

苯基乙酰甲基亚砷与碱土金属配合物的合成和晶体结构

李文先* 王宏胜 胡瑞珏 其其格

(内蒙古大学化学化工学院, 呼和浩特 010021)

摘要: 本文选取苯基乙酰甲基亚砷($\text{C}_6\text{H}_5\text{SOCH}_2\text{COCH}_3$)作为配体与碱土金属(钙、锶)的高氯酸盐反应得到配合物的单晶, 对它们进行了元素分析及红外光谱表征, 它们的化学式为 $[\text{ML}_6](\text{ClO}_4)_2$ ($\text{M}=\text{Ca}, \text{Sr}; \text{L}=\text{C}_6\text{H}_5\text{SOCH}_2\text{COCH}_3$)。并用 X-ray 单晶衍射法测定了钙、锶配合物的晶体结构。

关键词: 碱土金属; X-ray 晶体结构; 苯基乙酰甲基亚砷

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Synthesis and Crystal Structure of Phenyl-acetyl Methylene Sulfoxide Complexes with Alkaline-Earth Metal

LI Wen-Xian* WANG Hong-Shneg HU Rui-Jue QI Qi-Ge

(College of Chemistry & chemical Engineering, Inner Mongolia University, Huhhot 010021)

Abstract: Two complexes of alkaline-earth metals perchlorate with phenyl-acetylmethylene sulfoxide($\text{C}_6\text{H}_5\text{SOCH}_2\text{COCH}_3$) have been synthesized and characterized by elemental analysis and IR spectra. Composition of complexes are $[\text{ML}_6](\text{ClO}_4)_2$ ($\text{M}=\text{Ca}, \text{Sr}; \text{L}=\text{C}_6\text{H}_5\text{SOCH}_2\text{COCH}_3$). The crystal structures of the complexes of Ca and Sr were determined by X-ray single crystal diffraction analysis. CCDC: 23880 (Ca); 23881 (Sr).

Key words: alkaline-earth metals; X-ray crystal structure; phenyl-acetylmethylene sulfoxide

Sulfoxide as a kind of organic ligand has been numerously studied in Rare Earth Coordination Chemistry^[1-3]. Alkaline metals have the similar properties as Rare Earth. In recent years, many studies focus on Alkaline-Earth metals^[4-6]. In addition, some complexes of Alkaline-Earth metals can possibly be used as precursor of metal organic chemical vapour deposition (MOCVD)^[7,8]. In this paper phenyl-acetylmethylene sulfoxide as ligand reacted with Ca, Sr and Ba perchlorate, to obtain three complexes and single crystals of Ca and Sr complexes.

1 Experimental

1.1 Synthesis of ligand (L)

Sulfide($\text{C}_6\text{H}_5\text{SCH}_2\text{COCH}_3$) was synthesized accord-

ing to the methods of ref^[8,9]. Then oxidize the sulfide with H_2O_2 (30%) in acetone at room temperature, yellow oil was obtained, evaporate solvent and recrystallize yellow residue from alcohol, the colorless crystal was obtained(yield about 60%), m.p. 34~35 °C, Anal. Calc. for sulfoxide ($\text{C}_6\text{H}_5\text{SOCH}_2\text{COCH}_3$)(%): C, 59.31; H, 5.53. Found(%): C: 59.63; H, 5.31. Elemental analysis data of C, H were determined by PE-2400 elemental analyzer. IR using a KBr pellet was recorded on a Nicolet NEXUS 670 FTIR Spectrophotometer in the 4000~400 cm^{-1} range.

1.2 Synthesis of complexes

To an alcohol solution (5 mL) of sulfoxide (3 mmol), $\text{M}(\text{ClO}_4)_2$ (0.5 mmol, $\text{M}=\text{Ca}, \text{Sr}$) in alcohol was slowly added under stirring. The resulting solution was

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*通讯联系人。E-mail:nmgwlx@163.com

第一作者:李文先,44岁,女,教授;研究方向:稀土发光材料。

filtered and the white residue obtained (complex); the filtrate was allowed to stand in refrigerator, after a week, well-shaped colorless single crystals were obtained from the filtrate of Ca and Sr complexes.

1.3 Single crystal X-ray diffraction

Diffraction experiments of colorless crystals with dimensions $0.26\text{ mm} \times 0.22\text{ mm} \times 0.18\text{ mm}$ for Ca complex and $0.22\text{ mm} \times 0.18\text{ mm} \times 0.14\text{ mm}$ for Sr were performed with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) on a Bruker SMART 1000 CCD diffractometer at 293 K, 2 178 (Ca) and 2 231

(Sr) data were collected.

Data collection and reduction were performed using the SMART and SAINT software with frames of 0.3° oscillation in the θ ranges of $1.87^\circ < \theta < 26.34^\circ$ (Ca) and $1.86^\circ < \theta < 26.51^\circ$ (Sr). The structures were solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL program package. Summaries of crystallographic data and additional data collection parameters for the two complexes were given in Table 1.

CCDC: 23880 (Ca); 23881 (Sr).

Table 1 Crystal data and structure refinement for $[\text{CaL}_6](\text{ClO}_4)_2$ and $[\text{SrL}_6](\text{ClO}_4)_2$

	$[\text{CaL}_6](\text{ClO}_4)_2$	$[\text{SrL}_6](\text{ClO}_4)_2$
Empirical formula	$\text{C}_{54}\text{H}_{60}\text{Cl}_2\text{O}_{20}\text{S}_6\text{Ca}$	$\text{C}_{54}\text{H}_{60}\text{Cl}_2\text{O}_{20}\text{S}_6\text{Sr}$
Formula weight	1 332.36	1 379.90
Temperature / K	293(2)	293(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Rhombohedral	Rhombohedral
Space group	$R\bar{3}c$	$R\bar{3}c$
Hexagonal unit cell dimensions		
a / nm	1.351 55(18)	1.357 0(4)
c / nm	6.051 2(17)	6.077(3)
Volume / nm ³	9.573(3)	9.691(7)
Z	6	6
Calculated density / ($\text{Mg} \cdot \text{m}^{-3}$)	1.387	1.419
Absorption coefficient / mm^{-1}	0.448	1.180
$F(000)$	4 164	4 272
Crystal size / mm	$0.26 \times 0.22 \times 0.18$	$0.22 \times 0.18 \times 0.14$
Theta range for data collection / ($^\circ$)	1.87 to 26.34	1.86 to 26.51
Limiting indices	$-16 \leq h \leq 16, -14 \leq k \leq 16, -75 \leq l \leq 48$	$-16 \leq h \leq 15, -17 \leq k \leq 14, -37 \leq l \leq 75$
Reflections collected / unique	1 7189 / 2 178 [$R(\text{int})=0.041\,5$]	14 257 / 2 231 [$R(\text{int})=0.146\,7$]
Completeness to $\theta=26.34^\circ, \theta=26.51^\circ$	100.0%	99.2%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.79	1.00 and 0.59
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2 178 / 30 / 140	2 231 / 30 / 140
Goodness-of-fit on F^2	1.048	0.996
Final R indices [$I > 2\sigma(I)$]	$R_1=0.040\,1, wR_2=0.107\,8$	$R_1=0.054\,9, wR_2=0.122\,9$
R indices (all data)	$R_1=0.055\,5, wR_2=0.119\,8$	$R_1=0.117\,6, wR_2=0.149\,8$
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	477 and -536	506 and -646

2 Results and discussion

2.1 Composition of complexes

Elemental analysis data of three complexes were determined by PE-2400 elemental analyzer. The results is in Table 2.

Table 2 Composition analysis of complexes (%)

Complexes	C	H
$[\text{CaL}_6](\text{ClO}_4)_2$	48.39(48.68)	4.41(4.54)
$[\text{SrL}_6](\text{ClO}_4)_2$	46.89(47.00)	4.29(4.38)
$[\text{BaL}_6](\text{ClO}_4)_2$	45.62(45.36)	4.08(4.23)

2.2 Description of crystal structure

Fig.1 and Fig.2 show the crystal structure of the complexes of Ca and Sr, Fig.3 and Fig.4 are their structure of cell respectively. X-ray diffraction crystal structure analyses reveal that the two complexes are similar in their molecule structure. Each unit consists of one M^{2+} ($M=Ca, Sr$) and six neutral sulfoxides(L). C. N. of M^{2+} is six and M^{2+} coordinated with sulfoxides by the oxygen atom in sulfinyl group while the the oxygen atom in carbonyl group did not bond with M^{2+} . The distance of Ca-O is at the range of 0.231 49(18)~0.231 50(18) nm and Sr-O is all 0.245 36(18) nm; the bond angles of O-Ca-O and O-Sr-O are all close to 90° or 180° . Table 3 and Table 4 gives the selected

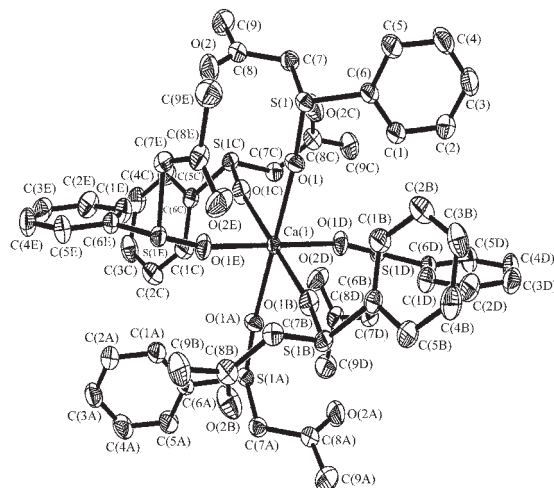


Fig.1 Crystal structure of $[CaL_6]^{2+}$

Table 3 Bond lengths (nm) and angles ($^\circ$) for $[CaL_6](ClO_4)_2$

Ca(1)-O(1)#1	0.231 49(18)	Ca(1)-O(1)#2	0.231 49(18)	Ca(1)-O(1)#3	0.214 9(18)
Ca(1)-O(1)#4	0.231 50(18)	Ca(1)-O(1)	0.231 50(17)	Ca(1)-O(1)#5	0.231 50(18)
S(1)-O(1)	0.149 69(18)	S(1)-C(6)	0.179 4(3)	S(1)-C(7)	0.180 6(3)
O(2)-C(8)	0.120 4(3)	C(1)-C(6)	0.137 8(4)	C(1)-C(2)	0.138 1(4)
C(1)-H(1)	0.093 00	C(2)-C(3)	0.137 1(5)	C(2)-H(2)	0.093 00
C(3)-C(4)	0.369(5)	C(3)-H(3)	0.093 00	C(4)-C(5)	0.138 8(4)
C(4)-H(4)	0.093 00	C(5)-C(6)	0.137 8(3)	C(5)-H(5)	0.093 00
C(7)-C(8)	0.150 6(4)	C(7)-H(7A)	0.097 00	C(7)-H(7B)	0.097 00
C(8)-C(9)	0.149 2(4)	C(9)-H(9A)	0.096 00	C(9)-H(9B)	0.096 00
C(9)-H(9C)	0.096 00				
O(1)#1-Ca(1)-O(1)#2	9.204(6)	O(1)#1-Ca(1)-O(1)#3	9.204(6)	O(1)#2-Ca(1)-O(1)#3	9.204(6)
O(1)#1-Ca(1)-O(1)#4	8.796(6)	O(1)#2-Ca(1)-O(1)#4	8.796(6)	O(1)#3-Ca(1)-O(1)#4	18.00
O(1)#1-Ca(1)-O(1)	8.796(6)	O(1)#2-Ca(1)-O(1)	18.00	O(1)#3-Ca(1)-O(1)	8.796(6)
O(1)#4-Ca(1)-O(1)	9.204(6)	O(1)#1-Ca(1)-O(1)#5	18.00	O(1)#2-Ca(1)-O(1)#5	8.796(6)
O(1)#3-Ca(1)-O(1)#5	8.796(6)	O(1)#4-Ca(1)-O(1)#5	9.204(6)	O(1)-Ca(1)-O(1)#5	9.204(6)
O(1)-S(1)-C(6)	10.604(11)	O(1)-S(1)-C(7)	10.668(12)	C(6)-S(1)-C(7)	9.763(12)
S(1)-O(1)-Ca(1)	16.826(12)	C(6)-C(1)-C(2)	11.87(3)	C(6)-C(1)-H(1)	12.07
C(2)-C(1)-H(1)	12.07	C(3)-C(2)-C(1)	12.06(3)	C(3)-C(2)-H(2)	11.97
C(1)-C(2)-H(2)	11.97	C(4)-C(3)-C(2)	12.03(3)	C(4)-C(3)-H(3)	11.99
C(2)-C(3)-H(3)	1.99	C(3)-C(4)-C(5)	12.03(3)	C(3)-C(4)-H(4)	11.99
C(5)-C(4)-H(4)	11.99	C(6)-C(5)-C(4)	11.87(3)	C(6)-C(5)-H(5)	12.06
C(4)-C(5)-H(5)	12.06	C(1)-C(6)-C(5)	12.14(3)	C(1)-C(6)-S(1)	12.007(19)
C(5)-C(6)-S(1)	11.84(2)	C(8)-C(7)-S(1)	11.150(18)	C(8)-C(7)-H(7A)	10.93
S(1)-C(7)-H(7A)	10.93	C(8)-C(7)-H(7B)	10.93	S(1)-C(7)-H(7B)	10.93
H(7A)-C(7)-H(7B)	10.80	O(2)-C(8)-C(9)	12.26(3)	O(2)-C(8)-C(7)	12.12(3)
C(9)-C(8)-C(7)	11.63(3)	C(8)-C(9)-H(9A)	10.95	C(8)-C(9)-H(9B)	10.95
H(9A)-C(9)-H(9B)	10.95	C(8)-C(9)-H(9C)	10.95	H(9A)-C(9)-H(9C)	10.95
H(9B)-C(9)-H(9C)	10.95				

Symmetry transformations used to generate equivalent atoms: #1: $y, -x+y+1, -z$; #2: $-x+2, -y+2, -z$; #3: $x-y+1, x, -z$; #4: $-x+y+1, -x+2, z$; #5: $-y+2, x-y+1, z$; #6: $-x+y+1, -x+1, z$; #7: $-y+1, x-y, z$.

Table 4 Bond lengths (nm) and angles (°) for [SrL₆](ClO₄)₂

Sr(1)-O(1)	0.245 35(18)	Sr(1)-O(1)#1	0.245 35(18)	Sr(1)-O(1)#2	0.245 36(18)
Sr(1)-O(1)#3	0.245 36(18)	Sr(1)-O(1)#4	0.245 36(18)	Sr(1)-O(1)#5	0.245 36(18)
S(1)-O(1)	0.150 30(17)	S(1)-C(6)	0.179 3(3)	S(1)-C(7)	0.181 0(2)
O(2)-C(8)	0.120 6(3)	C(1)-C(6)	0.138 0(4)	C(1)-C(2)	0.138 0(4)
C(1)-H(1)	0.093 00	C(2)-C(3)	0.137 2(4)	C(2)-H(2)	0.093 00
C(3)-C(4)	0.137 9(5)	C(3)-H(3)	0.093 00	C(4)-C(5)	0.137 4(4)
C(4)-H(4)	0.093 00	C(5)-C(6)	0.138 0(4)	C(5)-H(5)	0.093 00
C(7)-C(8)	0.150 9(4)	C(7)-H(7A)	0.097 00	C(7)-H(7B)	0.097 00
C(8)-C(9)	0.149 2(4)	C(9)-H(9A)	0.096 00	C(9)-H(9B)	0.096 00
C(9)-H(9C)	0.096 00				
O(1)-Sr(1)-O(1)#1	9.237(6)	O(1)-Sr(1)-O(1)#2	9.238(6)	O(1)#1-Sr(1)-O(1)#	9.237(6)
O(1)-Sr(1)-O(1)#3	8.763(6)	O(1)#1-Sr(1)-O(1)#3	8.763(6)	O(1)#2-Sr(1)-O(1)#3	18.00
O(1)-Sr(1)-O(1)#4	8.763(6)	O(1)#1-Sr(1)-O(1)#4	18.00	O(1)#2-Sr(1)-O(1)#4	8.763(6)
O(1)#3-Sr(1)-O(1)#4	9.237(6)	O(1)-Sr(1)-O(1)#5	17.9996(1)	O(1)#1-Sr(1)-O(1)#5	8.763(6)
O(1)#2-Sr(1)-O(1)#5	8.763(6)	O(1)#3-Sr(1)-O(1)#5	9.237(6)	O(1)#4-Sr(1)-O(1)#5	9.237(6)
O(1)-S(1)-C(6)	10.600(11)	O(1)-S(1)-C(7)	10.618(11)	C(6)-S(1)-C(7)	9.764(11)
S(1)-O(1)-Sr(1)	16.452(11)	C(6)-C(1)-C(2)	11.91(3)	C(6)-C(1)-H(1)	12.05
C(2)-C(1)-H(1)	12.05	C(3)-C(2)-C(1)	12.06(3)	C(3)-C(2)-H(2)	11.97
C(1)-C(2)-H(2)	11.97	C(2)-C(3)-C(4)	11.99(3)	C(2)-C(3)-H(3)	12.01
C(4)-C(3)-H(3)	12.01	C(5)-C(4)-C(3)	12.02(3)	C(5)-C(4)-H(4)	11.99
C(3)-C(4)-H(4)	11.99	C(4)-C(5)-C(6)	11.96(3)	C(4)-C(5)-H(5)	12.02
C(6)-C(5)-H(5)	12.02	C(1)-C(6)-C(5)	12.06(2)	C(1)-C(6)-S(1)	12.067(18)
C(5)-C(6)-S(1)	11.58(2)	C(8)-C(7)-S(1)	11.082(18)	C(8)-C(7)-H(7A)	10.59
S(1)-C(7)-H(7A)	10.95	C(8)-C(7)-H(7B)	10.95	S(1)-C(7)-H(7B)	10.95
H(7A)-C(7)-H(7B)	10.81	O(2)-C(8)-C(9)	12.29(3)	O(2)-C(8)-C(7)	12.31(2)
C(9)-C(8)-C(7)	11.58(2)	C(8)-C(9)-H(9A)	10.95	C(8)-C(9)-H(9B)	10.95
H(9A)-C(9)-H(9B)	10.95	C(8)-C(9)-H(9C)	10.95	H(9A)-C(9)-H(9C)	10.95
H(9B)-C(9)-H(9C)	10.95				

Symmetry transformations used to generate equivalent atoms: #1: $-y+2, x-y+1, z$; #2: $-x+y+1, -x+2, z$; #3: $x-y+1, x, -z$; #4: $y, -x+y+1, -z$; #5: $-x+2, -y+2, -z$; #6: $-y+1, x-y, z$; #7: $-x+y+1, -x+1, z$.

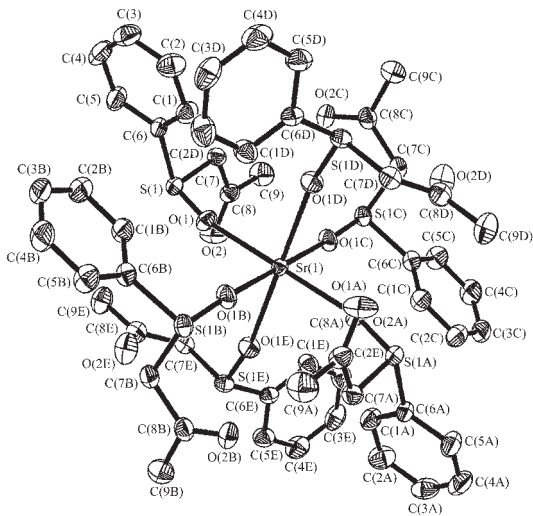


Fig.2 Crystal structure of [SrL₆]²⁺

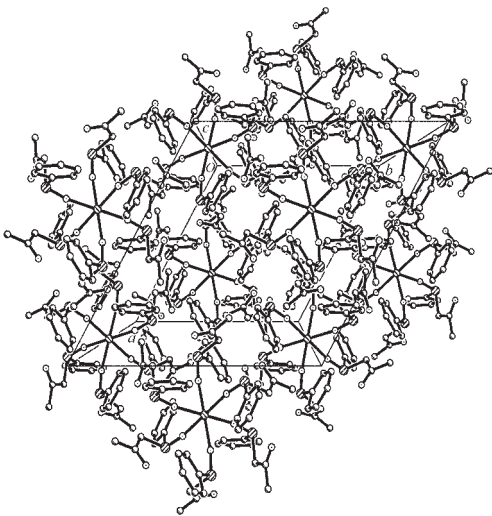


Fig.3 Packing of [CaL₆](ClO₄)₂

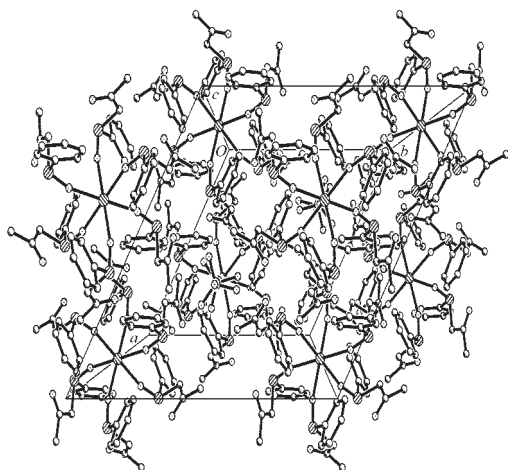


Fig. 4 Packing of $[\text{SrL}_6](\text{ClO}_4)_2$

bond lengths and bond angles of the Ca and Sr complexes respectively.

All the hydrogen atoms were omitted in Fig.1 and Fig.2 for clarity.

2.3 IR spectrum

Compare the IR spectrum of sulfoxide with their complexes, some conclusions can be obtained: In the ligand IR spectrum, there are two very strong peaks, the one at $1\,041\text{ cm}^{-1}$ ascribed to the $\text{S}=\text{O}$ group stretching and the other at $1\,709\text{ cm}^{-1}$ to $\text{C}=\text{O}$ group. In the complexes IR spectra, the $\text{S}=\text{O}$ groups stretching are at $1\,046\text{ cm}^{-1}$ (Ca), $1\,038\text{ cm}^{-1}$ (Sr) and $1\,026\text{ cm}^{-1}$ (Ba); the $\text{C}=\text{O}$ groups are at $1\,716\text{ cm}^{-1}$ (Ca), $1\,715\text{ cm}^{-1}$ (Sr) and $1\,714\text{ cm}^{-1}$ (Ba) respectively. In addition,

there are two additional peaks at $1\,089\text{ cm}^{-1}$ and 623 cm^{-1} , which are attributed to ClO_4^- group.

3 Conclusion

In the three complexes, each M^{2+} ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) coordinated with six ligands by oxygen atom in sulfinyl group. The molecule structure of Ca and Sr complexes is approximately an octahedron. The two ClO_4^- anions did not coordinate with M^{2+} .

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