Asian Journal of Chemistry; Vol. 25, No. 8 (2013), 4401-4403

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13992

# Synthesis, Crystal Structure and Antitumor Activity of 1D Coordination Polymer of Ca(II) and Na(I) with N-*p*-tolylsulfonyl-glycine

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(*Received*: 30 April 2012; *Accepted*: 11 February 2013) AJC-12974

1D coordination polymer formed by Ca(II) and Na(I) was synthesized by the reaction of calcium perchlorate, NaOH with N-*p*-tolylsulfonyl-glycine in the $CH_3CH_2OH/H_2O$ (v:v = 3:1). It was characterized by elemental analysis, IR and X-ray single crystal diffraction analysis. The crystal of the complex belongs to triclinic, space group P-1 with a = 0.95657(10) nm, b = 1.09171(11) nm, c = 1.8292(2) nm, α = 80.6790(10)°, β = 86.831(2)°, γ = 89.957(2)°, V = 1.8821(3) $nm^3$, Z = 2, $D_c$ = 1.599 Mg $m^{-3}$, μ = 0.507 $mm^{-1}$, $F_{(000)}$ = 936 and final $R_1$ = 0.0981, $wR_2$ = 0.2262. The complex comprises a seven-coordinated Ca(II) center, with a $O_7$ distorted pengonal coordination environment and a six-coordinated Na(I) center, with distorted octahedron environment. The molecules are connected by the oxygen atoms of carboxylates to form one dimensional chain structure. The antitumor activities against gastric cancer cells of free ligand and its Ca(II) complex were studied by MTT method.

**Key Words: N-*p*-Tolysulfonyl-glycine, Ca(II) complex, Synthesis, Crystal structure, Antitumor activity.**

## INTRODUCTION

In recent years, coordination polymers have attracted much attention owing to their enormous variety of interesting framework topologies and their wide range of potential applications in adsorption, separation, catalysis, biological property and luminescence[1-3]. To data, a large number of coordination polymers assembled from carboxylates and transition metals have been extensively investigated[4,5]. However, the coordination polymers of Ca(II) with carboxylates have rarely been studied due to the low coordination ability of Ca(II)[6]. So it is essential to design appropriate ligands to form the stable Ca(II) complex. In this paper, we report the synthesis and X-ray crystal structure of 1D coordination polymer formed by Ca(II) and Na(I). The antitumor activities against gastric cancer cells of free ligand and its Ca(II) complex were studied by MTT method.

## EXPERIMENTAL

The following A.R. grade chemicals were used for the preparation of the studied compound *e.g.*, calcium perchlorate, *p*-tolysulfonyl chloride, glycine, sodium hydroxide.

The carbon, hydrogen and nitrogen content in the newly synthesized compound were determined on a Elementar Vario III EL elemental analyzer. Infrared spectrum (4000-400 $cm^{-1}$) was recorded with KBr optics on a Nicolet AVATAR 360 FTIR spectrophotometer. The crystal data was collected on a Bruker smart CCD Area Detector.

**Synthesis of the ligand:** 10 mmol (0.7507 g) of glycine and 20 mmol (0.8 g) of sodium hydroxide were dissolved in 100 mL of water at room temperature and added drop by drop 10 mmol (1.9065 g) of *p*-tolylsulfonyl chloride by stirring at room temperature. The reaction solution was kept running for 4 h, then acidified with the solution of hydrochloric acid (V:V = 1:1) to pH = 2. The white solid precipitation were collected by filtration, washed and dried under vacuum (Fig. 1). Yield may reach up to over 65 %. Elementary analysis: calcd. (%) for $C_9H_{11}NSO_4$: C, 47.16; H, 4.80; N, 6.11; found (%): C, 47.58; H, 4.52; N, 6.39. IR (KBr, $\nu_{max}$, $cm^{-1}$): (C=O): 1719, (N-H): 3248.

**Synthesis of Ca(II) complex:** 1 mmol of N-*p*-tolylsulfonyl-glycine and 1 mmol (0.04 g) of sodium hydroxide were added to the 10 mL of $C_2H_5OH/H_2O$ (v:v = 3:1) solution. After being dissolved, 0.5 mmol of calcium perchlorate was added to the solution. The mixture was continuously stirred for 3 h at refluxing temperature. The mixture was cooled at room temperature and was collected by filtration. By evaporation in air at room temperature, the single crystal suitable for X-ray determination was obtained from methanol solution after 15 days. Yield: 57 %. Elementary analysis: calcd. (%) for $C_{27}H_{34}N_3O_{18}S_3ClCaNa_2$: C, 35.75; H, 3.75; N, 4.63; found (%): C, 35.58; H, 3.49; N, 4.72. IR (KBr, $\nu_{max}$, $cm^{-1}$): (C=O): 1680, (N-H): 3247, ($H_2O$): 3428, (Ca-O): 418.

**X-Ray crystallography:** A colourless block single crystal with dimensions of 0.48 mm × 0.47 mm × 0.23 mm was placed on a glass fiber and mounted on a CCD area detector. Diffraction data were collected by ϕ~ω scan mode using a graphite-monochromatic $MoK_\alpha$ radiation (λ = 0.71073 Å) at 293(2) K. A total of 9043 reflections were collected in the range 2.04-25.01°, of which 6031 were unique ($R_{int}$ = 0.0523) and 4640 were observed with I > 2σ(I). The data were corrected for Lp factors. The structure was solved by direct methods and refined by full-matrix least-squares techniques on $F^2$. The structure was solved by direct methods[7] using SHELXL-97 and expanded using Fourier techniques. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The final refinement by full-matrix least squares method was converged at R = 0.0981 and wR = 0.2262 ($w = 1/[\delta^2(Fo^2) + (0.1064P)^2 + 11.3326P]$, $P = (Fo^2 + 2Fc^2)/3$, S = 1.040, $(\Delta/\sigma)_{max} = 0.001$). The largest peak in the final difference Fourier map is 0.812 e/Å$^3$ and the minimum peak is -0.487 e/Å$^3$. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package[8]. The most relevant crystal data for complex are presented in Table-1 and the selected bond distances and angles are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR Ca(II) COMPLEX

| | |
|---|---|
| Formula | $C_{27}H_{34}N_3O_{18}S_3ClCaNa_2$ |
| Formula weight | 906.26 |
| Crystal system | Triclinic |
| Space group | P-1 |
| a (Å) | 9.5657(10) |
| b (Å) | 10.9171(11) |
| c (Å) | 18.292(2) |
| α (°) | 80.6790(10) |
| β (°) | 86.831(2) |
| γ (°) | 89.957(2) |
| Z | 2 |
| $F_{(000)}$ | 936 |
| Temperature (K) | 293(2) |
| V (Å$^3$) | 1882.1(3) |
| Calculated density (g cm$^{-3}$) | 1.599 |
| Crystal size (mm$^3$) | 0.48 × 0.47 × 0.23 |
| μ (mm$^{-1}$) | 0.507 |
| Limiting indices | -10 ≤ h ≤ 11, -11 ≤ k ≤ 12, -13 ≤ l ≤ 21 |
| Reflections collected | 9043 |
| Reflections unique | 6031 |
| $R_1$, $wR_2$ [all data] | 0.1187, 0.2391 |
| $R_1$, $wR_2$ [I > 2σ(I)] | 0.0981, 0.2262 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.812, -0.487 |

**Antitumor activity:** Gastric cancer cells were propagated continuously in culture and grown in RPMI 1640 medium with 10 % inactivated fetal calf serum and antibiotics. Cell harvested from exponential phase were seeded equivalently into 96 well plates and incubated for 24 h, then compounds studied were added in a concentration gradient. The final concentrations were maintained at c/(μg mL$^{-1}$) 5, 10, 20, respectively. The plates were maintained at 37 ºC in a humidified 5 % $CO_2$-90 % $N_2$-5 % $O_2$ atmosphere and incubated for 48 h, the MTT solution was added, the following procedure referred to[10]. The measurements of absorption of the solution concerned with the number of live cells were performed on spectrophotometer at 570 nm.

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR Ca(II) COMPLEX

| | | | |
|---|---|---|---|
| Ca1-O9 | 2.375(5) | Na1-O7 | 2.40(2) |
| Ca1$^{i}$-O10 | 2.442(4) | Na1$^{iii}$-O11 | 2.416(5) |
| Ca1$^{ii}$-O1 | 2.470(5) | Na1$^{ii}$-O1 | 2.433(5) |
| Ca1-O14 | 2.496(5) | Na1$^{i}$-O10 | 2.512(6) |
| Ca1-O6 | 2.534(5) | Na2$^{iv}$-O4 | 2.324(6) |
| Ca1-O13 | 2.568(5) | Na2$^{v}$-O12 | 2.325(5) |
| Ca1-O5 | 2.588(5) | Na2$^{i}$-O10 | 2.339(5) |
| Ca1$^{i}$-O19 | 3.231(6) | Na2-O13 | 2.435(6) |
| Na1-O3 | 2.347(6) | Na2$^{ii}$-O1 | 2.445(5) |
| Na1-O5 | 2.375(5) | Na2$^{iii}$-O11 | 2.521(6) |
| N1-C2 | 1.414(9) | N2-S2 | 1.619(7) |
| N1-S1 | 1.597(5) | N3-S3 | 1.585(5) |
| N2-C11 | 1.453(11) | – | – |
| O2$^{i}$-Ca1-O9 | 91.21(18) | O2$^{i}$-Ca1-O14 | 81.34(19) |
| O2$^{i}$-Ca1-O10$^{i}$ | 151.75(19) | O9-Ca1-O14 | 67.78(18) |
| O9-Ca1-O10$^{i}$ | 105.95(16) | O10$^{i}$-Ca1-O14 | 84.60(18) |
| O2$^{i}$-Ca1-O1$^{ii}$ | 107.88(17) | O1$^{ii}$-Ca1-O14 | 141.14(18) |
| O9-Ca1-O1$^{ii}$ | 146.12(19) | O2$^{ii}$-Ca1-O6 | 76.20(19) |
| O10$^{i}$-Ca1-O1$^{ii}$ | 69.65(15) | O3-Na1-O5 | 114.3(2) |
| O3-Na1-O7 | 79(3) | O14-Ca1-O6 | 137.71(18) |
| O5-Na1-O7 | 84(4) | O2$^{i}$-Ca1-O13 | 76.91(18) |
| O3-Na1-O1$^{ii}$ | 154.3(2) | O9-Ca1-O13 | 140.88(18) |
| O5-Na1-O1$^{ii}$ | 75.83(17) | O10$^{i}$-Ca1-O13 | 75.66(16) |
| O7-Na1-O1$^{ii}$ | 127(3) | O1$^{i}$-Ca1-O13 | 72.16(16) |
| O3-Na1-O10$^{i}$ | 88.30(19) | O14-Ca1-O13 | 73.59(17) |
| O11-Na2-O13$^{i}$ | 80.15(18) | O6-Ca1-O13 | 132.98(17) |
| O13-Na2-O1$^{ii}$ | 74.90(18) | O2$^{ii}$-Ca1-O5 | 127.16(18) |
| O9-Ca1-O6 | 77.27(17) | O9-Ca1-O5 | 74.71(18) |
| O10$^{i}$-Ca1-O6 | 128.83(17) | O10-Ca1-O5 | 79.77(16) |
| O1$^{ii}$-Ca1-O6 | 80.43(15) | O1$^{ii}$-Ca1-O5 | 71.45(15) |
| – | – | O14-Ca1-O5 | 133.24(17) |
| – | – | O6-Ca1-O5 | 51.17(16) |

Symmetry codes: (i) -x+1, -y+1, -z+1; (ii) x+1, y, z; (iii) x, y-1, z; (iv) -x+1, -y, -z+1; (v) -x+2, -y+1, -z+1.

## RESULTS AND DISCUSSION

**IR Spectra:** The free ligand exhibits characteristic the COOH stretching band at 1719 and 1436 cm$^{-1}$, which appeared at at 1718 cm$^{-1}$ was assigned as $\nu_{as}(COO^-)$ and that at 1435 cm$^{-1}$ as $\nu_s(COO^-)$ in the complex, the lower shifting of $COO^-$ stretching frequency verify the coordination of the carboxylate oxygen atoms with Ca(II) ion[10]. The -$SO_2$- stretching frequency occurs at 1336 and 1201 cm$^{-1}$, whereas for the complex which appears at 1288 and 1176 cm$^{-1}$. The -$SO_2$- stretching frequency is shifted to a lower frequency, suggesting that the Na-O bands are formed between the Na ion and oxygen atoms of -$SO_2$- groups. In addition, the band at 3426 cm$^{-1}$ shows that the complex contains water molecules, which are accordance with the results of elemental analysis.

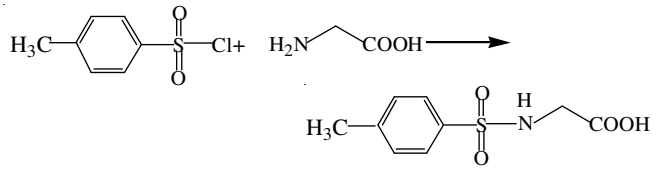


Fig. 1. Synthesis of ligand

**Structure description:** Perspective view of the molecule in a unit cell and molecular packing arrangement are shown in Figs. 2 and 3, respectively. It can be seen that the coordination environment of the Ca(II) atom consists of eight oxygen atoms from the coordinated water molecules and N-*p*-tolysulfonyl-glycinate ligand, making up a distorted pseudo square antiprismatic environment. In the complex molecule, it consists of two different Na ions. Na1 is coordinated by six oxygen atoms from the carboxylatos and S=O groups of N-*p*-tolysulfonyl-glycinate ligand, making up a distorted octahedral environment. $Na_2$ is coordinated by five oxygen atoms from the carboxylatos and S=O groups of N-*p*-tolysulfonyl-glycinate ligand and one oxygen atom from the coordinated water molecules, also making up a distorted octahedral environment. The distances of the Ca(1)-O bonds are in the range of 2.293(5)-2.588(5) Å, which are similar to the Ca-O bond lengths reported previously[11-13]. The distances of the Na(1)-O bonds are in the range of 2.347(6)-2.512(6) Å and that of Na (2)-O bonds are in the range of 2.324(6)-2.521(6) Å, respectively.

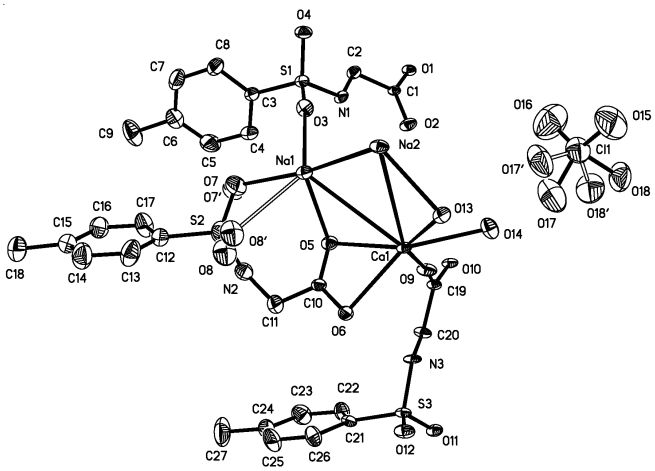


Fig. 2. Molecular structure of the complex, where the thermal ellipsoids were drawn at 30 % possibility

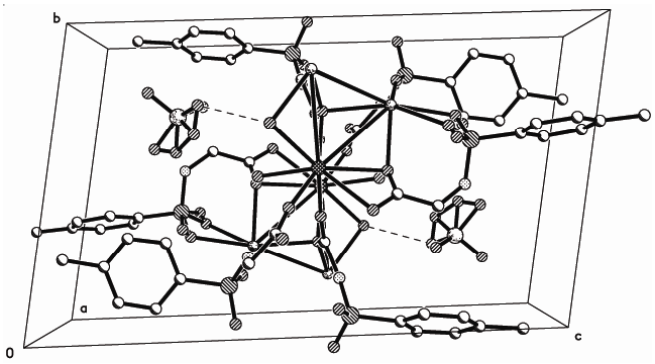


Fig. 3. Packing of the complex in the unit cell

The complex forms one dimensional chain structure by the bridging $NaO_6$ units, intramolecule and intermolecule hydrogen bonds and π-π stacking (Fig. 4).

As illustrated in Fig. 4, the complex molecules form one dimensional chained structure by the intramolecular and intermolecular hydrogen bonds [N1-H1···O2, 2.611 (8) Å; N1-H1···O14, 3.207(8) Å, symmetry code: 1-x, 1-y, 1-z; N3-H3···O6, 2.946 (7) Å; N3-H3···O9, 2.641 (7) Å; O13-H13B···O6, 2.827 (7) Å, symmetry code: 2-x, 2-y, 1-z; O14-H14B···O5, 2.883 (7) Å, symmetry code: 1-x, 1-y, 1-z.

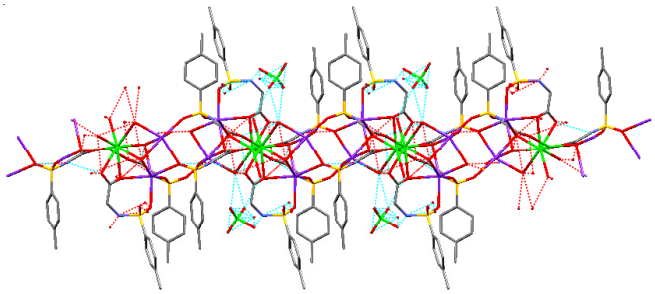

Fig. 4. One dimensional chained structure of complex

**Antibacterial activity:** The data of the antitumor activities of Ca(II) complex and ligand are given in Table-3. The concentration of DMSO was controlled under 1 % to assure not to affect the results[14]. As can be seen, the inhibitory rates of Ca(II) complex against gastric cancer cells increased with increasing of dose. The inhibitory effects of Ca(II) complex are higher than that of ligand.

TABLE-3
ANTITUMOR ACTIVITY OF AGAINST GASTRIC CANCER CELLS

| Compound | Dose (μg $mL^{-1}$) | Inhibitory rate (%) |
|---|---|---|
| Ca(II) complex | 5.0 | 16.0 |
| | 10.0 | 23.48 |
| | 20.0 | 32.99 |
| N-*p*-Tolylsulfonyl-glycine | 5.0 | 11.50 |
| | 10.0 | 18.93 |
| | 20.0 | 24.70 |

## ACKNOWLEDGEMENTS

The authors thank the National Natural Science Foundation of China (No. 21171132 and 20671073), the Promotive Research Fund for Excellent Young and Middle-aged Scientisits of Shandong Province (2010BSA07004) and Science Foundation of Weifang University.

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