk was significantly reduced. In addition to this, the western blot further confirmed the suppression activity of the compound 1 on AKT signaling pathway, but not compound 2. In conclusion, compound 1 can effectively inhibit ROS in oral mucosal cells, however, compound 2 conducts no influence on oral mucositis.

2 Experimental

2.1 Chemicals and measurements

Jinan Henghua Sci. & Tec company provided all the ligand and metal salts needed for the study with compensation. Other materials were obtained from other companies and applied without refinement. The elements of carbon, hydrogen and nitrogen were analyzed by the Vario MACRO cube elemental. In order to record the KBr pellets from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\), we used the FTIR–8400S Spectrometer to scan the samples. For powder X-ray diffraction (PXRD) measurement, we use the Rigaku D/Max–2500 PC diffractometer, with Cu Ka radiation in the range of 20 at 5–50\(^{\circ}\), which \(\lambda = 0.71073\) Å. At the same time, in order to carry out thermogravimetry (TG), we use a ZCT–A analyzer, and keep the nitrogen at 25-800°C and raise the temperature by 10°C every minute.

2.2 Preparation and characterization for \([\text{Cu}_2(\text{L})(\text{OH})] \cdot \text{H}_2\text{O}(1)\) and \([\text{Zn}(\text{HL})(\text{biz})]\) \(\text{(2)}\)

For complex 1, a mixture of Cu(NO\(_3\))\(_2\), 3H\(_2\)O (24 mg, 0.01 mmol), H\(_2\)L (110 mg, 0.35 mmol), trz (24 mg, 0.35 mmol) and 10.0 mL H\(_2\)O was added into a breaker which was adjusted to the pH of 7.5 using 1 M NaOH solution. Then the solution was poured into a 25.0 mL Teflon-lined autoclave and kept at 150°C for 72 hours. After cooling the reaction system at a rate of five degrees per hour, blue crystals of 1 with block shape was obtained. The final yield was 44.5 percent based on the weight of Cu\(^{2+}\) salts. Anal. Cald. for 1 (C\(_{20}\)H\(_{18}\)N\(_4\)O\(_9\)Cu\(_2\)) : the carbon content is 51.30; the hydrogen content is 3.44; and the nitrogen content is 7.98 percent. Meanwhile, the carbon content is 51.46; the hydrogen content is 3.23; and the nitrogen content is 7.65 percent. IR (KBr pellet, cm\(^{-1}\)) : 3200(\(s\)), 3080(\(w\)), 1766(\(s\)), 1649(\(s\)), 1551(\(m\)), 1420(\(w\)), 1250(\(s\)), 1200(\(s\)), 1055(\(m\)), 1026(\(m\)), 910(\(m\)), 750(\(s\)), 650(\(w\)).

For the synthesis of complex 2, a mixture of 30 mg Zn (NO\(_3\))\(_2\), 6H\(_2\)O, 111 mg H\(_2\)L, 41 mg biz and 10.0 mL H\(_2\)O was added into a beaker, which was adjusted to the pH of 7.5 using 1 M NaOH solution. Next, the solution was poured into a 25.0 mL Teflon-lined autoclave, then kept at 150°C for 72 hours. Set a cooling rate of five degrees per hour to cool the reaction mixture to room temperature, washed with water and dried in the air to afford the blue crystals of 2. The final yield was 44.5 percent, based on the weight of Zn\(^{2+}\) salts. Anal. Cald. for 2 (C\(_{30}\)H\(_{24}\)N\(_4\)O\(_9\)Cu\(_2\)) : the carbon content is 56.23; the hydrogen content is 3.28; and the nitrogen content is 5.58 percent. Meanwhile, the carbon content is 56.43; the hydrogen content is 3.20; and the nitrogen content is 5.58 percent. IR (KBr pellet, cm\(^{-1}\)) : 2965(\(w\)), 1734(\(s\)), 1690(\(s\)), 1598(\(s\)), 1460(\(m\)), 1285(\(s\)), 1206(\(s\)), 1121(\(m\)), 1057(\(m\)), 889(\(w\)), 765(\(m\)), 664(\(w\)), 531(\(w\)).

In order to obtain the data of X-ray, we use the Oxford Xcalibur E diffractometer. Statistical analysis of various strength data was performed using crysalispro software and the results were converted into HKL format. The program of SHELXS according to direct method was used to establish the initial structure models, and the program of SHELXL-2014 according to least square means was modified. The atom except hydrogen atom is refined by using different heterogenous parameters. Then all the H atoms by using AFIX command to geometrically fix on the C atom they are linked to. Table 1 shows the parameters and details of complexes 1 and 2.

2.3 ELISA detection

After compounds 1 and 2 were obtained, the effects of both compounds on the treatment of acute oral mucositis in orthodontics were analyzed separately. The ELISA was performed to measure the IL-1β and TNF-α content released from oral mucosa cells. This operation was performed under the manufacturers’ instructions with some changes. In brief the acute oral mucositis rat model was carried out at first. The experimental animals were obtained from research center of Zhejiang University. All animals are bred at 25°C and 45% humidity atmosphere, with proper food and water replenishment. Every procedure in the study are recognized by the Ethics Committee of the Experimental Animal Research Center. In this experiment, there are four groups: control group (sham operation), model group (treatment with PBS), compound 1 group (treatment with compound 1), compound 2 group (treatment with compound 2). After above treatment, the gingival crevicular fluid of different groups was gathered and the content of the TNF-α and IL-1β in the gingival crevicular fluid was evaluated with indicated ELISA detection kit. Three repeats were needed for all experiments.

2.4 Real time RT-PCR

To assess the treatment of compounds 1 and 2 on acute oral mucositis during orthodontic process, the expression of the relative expression of akt and jnk in the oral mucosa cells was evaluated by real time RT-PCR. This operation
was put into effect under the illustration of the manufacturers. Briefly, the acute oral mucositis rat model was constructed, followed by treatment of compound 1 or 2 at 5 mg/kg. Then, the oral mucosa cells were isolated and all RNA in the cells were extracted by TRIzol Reagent (Sigma, St. Louis, MO, USA), and the RNA was reversely transformed into cDNA by RNA reverse transcription equipment after RNA quality measurement. Finally, the RT-PCR was used to evaluate the relative expression level of akt and jnk in the oral mucosa cells. The final result was obtained from three experiments by using 2\(^{-ΔΔCt}\) method.

2.5 Western blot

The activation of the AKT signaling pathway after compounds treatment in the oral mucosa cells was further confirmed by western blot. In brief, the acute oral mucositis rat model was constructed, followed by treatment of compound 1 or 2 at 5 mg/kg. Then the oral mucosa cells were harvested and all the protein in the cells were collected by Total Protein Extraction kit. The all protein concentration was evaluated by BCA Protein Assay Kit and separated by SDS-PAGE gel electrophoresis, followed by electrophoretically transformed to a polyvinylidene fluoride (PVDF) film with thickness of 0.22 mm. After cultivated with primary antibody and suitable secondary antibody conjugated with horseradish peroxidase, the protein images were capture.

2.6 ROS detection

After the operation of the acute oral mucositis rat sample, compounds 1 and 2 were used for treatment. Then, the intracellular ROS accumulation in oral mucosa cells was evaluated by DCFH-DA assay. This study was finished under the illustration of the manufacturers. In brief, the cells were re-suspended in binding buffer, and the cells were placed in 10 μM DCFH-DA solution and kept at 37°C and 5% CO\(_2\) for 30 minutes. Next, the absorbance of all groups was measured with flow cytometer. Three times for all experiments.

### Table 1
Refinement details and crystallographic parameters for complexes 1 and 2.

| Identification code | 1               | 2               |
|---------------------|-----------------|-----------------|
| Empirical formula   | C\(_{30}\)H\(_{23}\)Cu\(_2\)N\(_4\)O\(_9\) | C\(_{23}\)H\(_{14}\)N\(_2\)O\(_7\)Zn |
| Formula weight      | 710.60          | 495.73          |
| Temperature/K       | 173.15          | 293.15          |
| Crystal system      | triclinic       | monoclinic      |
| Space group         | P-1             | P\(_2_1\)/c      |
| a/Å                 | 10.6310(10)     | 14.536(2)       |
| b/Å                 | 11.864(2)       | 7.519(3)        |
| c/Å                 | 11.923(3)       | 18.2140(10)     |
| α/°                 | 75.523(2)       | 90              |
| β/°                 | 86.679(2)       | 107.932(3)      |
| γ/°                 | 72.551(3)       | 90              |
| Volume/Å\(^3\)     | 1388.8(4)       | 1894.0(8)       |
| Z                   | 2               | 4               |
| \(ρ_{calc}\)/cm\(^3\) | 1.699           | 1.738           |
| \(μ/mm\(^{-1}\)     | 1.597           | 1.352           |
| Data/restraints/parameters | 4967/0/409 | 3546/0/298  |
| Goodness-of-fit on \(F^2\) | 1.007          | 1.010           |
| Final R indexes [I≥2σ (I)] | \(R_1 = 0.0629\), \(wR_2 = 0.1680\) | \(R_1 = 0.0533\), \(wR_2 = 0.1431\) |
| Final R indexes [all data] | \(R_1 = 0.1035\), \(wR_2 = 0.2026\) | \(R_1 = 0.0873\), \(wR_2 = 0.1634\) |
| Largest diff. peak/ hole / e Å\(^3\) | 0.93/–0.77 | 0.65/–0.85  |
| CCDC                | 1989934         | 1989935         |

3 Results and Discussion

3.1 Molecular structure

According to crystallographic analysis, the crystal of 1 is located in the group P-1, where is a triclinic space. In the asymmetric unit of 1, there are two Cu(II) atoms, two biz co-ligands, a L\(^{3-}\) ligand, one OH and a water molecule. Figure 1a shows that each CuI atom is a distorted octahe-
dral structure and contains a CuNO5 coordination polyhedron. At the same time, three carboxylic oxygen atoms of two different L^{2−} ligands (O6#1, O1, O2), an oxygen atom from μ3-OH, a carboxylic oxygen atom from L^{1−} ligand (O4#3) and a nitrogen atom from biz ligand (N1) are combined for coordination. The Cu2 atom has a similar CuNO4 coordination environment as Cu1, which is completed by two oxygen atoms from different μ1-OH, a nitrogen atom from biz co-ligand (Cu2), which are symmetrically related to Cu1A and Cu2A, form a[Cu4(μ−OH)3(μOCO)4] under the coordination of two μ1-OH from L^{1−} ligands and four carboxylic acid groups. The L^{1−} ligand shows a μ5-η2:η0:η1:η1:η1 coordination mode connecting with adjacent Cu4 clusters into a 2D layered framework (Fig. 1c). Every L^{1−} ligand connects the Cu4-based SBUs to form a 3-connected node; every Cu4-based SBUs combines with six L^{1−} ligands to form a 6-connected node. Finally, the shape of 1 is an indifferent 2-nodal(3,6)-connected frame. According to the topologic results of TOPOS program, the (3,6)-connected net with the (4^3) (4^0·6^0·8^0) topology (Fig. 1d).

According to the results of single crystal X-ray analysis, the crystal of 2 is located in the group P21/c, where is a monoclinic space. Among them, the asymmetric part contains a Zn(II) atom, a biz co-ligand and an HL^{2−} ligand. Figure 2a shows that Zn(II) atom combines with a nitrogen atom (N1) from a biz co-ligand and three carboxylic oxygen atoms (O2#2, O3#1, O4) from HL^{2−} ligands to form tetrahedral structure. Every biz co-ligand binds to a Zn(II) atom in a single dentate mode. With two carboxylic groups as mediators, every HL^{2−} ligand connects three CoII atoms. Figure 2b shows the coordination mode of HL^{2−} ligand (μ3-η1:η1:η0:η0:η0:η0). Due to the effect of unusual pH value, part of carboxybenzyloxy part of HL ligand is converted to HL^{2−}, and there is no coordination. Two Zn(II) atoms are linked by two carboxylic acid groups of two HL^{2−} ligands to form a[Zn4(CO3)]3 that the distance of Zn⋯Zn is 4.223(2) Å. A nitrogen atom from biz co-ligand and a carboxylate oxygen atom from HL^{2−} ligand combine with every Zn(II) atom of[Zn4(CO3)]3 to obtain Zn2-based SBUs [Zn4(CO3)2O6]. At the same time, HL^{2−} ligands connect Zn2-based SBUs to form a two-dimensional framework. Figure 2c shows that the non-deprotonated carboxybenzyloxy group points up and down to 2D tablets, respectively. Hydrogen bonding between all H atoms on every carboxylic acid group and the O atom on the adjacent carboxylic acid group (O6-H6A···O2, Fig. 2d) makes the two-dimensional structure of the complex 2 expand into a three-dimensional network. In the topological point of view, every HL^{2−} ligand is considered to be a linear connector between Zn2-based SBUs; although every Zn2-based SBU is considered to be a 4-connection node, the whole framework of 2 is a scalable impartial 4-connection framework with 8d symbols.

As shown in Fig. 3a, powder X-ray diffraction (PXRD) test was conducted on the powder-like samples by X-ray to
test the purity of the product. The experimental results are consistent with the simulated PXRD peaks, the simulated structure fully reflects the real structure of the crystals. Due to the different quality of the samples, it may lead to the strength difference within a certain range. To check the thermal stability of 1 and 2, we applied thermogravimetric analysis on the samples (Fig. 3b). When TGA curve is 1, the water molecules gradually disappear since the temperature reached 80 degrees (Obsd 3.2%, calcld 2.6%), and whole framework also decomposes. The residues were in accordance with oxide. According to the results of TGA analysis, 2 is stable in the range of room temperature to 260°C. The severe weight loss over 260°C is due to structural decomposition. The final product is metal oxide. Different crystal structures lead to different thermal behaviors.

3.2 Compound reduced the releasing of IL-1β and TNF-α in the gingival crevicular fluid

In the contrast of the acute oral mucositis during orthodontic process, there was an abnormal increased level of inflammatory response in the oral mucosa cells. Thus, after the formation of compounds 1 and 2, their treatment activity against acute oral mucositis was assessed with ELISA detection. As the results showed in Fig. 4, in this study, the level of TNF-α and IL-1β was higher in the gingival crevicular fluid than that in the control group. While, the release of TNF-α and IL-1β was suppressed after the compound 1 was used, but compound 2 is invalid of the inflammatory cytokines releasing.

3.3 Compound inhibited the relative expression of akt and jnk in the oral mucosa cells

After testifying the inhibitory effect of compound 1 on the number of TNF-α and IL-1β in the gingival crevicular fluid...
fluid, the related mechanism was still needed to be further explored. As the AKT signaling pathway influence the production of TNF-α and IL-1β in the gingival crevicular fluid. Thus, the relative expression of akt and jnk in the oral mucosa cells was evaluated by RT-PCR. Figure 5 indicates that the high level of akt and jnk in the oral mucosa cells could be reduced by compound 1, but compound 2 is invalid of the inflammatory gene expression.

3.4 Compound suppressed the activation of AKT signaling pathway in the oral mucosa cells

In addition to the RT-PCR determination about the relative expression of akt and jnk in the oral mucosa cells, the western bolt was further performed to evaluate the activation of AKT signaling route in the oral mucosa cells after compounds treatment. From Fig. 6, we got this information, the promoting ability of the AKT signaling route in the oral mucosa cells was up-regulated in the model group, there was obviously difference between the model and control groups. Compound 1 treatment significantly reduced the activation ability of the AKT signaling pathway. In consistence with the previous results, compound 2 had no influence on the AKT signaling pathway activation.

**Fig. 4** Reduced releasing of TNF-α and IL-1β in the gingival crevicular fluid after compound treatment. The acute oral mucositis rat model was constructed, followed by treatment of compound 1 or 2 at 5 mg/kg. ELISA detection was conducted to measure the quantity of TNF-α and IL-1β in the gingival crevicular fluid. "*" means $p<0.05$ and "***" means $p<0.005$.

**Fig. 5** Inhibited relative expression of akt and jnk in the oral mucosa cells after compound treatment. The acute oral mucositis rat model was constructed, followed by treatment of compound 1 or 2 at 5 mg/kg. The RT-PCR was conducted to measure the relative expression of akt and jnk in the oral mucosa cells after compounds treatment. "*" means $p<0.05$ and "***" means $p<0.005$. 
3.5 Compound inhibited the accumulation of ROS in oral mucosa cells

The accumulation of ROS in cells could trigger the inflammatory response. Therefore, in this study, the DCFH-DA assay was conducted according to the protocols to detect the accumulation of ROS in oral mucosa cells after compound treatment. Figure 7 indicated that there was significantly increased of ROS in model group, which is consistence with the higher inflammatory response in model group confirmed in the previous experiment. However, after using compound 1, the accumulation of ROS in oral mucosa cells had a big drop. Compound 2 still had no effect on the ROS collection in oral mucosa cells.

4 Conclusion

In summary, by modulating the metal centers to adjust the coordination surroundings of the products, two innovative composite-ligand coordination polymers have been successfully synthesized through mild hydrothermal
factors. In order to determine their structures, we used many instruments, such as single-crystal X-ray diffraction analysis, powder X-ray diffraction (PXRD), IR spectra, and thermogravimetric analysis. According to the results of structural analyses, complex 1 shows the 2D layer 4-connected $\text{SO}_{\text{4}}$ topology while complex 2 is a 2D sheet framework. In topology, complex 2 is a $(3,6)$-connected net with $(4^4)(6^68^3)$. The biological function of compounds 1 and 2 was measured, moreover, intrinsic mechanism was detected. The outcome of the ELISA indicated that the compound has better inhibitory activity against inflammatory cytokines TNF-$\alpha$ and IL-1$\beta$ releasing. The data of the $\beta$ and IL-1$\tau$ cytokines TNF-$\alpha$ showed no influence on the ROS production. In brief, the ROS in the oral mucosa cells was substantially reduced after compound 1 treatment, while compound 2 showed no influence on the ROS production. In brief, the compound 1 showed better treatment effect than compound 2 on acute oral mucositis during orthodontic process through reducing the inflammatory response in oral mucosa cells.

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