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Synthesis, Crystal Structure and Antibacterial Activity of a Calcium(II) Complex of 2-Formyl-benzenesulfonato-hydrazine

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A Schiff base complex, $[Ca(L)\cdot(H_2O)_4]\cdot 4H_2O$, has been synthesized and structurally characterized by elemental analyses and X-ray diffraction. In the complex, the Ca(II) atom is six-coordinated by two O atoms from the Schiff base ligands, 2-formyl-benzenesulfonato-hydrazine and four O atoms from four coordinated water molecules, forming a slightly distorted octahedral CaO_6 geometry. The complexes form one-dimensional chained structure by intermolucules and intramolecules hydrogen bonds and π-π interaction of benzene rings. 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*.

Key Words: Schiff base,; Ca(II) complex, Synthesis, Crystal structure.

INTRODUCTION

During recent years coordination compounds of Schiff base ligands have received much attention[1,2]. These compounds not only play important roles in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architecture[3-5], but also exhibit variety of biological activities[6-9]. Calcium(II) complexes with Schiff base ligand have received little attention. In this paper, a new Ca(II) complex from a Schiff base ligand condensed by 2-formylbenzenesulfonic acid sodium salt and hydrazine hydrate has been synthesized and structurally characterized. In this work, we report here the crystal structure of the calcium(II) complex of 2-formyl-benzene sulfonato-hydrazine. In the title mononuclear calcium(II) complex, $[(C_{14}H_{10}N_2O_6S_2)\cdot(H_2O)_4Ca]\cdot 4H_2O$, the Ca(II) atom is six-coordinated by two O atoms from the Schiff base ligands and four O atoms from four coordinated water molecules, forming a slightly distorted octahedral CaO_6 geometry.

EXPERIMENTAL

The following chemicals and solvents with A.R. grade: 2-formylbenzenesulfonic acid sodium salt, hydrazine hydrate and $Ca(ClO_4)_2\cdot 2H_2O$ were purchased from Aldrich.

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: 5 mmol (1.041 g) of 2-formylbenzene-sulfonic acid sodium was dissolved in 10 mL of 95 % ethanol at room temperature and added drop by drop 10 mmol (0.50 g) of hydrazine hydrate by stirring at sroom temperature. The reaction solution was kept running for 4 h. After evaporating some CH_3CH_2OH solvent, the white solid precipitation were collected by filtration, washed and dried under vacuum. Yield may reach up to over 85 %. Elementary analysis: calcd for $C_{14}H_{10}N_2S_2O_6Na_2$: C, 40.78; H, 2.43; N, 6.80 %; found: C, 40.58; H, 2.72; N, 6.57 %. IR ν_{max} (cm^{-1}): ν(C=N): 1650 cm^{-1}, ν(SO_3^-): 1335 cm^{-1}, 1202 cm^{-1}.

Synthesis of Ca(II) complex: 2-Formyl-benzenesulfonic acid sodium-hydrazine (412.0 mg, 1.0 mmol) and $Ca(ClO_4)_2\cdot 2H_2O$ (275.0 mg, 1.0 mmol,) were dissolved in 5 mL 95 % ethanol at room temperature. The mixture was refluxed for 4 h with stirring to give a clear solution and then filtered. Upon keeping the filtrate in air for 10 days, colourless block-shaped crystals of Ca(II) complex, suitable for X-ray crystal determination, formed at the bottom of vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with ethanol and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield: 67 %. Anal. calcd. for $[(C_{14}H_{10}N_2O_6S_2)\cdot(H_2O)_4Ca]\cdot 4H_2O$: C, 30.51 %; H, 4.72 %; N 5.09 %. Found: C, 30.36 %; H, 4.46 %; N 5.26 %.

X-ray crystallography: X-ray intensities of the complex were collected using a Bruker Smart-1000 CCD area detector equipped with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 298(2) K. Empirical absorption corrections were applied using the SADABS program[10]. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXTL program[11]. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in calculated positions. The contributions of these hydrogen atoms were included in the structure-factors calculations. A full-matrix least-square refinement of 1855 independent reflections with $I \geq 2\sigma(I)$ gave the final R_1 = 0.0299 and wR_2 = 0.0765 ($w = 1/[\sigma_2(F_0^2) + (0.0377P)^2 + 0.5108P]$) where $P = (F_0^2 + 2F_c^2)/3$. The largest peak and hole on the final difference-Fourier map were 0.221 and -0.389 e/Å^{-3}, respectively. Details of the crystal structure solutions and refinements are listed in Table-1. The selected bond lengths and bond angles are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR Ca(II) COMPLEX

Formula	$C_{14}H_{26}N_2O_{14}S_2Ca$
Formula weight	550.57
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.4202(12)
b (Å)	6.5879(10)
c (Å)	17.659(2)
α (º)	90.00
β (º)	95.625(2)
γ (º)	90.00
Z	2
F(000)	576
Temperature (K)	298(2)
V (Å^3)	1206.4(3)
Calculated density (g·cm^{-3})	1.516
Crystal size (mm^3)	0.50 × 0.47 × 0.46
μ (mm^{-1})	0.502
Limiting indices	$-11 \leq h \leq 12$, $-6 \leq k \leq 7$, $-20 \leq l \leq 20$
$(\Delta/\sigma)_{max}$	0.001
Reflections collected / unique	2123/1855
R_1, wR_2 [all data]	0.0362, 0.0810
R_1, wR_2 [I>2σ(I)]	0.0299, 0.0765
Largest diff. peak and hole (e Å^{-3})	0.221, -0.389

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

Ca1—O1	2.3089(13)	S1—O3	1.4457(15)
Ca1—O1^i	2.3089(13)	S1—O2	1.4535(14)
Ca1—O4^i	2.3295(15)	S1—O1	1.4577(14)
Ca1—O4	2.3295(15)	N1—C1	1.272(2)
Ca1—O5	2.3465(15)	S1—C3	1.7811(18)
Ca1—O5^i	2.3465(15)		
O1^i—Ca1—O1	180.0	O5^i—Ca1—O1^i	87.34(6)
O1—Ca1—O4	93.45(6)	O5^i—Ca1—O4	88.25(6)
O4—Ca1—O1^i	86.55(6)	O4^i—Ca1—O5^i	91.75(6)
O1—Ca1—O4^i	86.55(6)	O1—Ca1—O5	87.34(6)
O1^i—Ca1—O4^i	93.45(6)	O1^i—Ca1—O5	92.66(6)
O4^i—Ca1—O4	180.0(1)	O4—Ca1—O5	91.75(6)
O5^i—Ca1—O1	92.66(6)	O4^i—Ca1—O5	88.25(6)
O5^i—Ca1—O5	180.0	O3—S1—O2	112.71(9)
		O3—S1—O1	113.17(9)
		O1—S1—O2	111.12(9)

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1

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[12], 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. After 48 h of continuous incubation, the minimum bactericidal concentration was defined, too.

RESULTS AND DISCUSSION

IR Spectra: In the infrared spectra, the ν(C=N) vibrations of the free ligand are at 1650 cm^{-1}. For the complex, the vibration can be found at 1649 cm^{-1} was assigned as ν(C=N). It can be explained that the nitrogen atoms of ligands do not take part in the coordination with Ca atoms[13]. The ν(SO_3^-) vibrations of the free ligand are at 1335 cm^{-1} and 1202 cm^{-1}, respectively. For the complex, the vibration can be found at 1227 cm^{-1} and 1153 cm^{-1}, respectively. Which indicated that the oxygen atoms of ligands take part in coordination with Ca atoms. The new band at 389 cm^{-1} is assigned to the ν(Ca-O) vibration. The band corresponding to the ν(OH) at 3402 cm^{-1} shows that the complex contains water molecule, which is in accordance with the result of elemental analysis.

Structure description: The reaction of $Ca(ClO_4)_2{\cdot}2H_2O$ with Schiff base ligand condensed by 2-formylbenzenesulfonic acid sodium salt and hydrazine hydrate gave a new mononuclear Ca(II) complex. The Ca(II) complex was successfully crystallized and its structure was determined by single crystal X-ray diffraction analysis. The elemental analyses were in accordance with the proposed structure. Fig. 1 gives a perspective view of Ca(II) complex together with the atomic labeling system. In the Ca(II) complex, calcium(II) atom is six-coordinated by two O atoms from the Schiff base ligands, 2-formylbenzenesulfonato-hydrazine and four O atoms from four coordinated water molecules. The geometry around the calcium(II) center can be described as a slightly distorted octahedral CaO_6 geometry. The bond lengths of Ca-$O_{SO_3^-}$ [2.3089 (13) Å)] are shorter than that of Ca-OH_2O [2.3295(15) Å and 2.3465(15) Å], which shows that the strength of Ca-$O_{SO_3^-}$ bonds is stronger than Ca-OH_2O bonds. The angles subtended at the calcium(II) atom range from 86.55(6)º to 180.0º. Fig. 2 gives the molecular packing of the Ca(II) complex, viewed along the b axis. The Ca-O bond lengths are similar to the Ca-O bond lengths reported previously[14-18].

The complex forms one dimensional chain structure by intramolecule and intermolecule hydrogen bonds [O4-H4A···O2, 2.899(2) Å, symmetry codes: x, -1+y, z; O4-H4B···O6, 2.818(2) Å, symmetry codes: 1-x, 1-y, 1-z; O5-H5A···O7, 2.787(2) Å, symmetry codes: x, 1/2-y, -1/2+z; O5-H5B···O6, 2.875(2) Å, symmetry codes: 1-x, 2-y, 1-z; O6-

H6A···O7, 2.838(2) Å, symmetry codes: 1-x, 1/2+y, 3/2-z; O6-H6B···N1, 2.943(2) Å, symmetry codes: -1+x, y, z; O7-H7A···O3, 2.781(2) Å, symmetry codes: 1-x, -1/2+y, 3/2-z; O7-H7B···O2, 2.923(2) Å, symmetry codes: x, -1+y, z] and π-π stacking (Fig. 3).

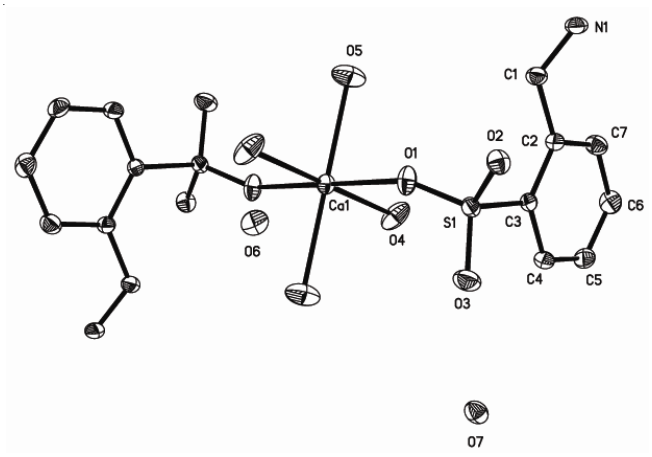

Fig. 1. Molecular structure of the complex, where the thermal ellipsoids were drawn at 30 % possibility

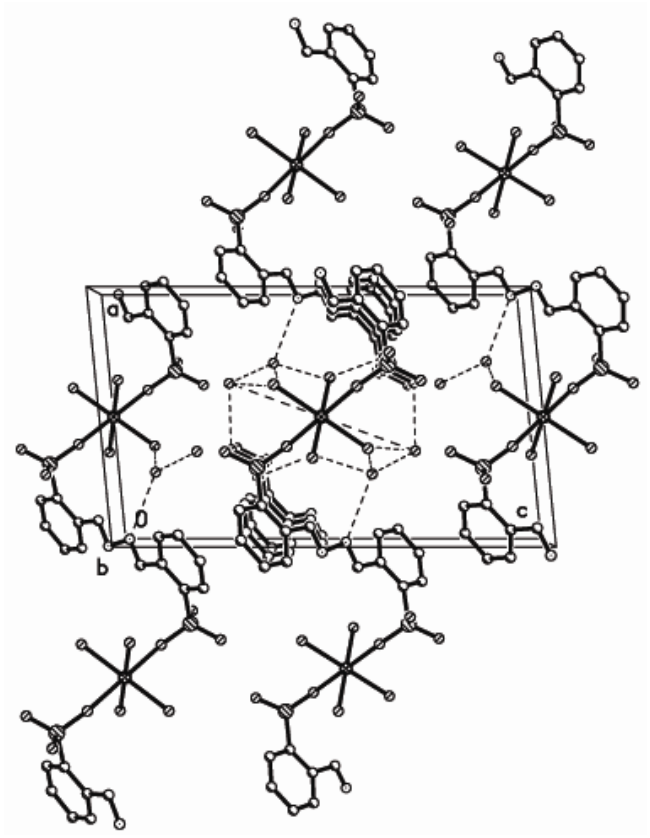

Fig. 2. Packing structure of the title complex

Antibacterial activity: The antibacterial activity of the calcium(II) complex was 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. So the complex will provide potential applications in the broad spectrum of the antibacterial field.

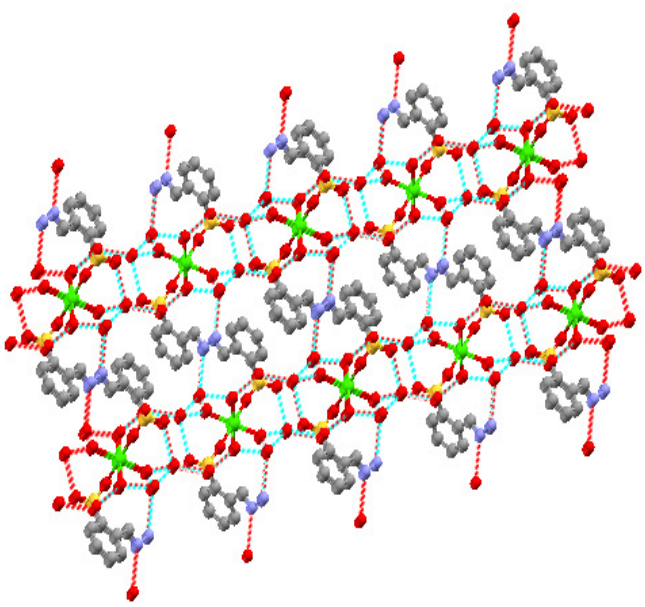

Fig. 3. One dimensional chain of the complex

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

Strains	MIC (mg/mL)	MBC (mg/mL)
Escherichia coli	0.615	0.675
Bacillus subtilis	0.625	0.625
Staphylococcus white	0.675	1.25

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) atom is six-coordinated by two O atoms from the Schiff base ligands, 2-formylbenzenesulfonato-hydrazine and four O atoms from four coordinated water molecules, forming a slightly distorted octahedral CaO_6 geometry. 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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