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Synthesis, Crystal Structure and Antibacterial Activity of Ca(II) Complex with 2-(Phenylsulfonamido)acetic Acid

TAI XI-SHI*, CHU SI-YUAN and TANG CHUN-YING

College of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, P.R. China

*Corresponding author: Fax: +86 536 8785363; Tel: +86 536 8785363; E-mail: taixs@wfu.edu.cn

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A new ligand 2-(phenylsulfonamido)acetic acid (L) and its Ca(II) complex have been synthesized and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. The results showed that the complex formed one dimensional chained structure through intramolecule and intermolecule hydrogen bonds and π-π stacking. The antibacterial assay of the Ca(II) complex and the lignd L was tested using a modified version of 2-fold serial dilution method. The Ca(II) complex shows considerable antibacterial activity against *Escherichia coli, Bacillus subtilis and Staphylococcus white*.

Key Words: 2-(Phenylsulfonamido)acetic acid, Ca(II) complex, Crystal structure, Antibacterial activity.

INTRODUCTION

Calcium is the indispensable element in biology. It is involved in several biochemical processes and is the essential cofactor required for the activation of a variety of enzymes. In the process of metabolism, calcium ions possess of a variety of coordination structures and play an important role in catalysis. It can be as the enzyme activator and bridged the adjacent carboxylates to strengthen the cell membrane in the lipoprotein[1-3]. In eucaryotes, calcium ions are involved in regulation of dozens of processes, such as mitosis, muscle contraction, proliferation and coagulation of blood, hormone secretion and differentiation in different types of cells. In addition, it also plays an integrating role in controlling coordinated function of different compartments, cells and organs. Thus, it is referred to the metal of life[4-6]. It is significant to study[7] on the structure and characteristic coordination of calcium for making sure about physiological and biochemical mechanisms of all lives.

Aromatic compounds with carboxylic acid are affluent in the coordination structures[8,9], their complexes are important for academic significance, but also possess potential application and prospect in many areas, such as material, biochemistry, medicinal preparation, catalytic behavior, micro-porosity, electrical conductivity, non-linear optical activity and cooperative magnetic behavior[10-14]. Herein, a novel calcium complex was synthesized by the reaction of calcium perchlorate tetrahydrate with 2-(phenylsulfonamido)acetic acid and was characterized by X-ray single crystal diffraction, indicating that the complex formed one-dimensional chain structure. The antibacterial assay of the Ca(II) complex was tested using a modified version of the 2-fold serial dilution method.

EXPERIMENTAL

The following AR grade chemicals were used for the preparation of the studied compound: calcium perchlorate tetrahydrate, benzenesulfonyl 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 (1.7662 g) of benzenesulfonyl 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. Yield may reach up to over 65 %. Elementary analysis: calcd. (%) for $C_8H_9NSO_4$: C, 44.65; H, 4.19; N, 6.51; found (%): C, 44.58; H, 4.52; N, 6.59. IR (KBr, ν_{max}, cm^{-1}): (C=O): 1718, (N-H): 3248 (Fig. 1).

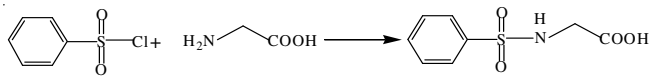

Fig. 1. Synthesis and structure of 2-(phenylsulfonamido)acetic acid

Synthesis of Ca(II) complex: 1 mmol (0.215 g) of 2-(phenylsulfonamido)acetic acid and 1 mmol (0.04 g) of sodium hydroxide were added to the 10 mL of CH_3OH/H_2O (v:v = 2:1) solution. After being dissolved, 0.5 mmol (0.138 g) of calcium perchlorate tetrahydrate 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 10 days. Yield: 56 %. Elementary analysis: calcd. (%) for $C_{24}H_{24}N_3O_{12}S_3CaNa$: C, 40.85; H, 3.43; N, 5.95; found (%): C, 40.58; H, 3.69; N, 5.72. IR (KBr, ν_{max}, cm^{-1}): (C=O): 1677, (N-H): 3248, (H_2O): 3423.

X-Ray crystallography: A colourless block single crystal with dimensions of 0.49 mm × 0.46 mm × 0.40 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_α radiation (λ = 0.71073 Å) at 298 (2) K. A total of 14432 reflections were collected in the range 1.39-25.01º, of which 5190 were unique (R_{int} = 0.045) and 3866 were observed with $I > 2\sigma(I)$. 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[15] 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 = 0.041 and wR = 0.1166 ($w = 1/[\delta^2(Fo^2) + (0.0507P)^2 + 2.4758P]$, $P = (Fo^2 + 2Fc^2)/3$, S = 1.055, $(\Delta/\sigma)_{max} = 0.001$). The largest peak in the final difference Fourier map is 0.512 e/Å^3 and the minimum peak is -0.513 e/Å^3. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package[16]. The most relevant crystal data for complex are quoted in Table-1 and the selected bond distances and angles are listed in Table-2.

Antibacterial assay: The ligand and the complex were dissolved in sterile water and tested against three reference strains for antibacterial activity, respectively. The antibacterial assay was performed using a modified version of the 2-fold serial dilution method[17], in which the concentration of compounds decreased half as many in a sterile culture medium containing broth as the nutrient and the strains were incubated 16 h in the culture mediums at the constant temperatures 37 ºC after being activated and misce bene after being added to the test tubes of chemical medicine, then readings were taken after 24 h of incubation at the constant temperatures 37 ºC. All other test conditions were standardized. The resultant turbidities in all tubes were estimated visually and the lowest drug concentrations were found, which is defined minimum inhibitory concentration (MIC). After 48 h of continuous incubation, the minimum bacterial concentration (MBC) was defined, too.

TABLE- 1
CRYSTALLOGRAPHIC DATA FOR Ca(II) COMPLEX

Formula	$C_{24}H_{24}N_3O_{12}S_3CaNa$
Formula weight	705.71
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	17.406(2)
b (Å)	8.7089(10)
c (Å)	20.069(3)
α (º)	90.00
β (º)	104.088(2)
γ (º)	90.00
Z	4
$F_{(000)}$	1456
Temperature (K)	298(2)
V (Å^3)	2950.8(6)
Calculated density (g cm^{-3})	1.589
Crystal size (mm^3)	0.49 × 0.46 × 0.40
μ (mm^{-1})	0.507
Limiting indices	$-16 \le h \le 20$, $-10 \le k \le 8$, $-23 \le l \le 23$
Reflections collected / unique	5190/3866
R_1, wR_2 [all data]	0.0621, 0.1166
R_1, wR_2 [$I > 2\sigma(I)$]	0.0405, 0.0989
Largest diff. peak and hole (e Å^{-3})	0.512, -0.513

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

Ca1-O10^{i}	2.322 (2)	Na1-O7^{iii}	2.377 (2)
Ca1-O9	2.323 (2)	Na1-O3^{iv}	2.403 (2)
Ca1-O2^{i}	2.339 (2)	Na1-O1	2.412 (2)
Ca1-O6^{ii}	2.362 (2)	Na1-O4^{v}	2.413 (2)
Ca1-O1	2.402 (2)	Na1-O8^{vi}	2.447 (2)
Ca1-O5	2.435 (2)	Na1-O5	2.456 (2)
O10^{i}-Ca1-O9	162.14 (8)	O7^{iii}-Na1-O3^{iv}	84.60 (9)
O10^{i}-Ca1-O2^{i}	81.60 (8)	O7^{iii}-Na1-O1	97.56 (8)
O9-Ca1-O2^{i}	80.91 (8)	O3^{iv}-Na1-O1	165.63 (9)
O10^{i}-Ca1-O6^{ii}	92.07 (9)	O7^{iii}-Na1-O4^{v}	83.47 (9)
O9-Ca1-O6^{ii}	82.15 (8)	O3^{iv}-Na1-O4^{v}	106.60 (9)
O2^{i}-Ca1-O6^{ii}	82.73 (8)	O1-Na1-O4^{v}	87.77 (9)
O10^{i}-Ca1-O1	88.51 (8)	O7^{iii}-Na1-O8^{vi}	101.33 (9)
O9-Ca1-O1	108.77 (8)	O3^{iv}-Na1-O8^{vi}	81.34 (9)
O2^{i}-Ca1-O1	169.79 (8)	O1-Na1-O8^{vi}	84.30 (8)
O6^{ii}-Ca1-O1	95.17 (7)	O4^{v}-Na1-O8^{vi}	171.20 (10)
O10^{i}-Ca1-O5	105.54 (8)	O7^{iii}-Na1-O5	163.22 (9)
O9-Ca1-O5	82.97 (8)	O3^{iv}-Na1-O5	103.79 (8)
O2^{i}-Ca1-O5	106.45 (8)	O1-Na1-O5	77.97 (7)
O6^{ii}-Ca1-O5	161.02 (8)	O4^{v}-Na1-O5	80.22 (8)
O1-Ca1-O5	78.57 (7)	O8^{vi}-Na1-O5	94.36 (9)

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

RESULTS AND DISCUSSION

IR spectra: In the infrared spectra, the ν(COOH) vibration of the free ligand are at 1718 cm^{-1}. For the complex, the vibration was shifted to 1677 cm^{-1}, which can be explained that the carboxylate oxygen atoms of 2-(phenylsulfonamido) acetic acid ligand are involved in the coordination with calcium atoms as bridging didentate[18]. The bands of the $-SO_2-NH-$ groups at 3248, 1320 and 1155 cm^{-1} show that there are uncoordinated atoms of the groups, because compared with the free ligand the strong absorption bands are not shifted. In addition, the band at 3423 cm^{-1} shows that the complex contains water

molecules, which are in accordance with the results of elemental analysis.

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 three oxygen atoms from the three 2-(phenylsulfonamido)acetic acid ligands and three oxygen atoms from the coordinated water molecules, making up a distorted octahedral environment. The coordination atoms (O(5), O(6), O(9), O(10)) are situated equatorial place and the coordination atoms (O(1), O(2)) are situated axial place. In the complex molecule, the Na(II) atom coordinates with two oxygen atoms from the two carboxylato group of two 2-(phenylsulfonamido)acetic acid ligands, one oxygen atom of S=O group and three oxygen atoms from the coordinated water molecules, also making up a distorted octahedral environment. The coordination atoms (O(1), O(3), O(4), O(8)) are situated equatorial place and the coordination atoms (O(5), O(7)) are situated axial place. The distances of the Ca(1)-O bonds are in the range of 2.322(2) 2 - 2.435(2) Å, which are similar to the Ca-O bond lengths reported previously[19].

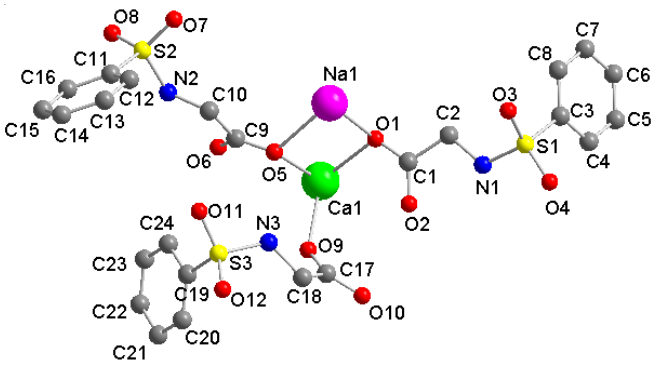

Fig. 2. Molecular structure of the complex, where the thermal ellipsoids were drawn at 30 % possibility. Ca-Na distance is 3.7567(11) Å

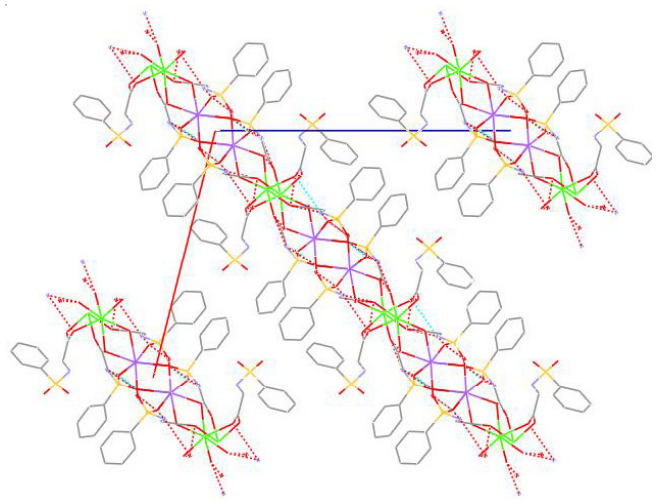

Fig. 3. One dimensional chain of the complex

The complex forms one dimensional chain structure along the b axis by intramolecule and intermolecule hydrogen bonds and π-π stacking. The coordination polyhedron of Ca and Na atoms in the complex and the 2D infinite net structure of complex viewed down the a axis is shown in Fig. 4.

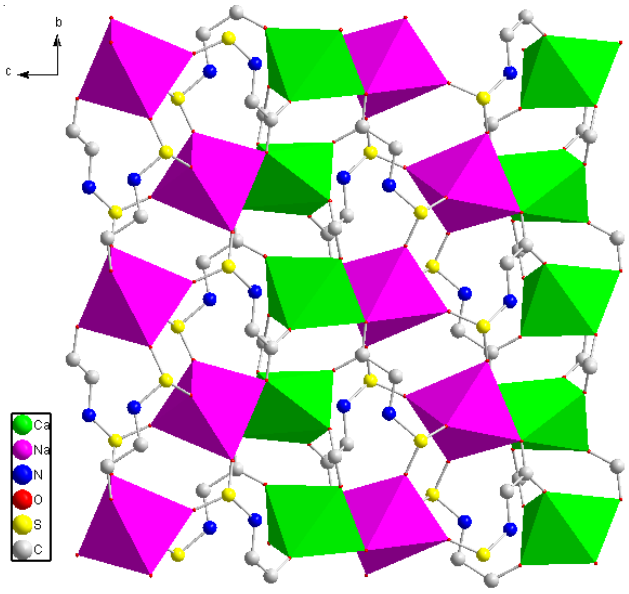

Fig. 4. Coordination polyhedron of Ca and Na atoms in the complex, and the 2D infinite net structure of complex viewed down the a axis. Hydrogen atoms and phenyl groups are omitted for clarity

Antibacterial activity: The antibacterial activity of the 2-(phenylsulfonamido)acetic acid ligand and Ca(II) complex were assayed using three bacterial strains (*Escherichia coli, Bacillus subtilis* and *Staphylococcus white*). The antibacterial results of the complex are listed in Table-3 and the results indicate that the Ca(II) complex shows considerable antibacterial activity. Compared with the complex, the N-2-(phenylsulfonamido)acetic acid ligand did not show antibacterial activity. So the complex will provide potential applications in the broad spectrum of the antibacterial field.

TABLE-3
MIC AND MBC OF COMPLEX AGAINST THREE BACTERIAL STRAINS

Strains	MIC (mg/mL)	MBC (mg/mL)
Escherichia coli	0.675	0.675
Bacillus subtilis	0.675	1.250
Staphylococcus white	0.625	0.625

MIC: Minimal inhibitory concentration. MBC: Minimal bactericidal concentration.

Conclusion

In summary, a novel Ca(II) complex has been synthesized and structurally characterized. The Ca(II) ion is coordinated by three oxygen atoms from the three 2-(phenylsulfonamido) acetic acid ligands and three oxygen atoms from the coordinated water molecules. The antibacterial activity of the Ca(II) complex indicates that the Ca(II) complex shows considerable antibacterial activity against *Escherichia coli, Bacillus subtilis* and *Staphylococcus white*.

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