

[Co(2, 3-tri)(men)Cl][ZnCl₄] 体系中三个经式异构体的晶体结构

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在 [Co(2, 3-tri)(men)Cl][ZnCl₄] (2, 3-tri = N-(2-氨基乙基)-1, 3-丙二胺; men = N-甲基乙二胺) 体系中可能的几何异构体的数目多达二十个, 其中经式异构体八个, 面式异构体十二个。用单晶 X-射线衍射分析方法解析了三个获得单晶的经式异构体, 它们的晶体学参数: (1) m3-[ZnCl₄] (monoclinic $P2_1/c$, $a = 8.0874(18)$, $b = 15.135(3)$, $c = 15.426(4)$ Å, $\beta = 99.303(6)^\circ$, $Z = 4$), (2) m4-[ZnCl₄] (orthorhombic $P2_12_12_1$, $a = 9.348(4)$, $b = 12.437(6)$, $c = 15.666(8)$ Å, $Z = 4$) and (3) m4'-[ZnCl₄] (orthorhombic $P2_12_12_1$, $a = 9.302(4)$, $b = 12.393(9)$, $c = 15.621(9)$ Å, $Z = 4$)。

关键词: 钴(III)配合物 几何经式异构体 晶体结构

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The Crystal Structures of three mer-[Co(2, 3-tri)(men)Cl][ZnCl₄] Isomers

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Among the twenty isomeric forms which are possible for [Co(2, 3-tri)(men)Cl][ZnCl₄] system (2, 3-tri = N-(2-Aminoethyl)-1, 3-propanediamine; men = N-methylethylenediamine), the structures of three mer-isomers have been determined by single crystal X-ray diffractions, crystal data: for (1) m3-[ZnCl₄] (monoclinic $P2_1/c$, $a = 8.0874(18)$, $b = 15.135(3)$, $c = 15.426(4)$ Å, $\beta = 99.303(6)^\circ$, $Z = 4$), for (2) m4-[ZnCl₄] (orthorhombic $P2_12_12_1$, $a = 9.348(4)$, $b = 12.437(6)$, $c = 15.666(8)$ Å, $Z = 4$) and for (3) m4'-[ZnCl₄] (orthorhombic $P2_12_12_1$, $a = 9.302(4)$, $b = 12.393(9)$, $c = 15.621(9)$ Å, $Z = 4$)。

Keywords: Co(III) complexes geometric mer-isomers crystal structures

0 Introduction

Amine complexes of cobalt(III) invariably undergo base catalysed substitution reactions in aqueous solution, and the source of the catalysis is via deprotonation of a bound amine; the resulting amine ion is a potent

labilizer for any potential leaving group^[1,2] and leads to the rate law:

$$k(\text{obsd}) = kK[\text{OH}^-] = k_{\text{OH}}[\text{OH}^-]$$

Most of the studies of this reaction have centred on tetraamine and pentaaminocobalt(III) species^[3,4], usually

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chloride as a leaving group. House has provided an immense amount of kinetic data on these systems^[13~11], while Tobe has provided a detailed consideration of the important factors in the mechanism^[12, 12]. Sargeson, Jackson, Buckingham and Marty and coworkers have concentrated on the stereochemical aspects which have elucidated some of the subtleties of the process, and some significant papers in this quest not covered in the recent reviews are cited^[13~20].

Outstanding problems in the complete understanding of the mechanism are (i) the effective site of deprotonation, and (ii), the factors controlling the reactivity of the aminate intermediate species. The latter shows a remarkable and enormous range in reactivity; rate enhancement up to 15 orders of magnitude relative to the parent amine complex is observed. Such an enormous rate acceleration is the key to the intense interest in the base catalysed reaction.

The tools of trade to probe the details of the mechanism are (i) to produce complexes with a single acidic proton in a specific position (e. g. cis or trans to the leaving group) which relate to the effective site of deprotonation directly, and (ii) to deal with systems in which the complex and its isomers are all chiral. Thus, careful investigations of reactant chirality and stereochemistry have to led a better understanding of the chemistry.

The $[\text{Co}(2, 3\text{-tri})(\text{men})\text{Cl}][\text{ZnCl}_4]$ system in this paper is such a system where the isomers are all chiral due to no any symmetric element in complex cation, and there are twenty possible geometric isomers (referring to Fig. 1), this paper describes the structures of three isomers of $[\text{Co}(2, 3\text{-tri})(\text{men})\text{Cl}][\text{ZnCl}_4]$ system corresponding to m3, m4 and m4' in Fig. 1.

1 Experimental

1.1 Synthesis

The isomers were prepared as described procedure of Duffy and House^[21], and Gainsford and House^[22] on the same scale. An aqueous solution (50mL) of 2, 3-tri (3.40g, $29.1 \times 10^{-3}\text{mol}$) and an equimolar amount of men(2.15g, $29.1 \times 10^{-3}\text{mol}$) were added to a stirred

solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (7.5g) and sodium perchlorate (17g) in water (70mL). A rapid stream of air was passed through the stirred solution at room temperature for four hr; during this period a grey-brown precipitate formed. The suspension was left at 4°C overnight and collected by filtration. The dark brown crystalline complexes (peroxo-bis[(men) (2, 3-tri) cobalt (III)]) were decomposed by heating in excess concentrated HCl for an hour, then loading onto a Dowex column, and eluting (HCl) in the usual way. Five well-separated bands developed, and the band-1, 2 and 4 proved to be the m4-Cl, m4'-Cl and m3-Cl species respectively. The ratio of five bands was 15 (m4): 35 (m4'): 20: 20 (m3): 10.

1.2 X-ray Crystal Structure Analysis

Single crystals of the isomers m3, m4 and m4' suitable for X-ray crystal structural determinations were obtained by gradually adding " H_2ZnCl_4 " ($2\text{mol} \cdot \text{dm}^{-3}$) to an aqueous solution of the chloride salts at room temperature. Crystals of the three mer-isomers are red-pink and air stable. Diffraction data were collected at ambient temperature on a Bruker P4 X-ray Four-circle Diffractometer with $\text{Mo K}\alpha$ Radiation. The details of the data collection and crystallographic data are summarised in Table 1.

The crystal structure was solved by direct method (SHELXS-97) which yielded the positions of part of non-hydrogen atoms and subsequent difference Fourier syntheses were employed to locate all of the remaining non-hydrogen atoms which did not show up in the initial structure. All of non-hydrogen atoms were refined anisotropically, and all of hydrogen atoms were located basing on difference Fourier Syntheses. All of atoms were refined by Least Square methods (by SHELXL-97) to convergence. The final atomic coordinates of non-hydrogen atoms are given in Table 2 and selected bond lengths and angles in Table 3. Perspective views are shown in Figs. 2 ~ 4 respectively. Particularly, the packing arrangement in unit cell of the m4- $[\text{ZnCl}_4]$ is shown in Fig. 5 where the cations are enantiomorph.

2 Results and Discussion

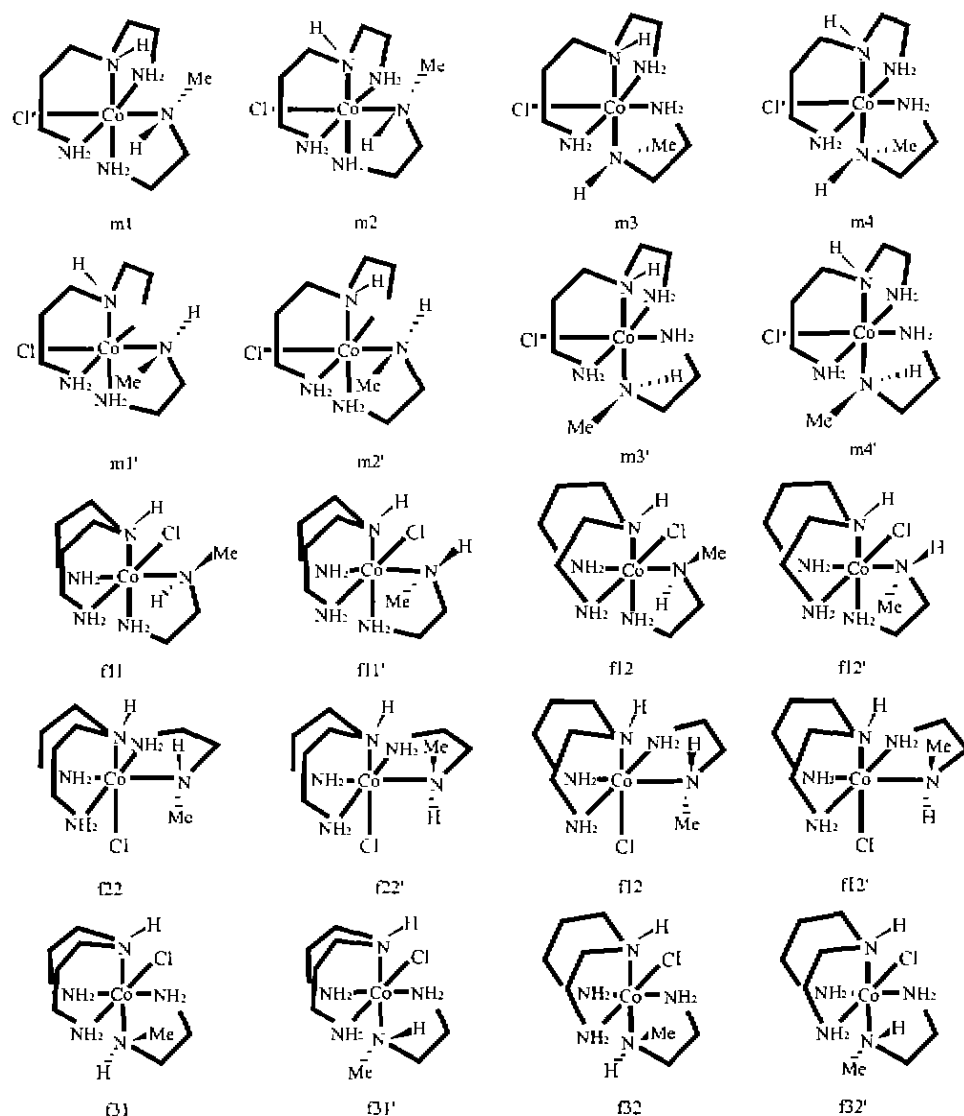


Fig. 1 Twenty possible geometric isomers for $[\text{Co}(2, 3\text{-tri})(\text{men})\text{Cl}]^{2+}$ system

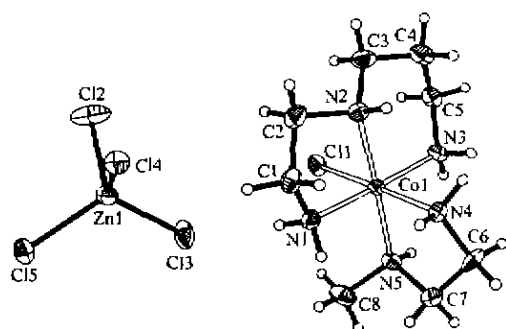


Fig. 2 A general view of the cation (m3) and $[\text{ZnCl}_4]^{2-}$

2.1 Description of the Structures of the $[\text{Co}(2, 3\text{-tri})(\text{men})\text{Cl}]^{2+}$ Isomers

The $[\text{Co}(2, 3\text{-tri})(\text{men})\text{Cl}]^{2+}$ system appears to be the first one which contains twenty possible geo-

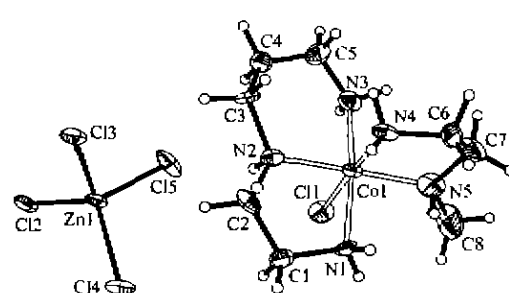


Fig. 3 A general view of cation (m4') and $[\text{ZnCl}_4]^{2-}$ metric isomers (Fig. 1) while a large number of $[\text{Co}(\text{triame})(\text{diamine})\text{Cl}]^{2+}$ systems have been synthesized and studied^[17, 18, 23-26]. For the $[\text{Co}(2, 3\text{-tri})(\text{asymmetric diamine})\text{Cl}]^{2+}$ system, three factors could lead

Table 1 Crystal Data and Data Collection Details for m3-, m4- and m4'-[Co(2, 3-tri)(men)Cl][ZnCl₄]

isomer	m3	m4	m4'
formula	C ₃ H ₂₅ N ₃ Cl ₅ ZnCo	C ₃ H ₂₅ N ₃ Cl ₅ ZnCo	C ₃ H ₂₅ N ₃ Cl ₅ ZnCo
f. w.	492.88	492.88	492.88
temperature	294(2)K	294(2)K	294(2)K
wave length	0.71073Å	0.71073Å	0.71073Å
crystal system	monoclinic	orthorhombic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	8.0874(18)	9.348(4)	9.302(4)
<i>b</i> /Å	15.135(3)	12.437(6)	12.393(9)
<i>c</i> /Å	15.426(4)	15.666(8)	15.621(9)
α /(°)	90	90	90
β /(°)	99.303(6)	90	90
γ /(°)	90	90	90
<i>V</i> /Å ³	1863.4(7)	1821.3(15)	1800.7(18)
<i>D_c</i> /(g·cm ⁻³)	1.757	1.798	1.818
<i>Z</i>	4	4	4
<i>F</i> ₀₀₀	1000	1000	1000
scan technique	ω -2 θ	ω -2 θ	ω -2 θ
scan range(θ /(°))	2.55~27.65	2.09~27.66	2.10~27.81
no. unique	7430	7064	7878
no. observed	4308	4186	4160
no. variables	182	168	157
<i>R</i> ^a	0.0573	0.0767	0.0699
<i>R_w</i> ^b	0.1307	0.1774	0.1864

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b R_w = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2} = 1/\sigma^2(F_o).$$

Table 2 Selected Atomic Coordinates and Equivalent Isotropic Thermal Parameters for m3-, m4-, and m4'-[Co(dien)(ibn)Cl][ZnCl₄]

atom	m3-[ZnCl ₄]				m4-[ZnCl ₄]				m4'-[ZnCl ₄]			
	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i> _{eq}	<i>x</i>	<i>Y</i>	<i>Z</i>	<i>U</i> _{eq}	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i> _{eq}
Co(1)	1803(1)	3808(1)	2282(1)	33(1)	-1423(1)	3267(1)	7526(1)	48(1)	-1427(1)	-3269(1)	-7528(1)	50(1)
Cl(1)	213(1)	5023(1)	2071(1)	58(1)	-455(2)	4918(1)	7756(1)	88(1)	-460(2)	-4924(1)	-7756(1)	89(1)
N(1)	2997(4)	4286(2)	3375(2)	47(1)	548(3)	2673(3)	7545(3)	73(1)	567(4)	-2642(3)	-7544(3)	75(1)
N(2)	3572(4)	4368(2)	1725(2)	46(1)	-1132(3)	3409(3)	6317(2)	60(1)	-1154(4)	-3436(3)	-6324(2)	62
N(3)	685(4)	3335(2)	1145(2)	43(1)	-3321(4)	3960(3)	7458(2)	66(1)	-3310(5)	-3954(3)	-7430(3)	77(2)
N(4)	3033(3)	2696(2)	2458(2)	41(1)	-2254(3)	1861(2)	7384(2)	58(1)	-2254(4)	-1869(3)	-7405(3)	66(1)
N(5)	148(4)	3219(2)	2914(2)	46(1)	-1664(5)	3015(3)	8742(3)	89(2)	-1662(6)	-3011(4)	-8729(3)	102(2)
Cl(1)	4704(5)	4582(3)	3275(3)	57(2)	1210(5)	2834(4)	6685(3)	82(2)	1218(6)	-2831(5)	-6703(3)	73
Cl(2)	4516(6)	5018(3)	2370(3)	71(2)	106(5)	2790(3)	5985(3)	72(2)	164(5)	-2798(4)	-5991(3)	73
Cl(3)	3130(6)	4769(3)	843(3)	66(2)	-2334(4)	3354(3)	5683(3)	67(1)	-2370(5)	-3333(4)	-5692(3)	67(1)
Cl(4)	2267(5)	4126(3)	183(3)	64(2)	-3580(6)	4133(4)	5927(4)	128(2)	-3566(7)	-4088(5)	-5926(4)	84
Cl(5)	597(5)	3854(3)	341(3)	56(1)	-4174(5)	3911(4)	6689(3)	93(2)	-4193(7)	-3892(6)	-6700(4)	111(1)
Cl(6)	1914(5)	1991(2)	2667(3)	65(2)	-2578(6)	1417(4)	8225(3)	102(2)	-2586(8)	-1407(5)	-8228(4)	113
Cl(7)	852(6)	2357(3)	3241(3)	72(2)	-2618(6)	2154(4)	8881(4)	95(2)	-2614(7)	-2137(5)	-8889(4)	105
Cl(8)	-496(5)	3703(3)	3636(3)	75(2)	-995(7)	3552(4)	9392(3)	110(2)	-1033(11)	-3564(7)	-9418(4)	157
Zn(1)	3934(1)	7142(1)	4591(1)	52(1)	942(1)	5249(1)	4316(1)	58(1)	942(1)	-5245(1)	-4316(1)	60(1)
Cl(2)	3325(2)	8199(1)	3522(1)	110(1)	1430(1)	6681(1)	3489(1)	75(1)	1440(1)	-6681(1)	-3488(1)	78(1)
Cl(3)	1888(2)	6163(1)	4316(1)	92(1)	2885(1)	4526(1)	4913(1)	80(1)	-261(2)	-3992(1)	-3544(1)	78(1)
Cl(4)	6566(1)	6656(1)	4483(1)	58(1)	-257(1)	3988(1)	3541(1)	74(1)	2885(1)	-4526(1)	-4915(1)	83(1)
Cl(5)	4034(2)	7809(1)	5899(1)	67(1)	-619(2)	5814(1)	5341(1)	106(1)	-608(2)	-5820(1)	-5348(1)	106(1)

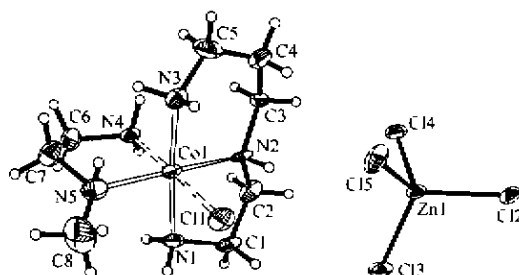
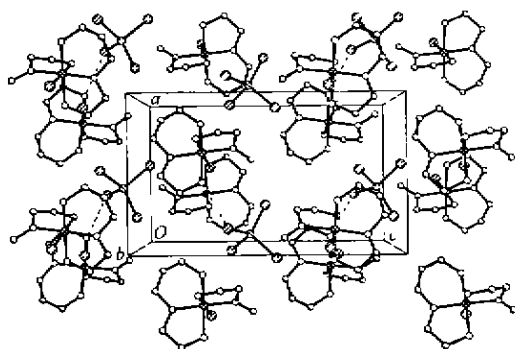
to increase the number of the isomers in the system. First, a R group replacing a -NH₂- or -CH₂- of en (= ethylenediamine) offers two possible end-to-end ar-

rangements of the asymmetrical diamine chelate, such as in the cases of m1 and m3 or f1 and f3. Second, one correlated end of the asymmetric diamine could be close

Table 3 Selected Bond Distances(Å), Bond Angles ($^{\circ}$) and Deviations of Angles for m3-, m4-, and m4'- $[\text{Co}(2,3\text{-tri})(\text{men})\text{Cl}][\text{ZnCl}_4]$

atom-atom	m3		m4		m4'	
Co(1)-Cl(1)	2.2378		2.2733		2.267	
Co(1)-N(1)	1.942		1.984		2.011	
Co(1)-N(2)	1.976		1.92		1.908	
Co(1)-N(3)	1.974		1.976		1.953	
Co(1)-N(4)	1.952		1.926		1.908	
Co(1)-N(5)	1.989		1.944		1.917	
Σ bonds	12.0708		12.0233		11.964	
N(1)-C(1)	1.483		1.496		1.467	
N(2)-C(2)	1.515		1.485		1.549	
N(2)-C(3)	1.48		1.501		1.507	
N(3)-C(5)	1.46		1.446		1.407	
N(4)-C(6)	1.468		1.461		1.441	
N(5)-C(7)	1.479		1.411		1.422	
N(5)-C(8)	1.495		1.368		1.404	
C(1)-C(2)	1.529		1.507		1.483	
C(3)-C(4)	1.497		1.563		1.498	
C(4)-C(5)	1.469		1.346		1.365	
C(6)-C(7)	1.44		1.376		1.372	
Σ bonds	28.3858		27.9833		27.879	

atom-atom-atom	angle($^{\circ}$)	deviation	angle($^{\circ}$)	deviation	angle($^{\circ}$)	deviation
N(1)-Co(1)-N(2)	85.64	4.36	85.33	4.67	86.11	3.89
N(1)-Co(1)-N(4)	91.76	1.76	92.21	2.21	91.25	1.25
N(1)-Co(1)-N(5)	91.23	1.23	91.86	1.86	91.6	1.6
N(2)-Co(1)-N(3)	91.62	1.62	91.91	1.91	89.75	0.25
N(2)-Co(1)-N(4)	92.37	2.37	91.56	1.56	93.06	3.06
N(3)-Co(1)-N(4)	87.74	2.26	91.6	1.6	92.7	2.7
N(3)-Co(1)-N(5)	91.48	1.48	91.09	1.09	91.48	1.48
N(4)-Co(1)-N(5)	85.07	4.93	85.43	4.57	84.28	5.72
N(1)-Co(1)-Cl(1)	90.75	0.75	87.95	2.05	88.93	1.07
N(2)-Co(1)-Cl(1)	91.36	1.36	90.94	0.94	90.26	0.26
N(3)-Co(1)-Cl(1)	89.93	0.07	88.36	1.64	88.58	1.42
N(5)-Co(1)-Cl(1)	91.32	1.32	92.07	2.07	92.4	2.4
N(1)-Co(1)-N(3)	177.19	2.81	175.36	4.64	175.16	4.84
N(2)-Co(1)-N(5)	175.91	4.09	175.81	4.19	176.46	3.54
N(4)-Co(1)-Cl(1)	175.66	4.34	177.5	2.5	176.68	3.32
total distortions*		58.26		63.67		61.9
N(1)-C(1)-C(2)	105.6	3.9	111.6	2.1	113.2	3.7
N(2)-C(2)-C(1)	106.5	3	105.1	4.4	104.9	4.6
N(2)-C(3)-C(4)	112	2.5	111.6	2.1	110.2	0.7
N(3)-C(5)-C(4)	111.8	2.3	120.2	10.7	117.3	7.8
C(7)-C(6)-N(4)	107.8	1.7	115.3	5.8	114.4	4.9
C(6)-C(7)-N(5)	111.4	1.9	111.9	2.4	111	1.5
C(1)-N(1)-Co(1)	111.3	1.8	108.7	0.8	107.9	1.6
C(2)-N(2)-Co(1)	108.4	1.1	114.1	4.6	112.4	2.9
C(3)-N(3)-Co(1)	119.5	10	122.9	13.4	122.5	13
C(5)-N(5)-Co(1)	120.8	11.3	121.5	12	124.2	14.7
C(6)-N(4)-Co(1)	109.8	0.3	108.8	0.7	111	1.5
C(7)-N(5)-Co(1)	108	1.5	110.2	0.7	111.7	2.2
C(8)-N(5)-Co(1)	119.2	9.7	126.7	17.2	128.5	19
C(3)-N(2)-C(2)	111	1.5	109.1	0.4	109.3	0.2
C(7)-N(5)-C(8)	109.9	0.4	123	13.5	119.8	10.3
C(5)-C(4)-C(3)	114.2	4.7	113.4	3.9	114.9	5.4
total distortions**		92.35		132.2		130.8

Fig. 4 A general view of cation (m4) and $[ZnCl_2]^{2-}$ Fig. 5 Packing arrangement in unit cell (m4- $[ZnCl_2]$)

to the five- or six-membered 2, 3-tri chelate ring for the facial isomers, such as in the cases of f11 and f12 or f31 and f32. Last, the two possible orientations of the replaced R (here is methyl) in asymmetric diamine could be closer to the five- or six-membered 2, 3-tri chelate ring, such as in the cases of m1 and m1' or f11 and f11'.

Table 3 shows selected bond lengths and angles of the title isomers. Co-Cl bond length has been considered to be related to the substitutional reactivity of a complex and some controversy has been arisen^[27, 28]. The recent works, we also noted that the sum of bond lengths of the isomers are almost the same^[28]. It is the case in this work, the order of the total bond length is $m3 > m4 > m4'$, and there is only slight difference between the isomers; 0.5 Å between m3 and m4'; 0.1 Å between m4 and m4', the differences are less than 2% of the total bond lengths (referring to Table 3). Thus, it is suggested that the bond length or sum of bond lengths is no obvious link with the reactivities. However, if we consider the deviations (absolute value) from the idealised octahedron or standard angles, such as $109^\circ 28'$ and 120° , for the different isomers, the obviously different total deviations or distortions

may tell some story. In the early works, the distortions of the isomers are consistent to their rates of base hydrolysis at least qualitatively^[28-30]. It is suggested that the total distortions of an isomer could link with the reactivity of this isomer.

Although we have not obtained all the geometric isomers, even all mer-isomers of $[Co(2, 3-tri)(men)Cl]^{2+}$, deviations of angles for the three mer-isomers listed in Table 3 are considered to predict the behavior of them in base hydrolysis. The order of the distortions is $m4 > m4' > m3$, and there is 1.4° difference between the two mer-isomers (m4 and m4'), but there is about a 40° difference between m3 and m4 or m4', the m4 or m4' forms showing the larger deviations. If ground state distortions are correlated with reactivity, the more severely distorted species should be more reactive. In base-hydrolysis, the m4 or m4' species are expected to be more reactive, whereas within each pair, m4 is more reactive than m4'.

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