[Co(bamp)(pi)Cl][$ZnCl_4$]·H_2O 一经式异构体的晶体结构及经式异构体的理论计算研究

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用 X- 射线单晶衍射法测定了 [Co(bamp)(pi)Cl][$ZnCl_4$] **体系的一经式异构体** (m2) **的晶体结构**, (bamp = 2, 6- **二** (**氨基甲基**) **吡啶**; pi = 1-(2- **氨基乙基**) **哌啶**) **晶体属于三斜晶系, 空间群** $P\bar{1}$(#2), a = 11.323(4) Å, b = 11.747(3) Å, c = 10.617(3) Å, α = 115.45(2)°, β = 113.32(2)°, γ = 77.95(3)°, V = 1169.7(6) Å^3, D_c = 1.661 g·cm^{-3}, Z = 2, F_{000} = 596.00, μ(Mo $K\alpha$) = 23.20 cm^{-1}, R = 0.032, R_w = 0.044**。用量子化学从头计算方法, 在赝势基组** RHF/LANL2DZ **的水平上对该体系的两经式异构体在不同介质中的稳定性进行比较, 其能量差分别为** 11.3 kJ·mol^{-1} (**气相**) **和** 27.3 kJ·mol^{-1} (**水介质**)**。从而解释了在水介质条件下难于合成分离出另一经式异构体**(m1)**。**

关键词: **钴(Ⅲ)配合物** **晶体结构** **量化计算**
分类号: O614.81$^+$2

Crystal Structure and Computational Study on the Isomers of *mer*-[Co(bamp)(pi)Cl][$ZnCl_4$]·H_2O

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The crystal structure of the m2 isomer of [Co(bamp)(pi)Cl][$ZnCl_4$] has been determined (bamp = 2, 6-bis(2-aminomethyl) pyridine; pi = 1-(2-aminomethyl) piperidine) by single crystal X-ray diffraction analysis. Crystal data: triclinic, $P\bar{1}$(#2), a = 11.323(4) Å, b = 11.747(3) Å, c = 10.617(3) Å, α = 115.45(2)°, β = 113.32(2)°, γ = 77.95(3)°, V = 1169.7(6) Å^3, D_c = 1.661 g·cm^{-3}, Z = 2, F_{000} = 596.00, μ(Mo $K\alpha$) = 23.20 cm^{-1}, R = 0.032, R_w = 0.044. A comparison of the crystal structure of the m2-[Co(bamp)(pi)Cl][$ZnCl_4$] complex with an *ab initio* computational result (RHF/LANL2DZ optimised structure) suggests why the m1 isomer has not been isolated or even observed. The energies of the two isomers are calculated, the results show that the m1 isomer is

收稿日期: 2001-04-09。**收修改稿日期**: 2001-08-03。
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11.3kJ · mol^{-1} less stable than the m2 isomer in the gas phase, and 27.3kJ · mol^{-1} less stable when the effect of solvent (water) is included using the Onsager model within the solvent continuum reaction field method.

Keywords: cobalt (Ⅲ) complex crystal structure *ab initio*

0 Introduction

Octahedral cobalt (Ⅲ) complexes has been extensively studied for some decades, particularly the base hydrolysis reaction for dichlorotetraamine and chloropentaaminecobalt (Ⅲ) species[1~6]. Lacking are theoretical studies of the rates of such reactions[7], and even the relative energies of isomeric complexes used in these studies are a complex problem. Most calculations have been for the gas phase, and comparisons made with solid state crystal structural data. Solvent effects are appreciable, and this remains an outstanding theoretical difficulty.

The present study was motivated by a need to predict the relative stabilities of closely related isomers in water as solvent. We deal with the case of the title [Co(bamp)(pi)Cl]$^{2+}$ system[8]. The crystal structure of the only presently known isomer has been determined(m2, Fig. 1), and we consider why attempts to make the m1 form have been unsuccessful. This comment need be viewed in the light of the fact that, for the [Co(triamine)(diamine)Cl]$^{2+}$ systems in general, most isomers have been experimentally accessible, including particularly unstable species, by exploiting kinetic methods for trapping such ions. These experiments do not impinge on the relative stability of alternative isomers(but, rather, rely on the kinetic stability of trapped thermodynamically unstable ions).

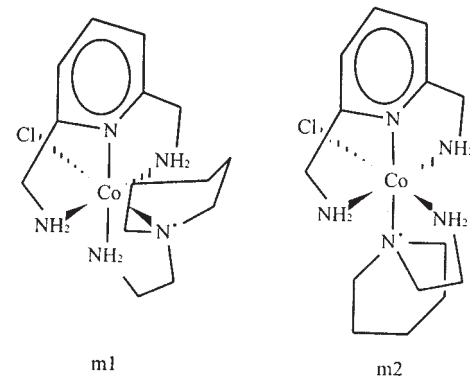

Fig. 1 Two possible *mer*-[Co(bamp)(pi)Cl]$^{2+}$ isomers

The energy difference between the structures of the two isomers in the gas phase and in aqueous solution has been calculated by using an *ab initio* method. Comparison of the crystal structural results for the m2 isomer of [Co(bamp)(pi)Cl]$^{2+}$ with the optimised structure calculated with the RHF/LANL2DZ model reveals a maximum error of ±3%.

1 Experiment

1.1 Determination of the Crystal Structure of the Title Complex

The general procedures of Duffy and House[9], and Gainsford and House[10] were followed on the same scale. An aqueous solution(50mL) of bamp(4.0g, 29.1×10^{-3}mole) and an equimolar amount of pi(3.73g, 29.1×10^{-3}mole) were added to a stirred solution of $Co(NO_3)_2\cdot6H_2O$(7.5g) and sodium perchlorate(17.5g) in water(60mL). A rapid stream of air was passed through the stirred

solution at room temperature for 3hrs, and in this period a grey-brown precipitate formed. The suspension was left at 4℃ overnight and collected by filtration. The dark brown crystalline complexes (peroxo-bis[(pi) (bamp) cobalt(Ⅲ)]) were decomposed by heating in excess concentrated HCl at 100℃ for 40min, then diluting substantially with water before loading onto a Dowex column, and eluting with hydrochloric acid in the usual way. Only one red band was collected. After rotary evaporation, the isomer was characterised as chloride. Perchlorate and tetrachlorozincate salts were also obtained from concentrated solutions of the chlorides using one-fifth volume of the appropriate precipitant (70% $HClO_4$ or 2mol·dm^{-3} "H_2ZnCl_4").

Single crystals of the isomer m2 suitable for X-ray crystal structural determination was obtained by gradually adding "H_2ZnCl_4" (2mol·dm^{-3}) to an aqueous solution of the chloride salts at room temperature.

1.2 Determination of the Crystal Structure of the Title Complex

A suitable crystal was mounted with epoxy resin on a glass fibre. The diffraction work was performed on a Rigaku AFC7R four-cycle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation. The cell parameters were obtained and refined by 19 reflections with $18.3° < \theta < 21.7°$. The reflections were collected in the range of $6° < \theta < 52°$ using the ω-2θ scanning mode. A total of 3720 unique reflections were measured, of which 3391 reflections were used for the structure solution and refinements. Direct methods(SHELXS86) were used for the structure solution. The hydrogen atoms were refined in calculated positions assuming idealised geometries.

1.3 Computational Method

Pre-optimized configurations of the $[Co(bamp)(pi)Cl]^{2+}$ isomers were built using INDO/1 in the Hyperchem program. Starting with these geometries, optimisation of the structures at the RHF/LANL2DZ level was carried out using the Guassian 98 package at Zhejiang University. The Onsager model was then used to calculate the solvent(H_2O) effect.

2 Results and Discussion

2.1 Characteristics of m2-$(ClO_4)_2$

Analysis: Calculated for m2-[Co(bamp) (pi) Cl] $(ClO_4)_2$: C, 28.76; H, 4.99; N, 12.09%. Found: C, 28.36; H, 4.96; N, 11.84%. (method: CE 1106).

^{13}C and ^{1}H NMR spectra were recorded on a Unity-400 instrument at 20℃ in Me_2SO-d_6 with the central peak of the CD_3 septet as the reference(13C, δ 39.37; 1H, δ 2.49, relative to $SiMe_4$). The mer-isomers have a plane of symmetry, thus for the 14 carbon atoms in the molecule, the number of lines expected in the 1D ^{13}C NMR spectrum is 9($5 \times 2C$, $4 \times 1C$). The ^{13}C NMR spectrum shows that there are nine resonances; the intensities of four signals are double the others, as expected; the intensity of the quaternary carbon in bamp at 163.18ppm is weaker, which is normal for such a carbon. Clearly this is a mer isomer. The mer symmetry is also clearly reflected in the ^{1}H NMR spectrum, particularly the resonances of the pyridiyl residue at 7.54ppm(2H) and 8.02ppm(1H). The splitting pattern, as for the ^{13}C NMR spectrum, is unique to the mer configuration. The 1D NMR spectra cannot indicate which mer isomer this is (m1 or m2).

Visible absorption spectral data [λ/nm(ε/(L · mol^{-1} · cm^{-1}))] for m2-[Co(bamp)(pi)Cl]$^{2+}$ in 0.01mol · L^{-1} $HClO_4$ at 25℃ are 508(156.4) and 368(195.4).

2.2 Crystal Structure of the Title Complex and Comparison with the Calculation Results

The m2-[Co(bamp)(pi)Cl][$ZnCl_4$] salt belongs to the triclinic system, space group $P\bar{1}$(#2), a = 11.323(4) Å, b = 11.747(3) Å, c = 10.617(3) Å, α = 115.45(2)°, β = 113.32(2)°, γ = 77.95(3)°, V = 1169.7(6)Å^3, D_c = 1.661g · cm^{-3}, Z = 2, F_{000} = 596.00, μ(Mo $K\alpha$) = 23.20cm^{-1}, R = 0.032, R_w = 0.044. Positional and thermal parameters are listed in Table 1. Selected bond distances and angles are given in Tables 2 and 3, respectively. The structure of the title complex is shown in Fig. 2.

Table 1 Positional (Å) and Thermal Parameters for the m2-[Co(bamp)(pi)Cl][$ZnCl_4$] · H_2O

atom	X	Y	Z	B(eq)	atom	X	Y	Z	B(eq)
Co	0.70966(4)	0.27506(3)	0.22650(4)	1.83(1)	C(5)	0.6497(4)	0.5902(3)	0.5705(4)	3.51(8)
Cl(5)	0.51982(7)	0.19939(7)	0.16342(9)	2.73(2)	C(6)	0.6508(3)	0.5052(3)	0.4330(3)	2.45(6)
N(1)	0.7914(2)	0.1570(2)	0.3276(3)	2.44(5)	C(7)	0.6022(3)	0.5320(3)	0.2949(3)	2.81(7)
N(2)	0.6994(2)	0.3868(2)	0.4133(3)	2.17(5)	C(8)	0.9169(4)	0.2929(4)	0.1523(4)	4.9(1)
N(3)	0.6158(2)	0.4157(2)	0.1666(3)	2.29(5)	C(9)	0.8710(4)	0.1729(5)	0.0507(5)	5.6(1)
N(4)	0.8749(2)	0.3407(2)	0.2801(3)	2.44(5)	C(10)	0.7233(4)	0.0210(3)	−0.0107(4)	3.37(7)
N(5)	0.7348(2)	0.1583(2)	0.0271(3)	2.35(5)	C(11)	0.7387(4)	−0.0672(3)	−0.1595(4)	3.83(8)
C(1)	0.7864(3)	0.2100(3)	0.4808(3)	3.01(7)	C(12)	0.6419(4)	−0.0333(4)	−0.2849(4)	4.02(8)
C(2)	0.7451(3)	0.3470(3)	0.5264(3)	2.58(6)	C(13)	0.6477(4)	0.1045(4)	−0.2516(4)	4.23(9)
C(3)	0.7469(4)	0.4288(3)	0.6660(4)	3.52(8)	C(14)	0.6396(4)	0.1901(3)	−0.0989(4)	3.71(8)
C(4)	0.6997(4)	0.5522(3)	0.6888(4)	3.85(8)					

Table 2 Non-hydrogen Bond Lengths (Å) in m2-[Co(bamp)(pi)Cl][$ZnCl_4$] · H_2O and *ab initio* Calculations

atom-atom	m2	m2*	error	m1*	atom-atom	m2	m2*	error	m1*
Co-Cl(5)	2.237(1)	2.2947	2.58	2.3211	N(5)-C(14)	1.487(4)	1.5262	2.64	1.5207
Co-N(1)	1.972(2)	2.0320	3.04	2.0283	C(1)-C(2)	1.496(4)	1.5064	0.70	1.5096
Co-N(2)	1.884(2)	1.9289	2.38	1.9114	C(2)-C(3)	1.371(4)	1.3862	1.11	1.3845
Co-N(3)	1.974(2)	2.0344	3.06	2.0267	C(3)-C(4)	1.387(5)	1.3960	0.65	1.3972
Co-N(4)	1.950(3)	2.0101	3.08	1.9879	C(4)-C(5)	1.382(5)	1.3991	1.24	1.3972
Co-N(5)	2.065(2)	2.0868	1.06	2.1313	C(5)-C(6)	1.373(4)	1.3830	0.73	1.3846
∑ bonds 1	12.082	12.3869	2.52	12.4067	C(6)-C(7)	1.496(4)	1.5088	0.86	1.5096
N(1)-C(1)	1.491(4)	1.5093	1.23	1.5105	C(8)-C(9)	1.406(6)	1.5201	8.12	1.5214
N(2)-C(2)	1.349(4)	1.3402	−0.65	1.3420	C(10)-C(11)	1.528(5)	1.5360	0.52	1.5377
N(2)-C(6)	1.343(4)	1.3435	0.04	1.3423	C(11)-C(12)	1.500(5)	1.5338	2.25	1.5335
N(3)-C(7)	1.492(4)	1.5040	0.80	1.5080	C(12)-C(13)	1.511(5)	1.5341	1.53	1.5338
N(4)-C(8)	1.458(4)	1.5015	2.98	1.5014	C(13)-C(14)	1.525(5)	1.5389	0.91	1.5399
N(5)-C(9)	1.496(5)	1.5064	0.70	1.5096	∑ bonds 2	39.679	40.3901	1.79	40.4107
N(5)-C(10)	1.506(4)	1.5297	1.57	1.5205					

* *ab initio* computational results

The calculated data are also listed in Table 2 and 3 for comparison. Bond lengths and bond angles differences between the experimental and calculated results are all less than 3%, the only exception being the C8-C9 bond length (+8%) which seems anomalous.

If one examines the distortion, that is the total bond angle deviations (absolute value of the bond angle from the ideal angle, such as 90° or 109.28° or 120°), these are 108.78° for m2 and 133.68° for the m1 isomer. We interpret the increased distortions for the m1 form as indication of its in-

Table 3　Non-hydrogen Angles (°) in m2-[Co(bamp)(pi)Cl][$ZnCl_4$]·H_2O and *ab initio* Calculations, and some Statistical Parameters

atom-atom-atom	m2	m2*	error	m1*	deviation(m2)	deviation(m2*)	deviation(m1*)
Cl(5)-Co-N(1)	88.13(8)	89.34	1.37	85.66	1.87	0.66	4.34
Cl(5)-Co-N(2)	90.27(8)	89.78	−0.54	90.19	0.27	0.22	0.19
Cl(5)-Co-N(3)	88.61(8)	86.64	−2.22	85.41	1.39	3.36	4.59
Cl(5)-Co-N(4)	179.64(7)	—		86.97	0	0	3.03
Cl(5)-Co-N(5)	94.25(7)	93.89	−0.38	—	4.25	3.89	0
N(1)-Co-N(2)	84.0(1)	82.00	−2.38	83.88	6	8	6.12
N(1)-Co-N(3)	166.6(1)	—		—	0	0	0
N(1)-Co-N(4)	92.1(1)	92.82	0.78	96.15	2.1	2.82	6.15
N(1)-Co-N(5)	96.0(1)	96.34	0.35	97.17	6	6.34	7.17
N(2)-Co-N(3)	83.0(1)	82.64	−0.43	83.43	7	7.36	6.57
N(2)-Co-N(4)	90.1(1)	90.88	0.87	—	0.1	0.88	0
N(2)-Co-N(5)	175.5(1)	—		97.91	0	0	7.91
N(3)-Co-N(4)	91.3(1)	91.38	0.09	96.08	1.3	1.38	6.08
N(3)-Co-N(5)	97.2(1)	99.25	2.11	93.47	7.2	9.25	3.47
N(4)-Co-N(5)	85.4(1)	85.51	0.13	84.94	4.6	4.49	5.06
Co-N(1)-C(1)	111.5(2)	111.20	−0.27	111.34	2	1.7	1.84
Co-N(2)-C(2)	119.0(2)	119.07	0.06	118.80	1	0.93	1.2
Co-N(2)-C(6)	119.8(2)	118.67	−0.94	118.52	0.2	1.33	1.48
Co-N(3)-C(7)	112.8(2)	110.30	−2.22	111.10	3.3	0.8	1.6
Co-N(4)-C(8)	111.1(2)	109.27	−1.65	112.15	1.6	0.23	2.65
Co-N(5)-C(9)	105.2(2)	105.93	0.69	103.69	4.3	3.57	5.81
Co-N(5)-C(10)	112.7(2)	112.13	−0.51	112.62	3.2	2.63	3.12
Co-N(5)-C(14)	111.8(2)	110.63	−1.05	118.80	2.3	1.13	9.3
C(9)-N(5)-C(10)	106.5(3)	109.61	2.92	110.17	3	0.11	0.67
C(2)-N(2)-C(6)	121.2(3)	121.97	0.64	121.99	1.2	1.97	1.99
C(9)-N(5)-C(14)	113.1(3)	111.15	−1.72	110.81	3.6	1.65	1.31
C(10)-N(5)-C(14)	107.6(2)	107.43	−0.16	107.21	1.9	2.07	2.29
N(1)-C(1)-C(2)	110.9(2)	109.07	−1.65	110.05	1.4	0.43	0.55
N(2)-C(2)-C(1)	113.5(3)	114.81	1.15	115.65	6.5	5.19	4.35
N(2)-C(2)-C(3)	120.2(3)	120.60	0.33	120.48	0.2	0.6	0.48
N(2)-C(6)-C(5)	120.6(3)	120.53	−0.06	120.49	0.6	0.53	0.49
N(2)-C(6)-C(7)	113.9(2)	115.11	1.06	115.82	6.1	4.89	4.18
N(3)-C(7)-C(6)	110.0(2)	110.07	0.06	110.51	0.5	0.57	1.01
N(4)-C(8)-C(9)	112.1(3)	107.04	−4.51	107.56	2.6	2.46	1.94
N(5)-C(9)-C(8)	113.7(3)	110.43	−2.88	110.39	4.2	0.93	0.89
N(5)-C(10)-C(11)	113.7(3)	113.92	0.19	114.46	4.2	4.42	4.96
N(5)-C(14)-C(13)	115.2(3)	114.94	−0.23	115.13	5.7	5.44	5.63
C(1)-C(2)-C(3)	126.3(3)	124.59	−1.35	123.85	6.3	4.59	3.85
C(2)-C(3)-C(4)	119.3(3)	118.30	−0.84	118.36	0.7	1.7	1.64
C(3)-C(4)-C(5)	119.7(3)	120.19	0.41	120.18	0.3	0.19	0.18
C(4)-C(5)-C(6)	119.0(3)	118.36	−0.54	118.36	1	1.64	1.64
C(5)-C(6)-C(7)	125.5(3)	124.26	−0.99	123.67	5.5	4.26	3.67
C(10)-C(11)-C(12)	111.4(3)	111.04	−0.32	111.20	1.9	1.54	1.7
C(11)-C(12)-C(13)	110.4(3)	109.93	−0.43	109.93	0.9	0.43	0.43
C(12)-C(13)-C(14)	112.1(3)	111.70	−0.36	111.65	2.6	2.2	2.15
distortion					120.88	108.78	133.68

* *ab initio* computational results

creased strain and reactivity, these are consistent with the fact that the m1 isomer is not yet to be synthesised.

2.3 Relative Energies

The calculated gas phase energies of the m1 and m2 iomers are −976.2987 and −976.3030 (a.u.) respectively, the difference being 0.0043 (a.u.) or 11.3kJ·mol^{-1}; m2 is the more stable. The results using the solvent continuous reaction field model show that total electronic energies are −976.2988 and −976.3092 (a.u.) respectively. Thus solvation (hydration) hardly influences the energy of the m1 isomer but stabilises the m2 form by a further 0.0062(a.u.) or 16.26kJ·mol^{-1}, producing a total SCRF energy difference of 27.3kJ·mol^{-1} in favour of the m2 isomer. It would seem this energy difference is sufficient to prevent isolation of the m1 isomer under ordinary experimental conditions.

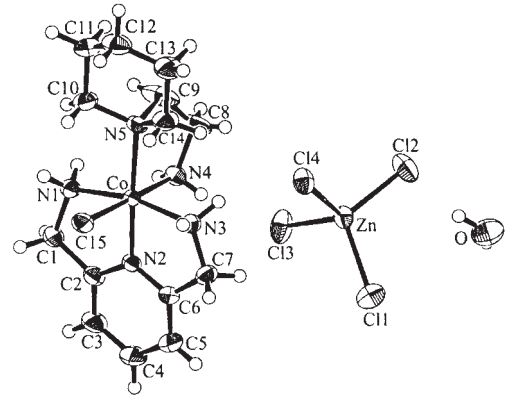

Fig. 2　Perspective view of the m2-[Co(bamp)(pi)Cl]$^{2+}$ cation, $[ZnCl_4]^{2-}$ anion, and lattice water

In summary, in comparing the single crystal data with the calculated ab initio results, the agreement is excellent(within ±3%). We are therefore confident in the calculated data for the unknown m1 isomer.

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