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$C–H\cdots\pi$ interactions in the $[Co(N\text{-}(2\text{-pyridylmethyl})\text{-}1,3\text{-diaminopropane})(2\text{-aminomethylpyridine})Cl]^{2+}$ system: syntheses, 2D NMR spectroscopy, X-ray structures and energy minimisations

Lin Rong-Guang [a,b], Tao Zhu [a,*], Xue Sai-Feng [a], Zhu Qian-Jiang [a], W. Gregory Jackson [c,*], Wei Zhan-Bing [d], Long La-Sheng [d]

[a] *Institute of Applied Chemistry, Guizhou University, Guiyang 550025, People's Republic of China*
[b] *Fuqing Branch of Fujian Normal University, Fuqing 350300, People's Republic of China*
[c] *School of Chemistry, University College (UNSW), Australian Defence Force Academy, Canberra, ACT 2600, Australia*
[d] *Department of Chemistry, Xiamen University, Xiamen, People's Republic of China*

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Abstract

Ten asymmetric isomers exist for $[Co(ptma)(ampy)Cl]^{2+}$ (ptma = *N*-(2-pyridylmethyl)-1,3-diaminopropane, ampy = 2-aminomethylpyridine) each involving unsymmetrical triamine and diamine ligands. Two of these, the m3 and m4 forms, have been synthesized, and under a variety of conditions none of the other eight has been observed. As for the related $[Co(pema)(ampy)Cl]^{2+}$ system, ab initio energy calculations again show that the isomers containing a $C–H\cdots\pi$ interaction are the more stable forms; the m4 isomer is the most stable. The structures for the two isolated chloro isomers are deduced from the 2D NMR spectra and are confirmed by the X-ray crystal structure determinations.
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Keywords: Cobalt(III) isomers; $C–H\cdots\pi$ Interaction; X-ray crystal structures; 2D NMR; Energy minimisation

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1. Introduction

In previous work we reported on intramolecular $C–H\cdots$aromatic π interactions for metal complexes [1–4]. While such interactions are important for a wide range of phenomena [5–13], the details of such interactions remain not well understood.

Following a substantial amount of research on $[Co(dien)(diamine)X]^{n+}$ complexes involving unsymmetrical diamines with aromatic pyridine nitrogen donors, we shifted our attention to the unsymmetrical triamine pema which has one terminal pyridine donor. This allows for a system of $[Co(triamine)(diamine)X]^{n+}$ isomers (X = Cl, OH) where some have $C–H\cdots\pi$ interactions and others do not. Of the 10 possible isomers, four (f3, f2′, m3 and m4) involve a specific $C–H\cdots\pi$ interaction, shown for the related ptma ligand (Fig. 1) in Fig. 2. This $C–H\cdots\pi$ interaction involves one aromatic proton of pema or ptma (H13) interacting with the π system of ampy for three of the isomers, whereas for the f2′ isomer, it involves one aromatic C–H (H21) of ampy and the π system of the terminal pyridine of the pema or ptma tridentate ligand. These four isomers were anticipated to be stabilized relative to the other six due to these favourable $C–H\cdots\pi$ interactions.

In a previous publication we reported the structures of four of these isomers, and energy calculations for all 10 possible forms, and argued that the specific $C–H\cdots\pi$ interactions were indeed responsible for the stability of the four isolated complexes [5]. We wanted to test the arguments by introducing an additional variable – ring size – which is known to affect the relative stability of geometric isomers, and to see if the relative energies

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[*] Corresponding authors. Fax: +61-2-6268-8090.
E-mail address: wgj@adfa.edu.au (W. Gregory Jackson).

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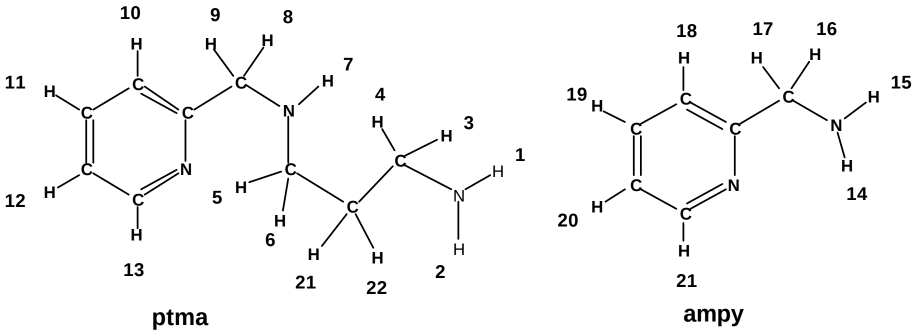

Fig. 1. The ligands and proton numbering scheme.

could still be reliably calculated, and to examine the proposition that the stabilizing π interaction remains a dominant contributor.

The ligand ptma was thus chosen (Fig. 1). It is related to pema with an extra methylene in the aminoalkyl arm of the tridentate which gives rise to the 6-membered ring rather than 5-membered ring formation on complexation (the previous numbering scheme is retained, and the extra protons are thus H22 and H23, Fig. 1). There was an expectation that the energy of the facial isomers relative to the mer might be raised, given the differences between the [Co(2,2-tri)(diamine)X]$^{n+}$, [Co(2,3-tri)(diamine)X]$^{n+}$ and [Co(3,3-tri)(diamine)X]$^{n+}$ systems (tri = $H_2N(CH_2)_mNH(CH_2)_nNH_2$; $m, n = 2$ or 3). Although calculations are yet to be carried out on these systems, it is generally recognized that the introduction of one or two 6-membered rings renders any of the facial isomers difficult to synthesise in any reasonable quantity.

2. Experimental

All chemicals were AnalaR or an equivalent grade. ^{13}C and ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 MHz instrument at 20 °C. Solvents used were Me_2SO-d_6 with the central peak of the CD_3 septet or CHD_2 quintet as the references (^{13}C, δ 39.37 ppm; ^{1}H, δ 2.49 ppm relative to $SiMe_4$). ^{1}H NMR spectra reported for Me_2SO-d_6 are for the $ZnCl_4^{2-}$ salts. The cation exchange medium used was Dowex 50WX2 (H^+ form, 200–400 mesh; Biorad).

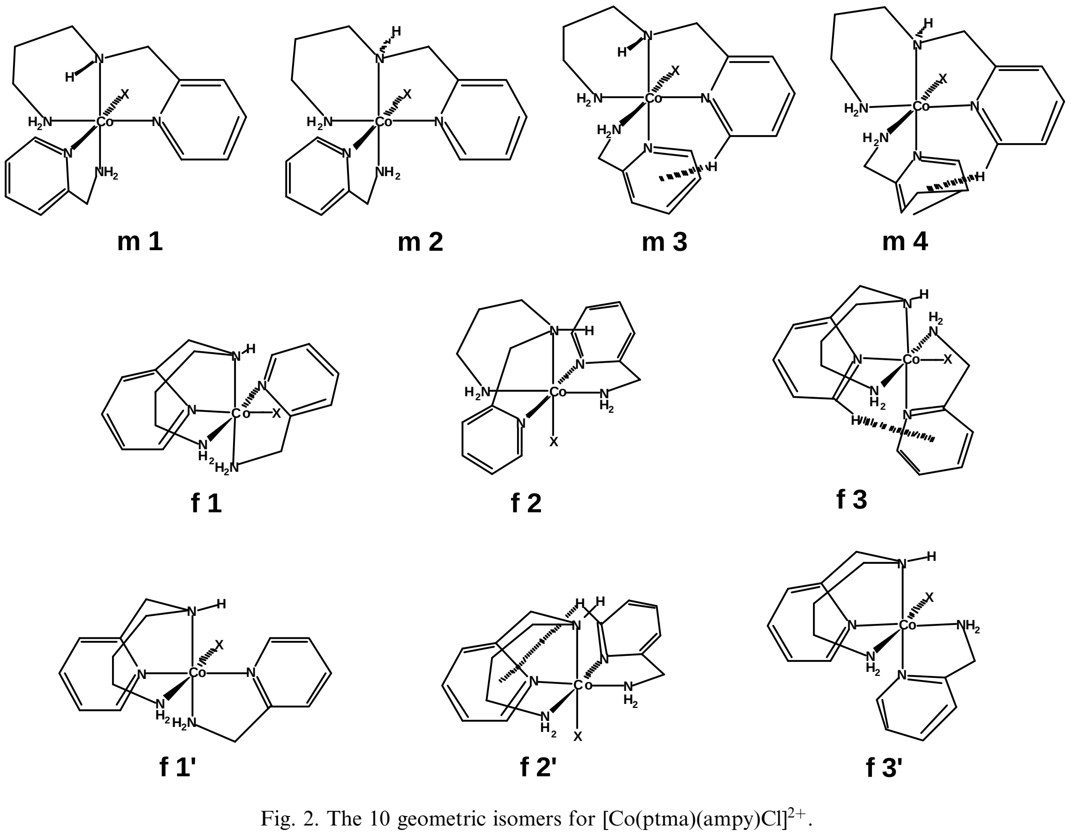

Fig. 2. The 10 geometric isomers for [Co(ptma)(ampy)Cl]$^{2+}$.

2.1. Synthesis of m3- and m4-[Co(ptma)(ampy)Cl]ZnCl$_4$

The general procedures of Duffy et al. [14] and Gainsford and House [15] were followed on similar scales. The ligand ptma was synthesized as for pema using the method of Larsen et al. for the related picam but substituting 1,3-diaminopropane for 2-picolylamine or 1,2-diaminoethane [4,16]. It was isolated as the hydrochloride salt. An aqueous solution (50 mL) of *N*-(2-aminomethylpyridyl)-1,3-diaminopropane (ptma · 3HCl; 7.99 g, 0.0291 mol), NaOH (3.49 g; 0.0873 mol) and 2-aminomethylpyridine (ampy; 3.18 g, 0.0291 mol; Aldrich) were added to a stirred solution of $Co(NO_3)_2 \cdot 6H_2O$ (8.46 g, 0.0291 mol) and sodium perchlorate (17 g) in water (70 mL). A rapid stream of air was passed through the stirred solution at room temperature for 4 hr; during this period a brown precipitate formed. The suspension was left at 4 °C overnight and collected by filtration. The dark brown crystalline complex (peroxo-bis((ptma)(ampy)cobalt(III)) was decomposed by heating in excess concentrated HCl for an hour, then diluted substantially with water before loading onto a Dowex column. The column was eluted with 1–4 M HCl to yield two well-separated red bands, m4 followed by m3, in the ratio 80:20. The syn isomer elutes in front of the anti form, and this is usual. The bands were evaporated to dryness to yield the crude chloride salts. They were crystallised from a minimum volume of water by addition of a fifth volume of 'H_2ZnCl_4' (2 M) to yield the $ZnCl_4^{2-}$ salts. Yields: 8.0 g (m4), 2.1 g (m3; monohydrate); total 59%.

2.2. Kinetic and equilibrium isomer distributions in base hydrolysis

A sample (5 g) of m4-[Co(ptma)(ampy)Cl]Cl$_2$ was dissolved in water (50 mL), and the pH of the solution was adjusted to 14 by adding NaOH (6 M). Concentrated HCl (12 M, 25 mL)) was added, and the solution was heated for one hour at 90 °C. After rota-evaporation to dryness, the residue was dissolved in water and loaded onto a Dowex column. Elution with 2 M HCl again yielded the same m4 (80%) and m3 (20%) isomers (95% recovery).

In other experiments, the chloride salt of m3- or m4-[Co(ptma)(ampy)Cl]$^{2+}$ was dissolved in 10 times its weight of water, and the pH of the solution was adjusted to *ca.* 10 by adding NaOH (1 M) gradually. After 24 hr at room temperature, the solution was worked up as described in the previous paragraph to again yield the m4 (80%) and m3 (20%) isomers.

2.3. X-ray crystal structure analysis

Suitable crystals were mounted with epoxy resin on glass fibres. The diffraction work was performed on a Smart APEX CCD with graphite-monochromatized Mo Kα radiation. Direct methods (SHELXS-97) were used for the structure solutions. The hydrogen atoms were refined in calculated positions assuming idealised geometries. The structure was solved by Patterson methods (SHELXL-97) and refined using empirically corrected absorption data.

3. Results and discussion

3.1. 1D and 2D NMR spectra

All 10 isomers of [Co(ptma)(ampy)Cl]$^{2+}$ are asymmetric and 15 lines are expected for each isomer in the ^{13}C NMR spectrum irrespective of configuration. The two isolated isomers displayed this asymmetry (Fig. 3).

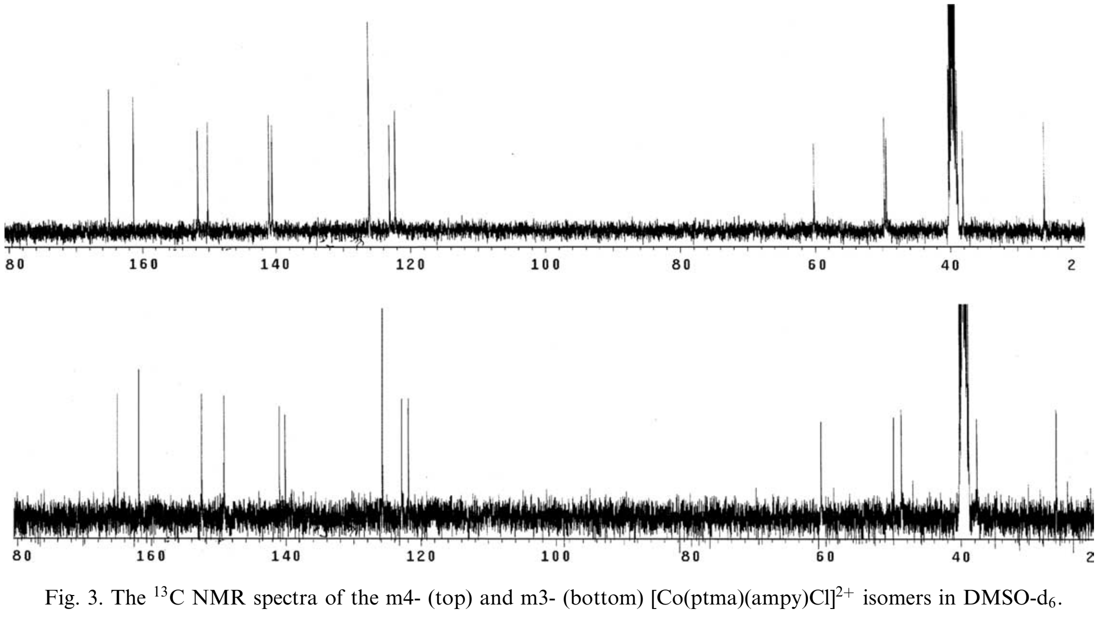

Fig. 3. The ^{13}C NMR spectra of the m4- (top) and m3- (bottom) [Co(ptma)(ampy)Cl]$^{2+}$ isomers in DMSO-d$_6$.

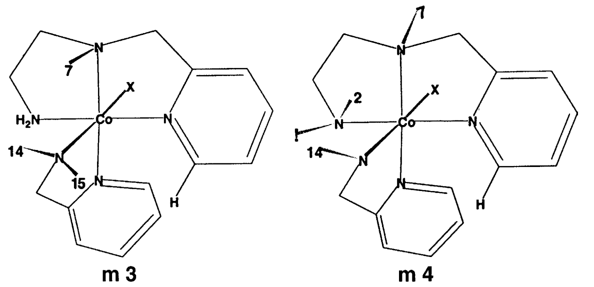

Fig. 4. The H-atom labeling scheme for the two isolated $[Co(ptma)(ampy)Cl]^{2+}$ isomers.

The proton numbering scheme is shown in Fig. 4.

The DQCOSY spectra correlate the resonances of scalar(*J*) coupled hydrogens [3,4,17]. In the [Co(ptma)(ampy)Cl]$^{2+}$ cations, there are two NH_2 groups H1/H2 and H14/H15 which are normally at δ 5~7, and one NH proton H7 which is normally at δ 7.5~9. For the ampy ligand, H14 and H15 correlate with the α-CH_2 protons H16 and H17 which are generally at δ 4~5. For the ptma ligand, the amine protons H1 and H2 correlate with the –CH_2- protons H3 and H4 which are generally at ~δ 3. Thus, one can differentiate the sets of terminal NH_2 protons H1/H2, H14/H15 and the unique sec-NH H7.

From the DQCOSY spectrum of the m4 isomer (Fig. 5 (top)), the pair of amine proton signals H1 and H2 are at δ 5.41 and 5.11, while H14 and H15 are at δ 5.83 and 5.80 and H(7) at δ 7.17.

From the DQCOSY spectrum of the m3 isomer (Fig. 6 (top)), the corresponding pair of amine proton signals H1 and H2 are at δ 5.43 and 5.11, while H14 and H15 are at δ 5.96 and 5.59, with H7 at δ 8.05.

To differentiate m3 and m4, the cross peaks of proton H7 with H16 and H17, or their absence, in the NOESY spectra are the key. They are correlated in the syn (m3) but not the anti (m4) form. The NOESY spectrum of the m3 isomer bears this out, Fig. 6 (bottom).

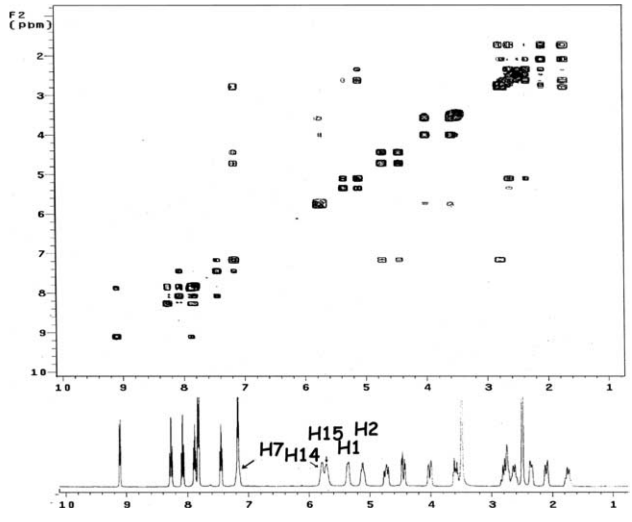

Fig. 5. DQCOSY (top) and 1D (bottom) ^1H spectra of m4-$[Co(ptma)(ampy)Cl]ZnCl_4 \cdot H_2O$ in DMSO-d_6.

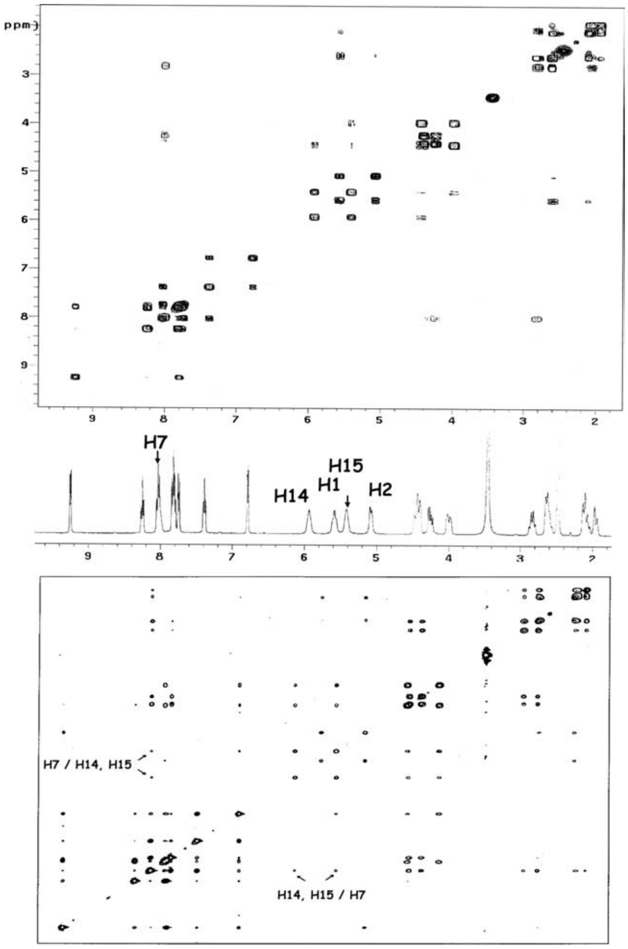

Fig. 6. DQCOSY (top), 1D (middle) and NOESY (bottom) ^1H spectra of m3-$[Co(ptma)(ampy)Cl]ZnCl_4$ in DMSO-d_6.

These assignments were assisted by the fact the inner aromatic C–H protons are triplets, while the outer protons are doublets in the 1D spectra; H15 (m4 at δ 7.2 ppm and m3 at δ 6.8ppm) appears at highest field for the aromatic CH protons because it is shielded by the pyridyl of ampy (Fig. 2). Conversely, the deshielding of H7 by the ampy ligand for m3 but not for the m4 isomer is a decisive feature – the shifts differ by almost 1 ppm.

3.2. X-ray crystal structural data

The details of the data collection and crystallographic data are summarised in Table 1. Perspective views of the cations are shown in Figs. 7 and 8, and corresponding unit cells in Figs. 8S and 10S (Supplementary Material).

A structure for the m3 isomer has appeared previously [18]. That material ($ZnCl_4 \cdot 0.5H_2O$; Cc1 space group) is different in the solid state to the present structure, and clearly it was crystallized under different conditions. The molecular dimensions are of course very similar. Interestingly, we have observed this dimorphism

Table 1
Crystal data and data collection details for the two [Co(ptma)(ampy)Cl] $ZnCl_4$ isomers

	m3	m4
Formula	C15H25N5Cl5OZnCo	$C_{15}H_{23}N_5Cl_5ZnCo$
f.w.	592.95	574.93
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$p21/c$
a (nm)	1.13859(8)	0.78692(6)
b (nm)	1.22869(9)	1.78041(13)
c (nm)	1.63378(11)	1.65711(12)
α (°)	90	90
β (°)	90	94.0680(10)
γ (°)	90	90
V (nm^3)	2.2856(3)	2.3158(3)
$\rho_{calc.}$ ($Mg\ m^{-3}$)	1.723	1.649
Z	6	4
F_{000}	1200	1160
μ (mm^{-1})	2.376	2.34
Scan technique	$\omega - 2\theta$	$\omega - 2\theta$
Scan range (2θ)	4.14–50.00	3.36–50.00
Number of unique reflections	4014	4072
Number observed reflections	3946	3890
Number of variables	259	244
R^a	0.0888	0.0912
$R_w{}^b$	0.1839	0.1872

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

phenomenon before for pentaaminechlorocobalt(III) complexes [19]. Furthermore, the present m3 salt crystallizes in the chiral space group $P2_12_12_1$, and it provides yet another example of conglomerate formation (spontaneous resolution).

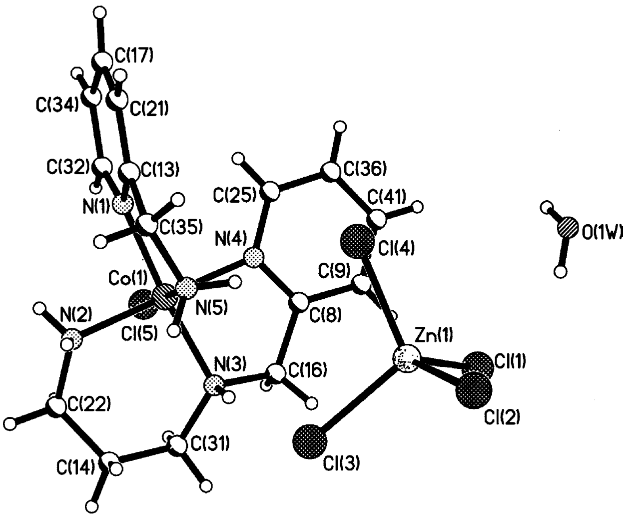

Fig. 7. Molecular structure for one enantiomer (arbitrary) of m3-[Co(ptma)(ampy)Cl]$ZnCl_4 \cdot H_2O$.

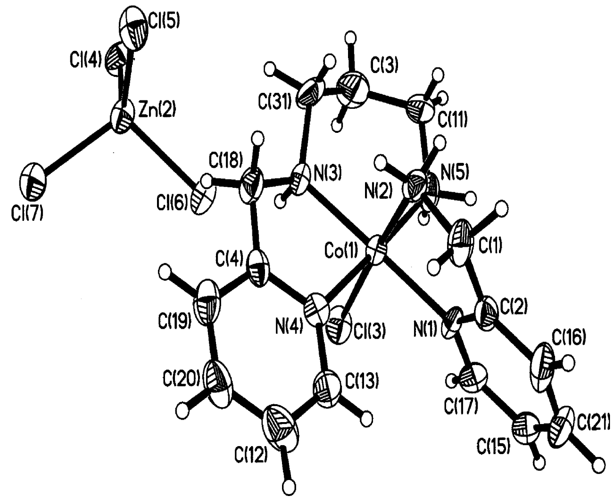

Fig. 8. The molecular structure of one enantiomer (arbitrary) of m4-[Co(ptma)(ampy)Cl]$ZnCl_4$.

3.3. Computations

Pre-optimized configurations of the [Co(ptma)(ampy)Cl]$^{2+}$ isomers were built using INDO/1 in the HYPERCHEM program [3]. Starting with these geometries, optimisation of the structures at the RHF/LANL2DZ level was carried out using the GAUSSIAN 98 package at Zhejiang University.

3.4. Comparison of the crystal and calculated structures

Selected interatomic distances and angles with their estimated standard deviations are given in Tables 2–5. The calculated structural data and the errors between crystal and calculated data are also listed. It can be seen that bond length and bond angle differences between the experimental and calculated results are all less than 3.5%, with most of them less than 1%. Again it is clear that crystal structure data can be satisfactorily reproduced by ab initio calculation [3,12,17,20].

3.5. Relative stability and preference of the isomers in the [Co(ptma)(ampy)Cl]$^{2+}$ system

The relative stability of the all possible geometric isomers in the [Co(ptma)(ampy)Cl]$^{2+}$ systems has been modelled theoretically using the ab initio methods described herein and previously [3,12,17,20]. Table 6 shows the energy calculations for both the gas phase and also for the ions immersed in a solvent dielectric continuum.

One can see immediately that in both the gas phase and in aqueous solution the energies of the m3 and m4 isomers in which a C–H···π interaction exists are significantly higher than the rest. The data in the fourth column indicate that aqueous solvation stabilises all the isomers, particularly m3, such that m3 and m4 have almost the same total energy.

Table 2
Selected experimental and calculated bond distances (nm) for m3-[Co(ptma)(amp)Cl]ZnCl$_4$

Atom–atom	Observed	Calculated	Error (%)
Co(1)–N(5)	0.1949(9)	0.20018	2.71
Co(1)–N(4)	0.1965(8)	0.19985	1.70
Co(1)–N(3)	0.1975(8)	0.20193	2.24
Co(1)–N(1)	0.1976(9)	0.20017	1.30
Co(1)–N(2)	0.1996(9)	0.20161	1.01
Co(1)–Cl(5)	0.2229(3)	0.22863	2.57
N(3)–C(16)	0.1472(14)	0.15015	2.00
N(3)–C(31)	0.1486(15)	0.15125	1.78
N(4)–C(8)	0.1337(14)	0.13477	0.80
N(4)–C(25)	0.1343(14)	0.13517	0.65
N(5)–C(35)	0.1487(16)	0.14991	0.81
N(2)–C(22)	0.1487(15)	0.15123	1.70
C(8)–C(9)	0.1372(18)	0.1388	1.17
C(8)–C(16)	0.1490(17)	0.15019	0.80
C(9)–C(41)	0.135(2)	0.1392	3.11
N(1)–C(32)	0.1334(16)	0.13524	1.38
N(1)–C(13)	0.1352(15)	0.13531	0.08
C(13)–C(21)	0.1365(18)	0.13845	1.43
C(35)–C(13)	0.151(2)	0.151	0.00
C(14)–C(22)	0.1506(19)	0.15247	1.24
C(14)–C(31)	0.1515(19)	0.15255	0.69
C(21)–C(17)	0.132(3)	0.13576	2.85
C(34)–C(17)	0.136(3)	0.13941	2.51
C(36)–C(25)	0.1362(17)	0.13819	1.46
C(41)–C(36)	0.138(2)	0.13981	1.31
C(32)–C(34)	0.1398(19)	0.13872	0.77

Table 3
Selected experimental and calculated bond distances (nm) for m4-[Co(ptma)(amp)Cl]ZnCl$_4$

Atom–atom	Observed	Calculated	Error (%)
Co(1)–N(2)	0.1951(7)	0.20124	3.15
Co(1)–N(1)	0.1952(6)	0.2001	2.51
Co(1)–N(4)	0.1964(6)	0.19966	1.66
Co(1)–N(3)	0.1971(6)	0.20121	2.09
Co(1)–N(5)	0.1970(7)	0.20134	2.20
Co(1)–Cl(3)	0.2247(2)	0.23217	3.32
N(1)–C(17)	0.1332(11)	0.13532	1.59
N(1)–C(2)	0.1354(10)	0.13529	0.08
N(2)–C(1)	0.1484(10)	0.14986	0.98
N(3)–C(18)	0.1486(10)	0.14945	0.57
N(3)–C(31)	0.1497(11)	0.15052	0.55
N(4)–C(13)	0.1342(11)	0.13476	0.42
N(4)–C(4)	0.1349(10)	0.13502	0.09
N(5)–C(11)	0.1472(11)	0.15047	2.22
C(4)–C(19)	0.1392(12)	0.13855	0.47
C(4)–C(18)	0.1473(12)	0.15058	2.23
C(3)–C(31)	0.1486(13)	0.15274	2.79
C(3)–C(11)	0.1505(13)	0.15266	1.44
C(2)–C(16)	0.1381(12)	0.1386	0.36
C(1)–C(2)	0.1463(13)	0.15088	3.13
C(13)–C(12)	0.1361(13)	0.13843	1.71
C(20)–C(12)	0.1372(14)	0.13952	1.69
C(17)–C(15)	0.1368(13)	0.13853	1.26
C(15)–C(21)	0.1378(16)	0.13959	1.30
C(16)–C(21)	0.1385(15)	0.13957	0.77
C(19)–C(20)	0.1358(14)	0.13947	2.70

Table 4
Selected observed and calculated bond angles (°) for m3-[Co(ptma)(amp)Cl]ZnCl$_4$

Atom–atom–atom	Observed	Calculated	Error (%)
N(5)–Co(1)–N(4)	90.1(4)	89.5288	0.63
N(5)–Co(1)–N(3)	90.1(4)	92.4385	2.60
N(4)–Co(1)–N(3)	84.1(4)	82.4863	1.92
N(5)–Co(1)–N(1)	84.6(5)	82.3296	2.68
N(1)–Co(1)–N(4)	92.1(4)	94.1553	2.23
N(3)–Co(1)–N(1)	173.4(4)		
N(2)–Co(1)–N(5)	89.4(4)	91.2992	2.12
N(4)–Co(1)–N(2)	179.2(4)		
N(2)–Co(1)–N(3)	95.3(4)	95.912	0.64
N(2)–Co(1)–N(1)	88.5(4)	87.5083	1.12
N(5)–Co(1)–Cl(5)	179.4(3)		
N(4)–Co(1)–Cl(5)	89.4(3)	91.1742	1.98
Cl(5)–Co(1)–N(3)	90.1(3)	89.9344	0.18
N(1)–Co(1)–Cl(5)	95.2(4)	95.3238	0.13
N(2)–Co(1)–Cl(5)	91.1(3)	88.0616	3.34
C(16)–N(3)–C(31)	110.2(9)	109.5691	0.57
Co(1)–N(3)–C(16)	109.0(7)	107.7487	1.15
Co(1)–N(3)–C(31)	118.7(7)	119.0542	0.30
C(8)–N(4)–C(25)	117.8(9)	119.2126	1.20
Co(1)–N(4)–C(8)	114.7(7)	114.1379	0.49
Co(1)–N(4)–C(25)	127.4(8)	126.4141	0.77
Co(1)–N(5)–C(35)	111.8(8)	111.477	0.29
Co(1)–N(2)–C(22)	117.8(8)	120.6197	2.39
N(4)–C(8)–C(9)	122.4(11)	121.8062	0.49
N(4)–C(8)–C(16)	115.0(9)	115.8769	0.76
C(16)–C(8)–C(9)	122.5(11)	122.2641	0.19
C(8)–C(9)–C(41)	119.3(13)	119.0126	0.24
C(13)–N(1)–C(32)	119.9(10)	119.4367	0.39
Co(1)–N(1)–C(32)	125.4(9)	124.8554	0.43
Co(1)–N(1)–C(13)	113.5(8)	115.7073	1.94
N(1)–C(13)–C(21)	119.9(14)	121.7995	1.58
N(1)–C(13)–C(35)	115.0(10)	116.6151	1.40
C(35)–C(13)–C(21)	125.0(13)	121.5691	2.74
C(22)–C(14)–C(31)	113.3(11)	112.6687	0.56
N(3)–C(16)–C(8)	111.9(9)	109.7349	1.93
C(21)–C(17)–C(34)	119.0(14)	119.1642	0.14
C(13)–C(21)–C(17)	121.5(17)	118.9152	2.13
N(2)–C(22)–C(14)	112.7(10)	112.2728	0.38
N(4)–C(25)–C(36)	122.1(12)	122.1464	0.04
C(41)–C(36)–C(25)	119.3(13)	118.733	0.48
C(9)–C(41)–C(36)	118.9(13)	119.0834	0.15
N(3)–C(31)–C(14)	113.6(10)	112.8498	0.66
N(1)–C(32)–C(34)	119.4(14)	121.7012	1.93
N(5)–C(35)–C(13)	108.9(9)	109.7715	0.80
C(32)–C(34)–C(17)	119.7(15)	118.9809	0.60

Experimentally, the m3 and m4 chloro complexes were the only two isomers to be synthesized (m4:m3 = 80:20), by kinetic or equilibration routes, a result consistent with the calculations.

There are a number of common features of these calculations for the pema and present ptma systems: 1. The f1, f1′, f2, m1 and m2 isomers have very high energies and are never observed; 2. The f3′ isomers have a strong steric clash between the CH protons α to the pyridyl nitrogens, similar to that evident in the sym-[Co(dmptacn)X]$^{n+}$ and [Co(dmpmetacn)X]$^{n+}$ species [21]; consequently, none of these configurations have

Table 5
Selected observed and calculated bond angles (°) for m4-[Co(ptma)(amp)Cl]ZnCl$_4$

Atom–atom–atom	Observed	Calculated	Error (%)
N(2)–Co(1)–N(1)	83.3(3)	82.7261	0.69
N(2)–Co(1)–N(4)	88.7(3)	89.6139	1.03
N(1)–Co(1)–N(4)	94.0(3)	95.5213	1.62
N(2)–Co(1)–N(3)	95.2(3)	94.5313	0.70
N(1)–Co(1)–N(3)	177.3(3)		
N(4)–Co(1)–N(3)	83.8(3)	83.1186	0.81
N(5)–Co(1)–N(2)	92.0(3)	93.3361	1.45
N(5)–Co(1)–N(1)	88.0(3)	88.276	0.31
N(4)–Co(1)–N(5)	178.0(3)		
N(5)–Co(1)–N(3)	94.2(3)	93.205	1.06
N(2)–Co(1)–Cl(3)	175.8(2)		
N(1)–Co(1)–Cl(3)	93.3(2)	95.2174	2.06
N(4)–Co(1)–Cl(3)	89.3(2)	89.3515	0.06
Cl(3)–Co(1)–N(3)	88.1(2)	87.4955	0.69
N(5)–Co(1)–Cl(3)	90.1(2)	87.8289	2.52
C(2)–N(1)–C(17)	119.3(7)	119.3746	0.06
Co(1)–N(1)–C(17)	126.6(6)	125.4358	0.92
Co(1)–N(1)–C(2)	114.0(5)	115.181	1.04
Co(1)–N(2)–C(1)	109.9(5)	111.435	1.40
C(18)–N(3)–C(31)	110.3(7)	110.9866	0.62
Co(1)–N(3)–C(18)	109.8(5)	109.6356	0.15
Co(1)–N(3)–C(31)	119.8(5)	120.8425	0.87
C(4)–N(4)–C(13)	119.0(7)	119.316	0.27
Co(1)–N(4)–C(13)	126.9(6)	125.5926	1.03
Co(1)–N(4)–C(4)	114.1(5)	114.6592	0.49
Co(1)–N(5)–C(11)	122.4(5)	121.8089	0.48
N(4)–C(4)–C(19)	120.5(8)	121.8034	1.08
N(4)–C(4)–C(18)	116.2(7)	115.7211	0.41
C(18)–C(4)–C(19)	123.2(8)	122.4579	0.60
C(11)–C(3)–C(31)	114.7(9)	113.5521	1.00
N(1)–C(2)–C(16)	121.1(9)	121.809	0.59
N(1)–C(2)–C(1)	115.8(7)	116.5057	0.61
C(1)–C(2)–C(16)	123.1(8)	121.6244	1.20
N(2)–C(1)–C(2)	110.2(7)	109.5952	0.55
N(5)–C(11)–C(3)	111.7(7)	111.8012	0.09
C(13)–C(12)–C(20)	119.5(10)	118.7755	0.61
N(4)–C(13)–C(12)	122.0(9)	122.0613	0.05
C(17)–C(15)–C(21)	118.8(10)	118.9981	0.17
C(2)–C(16)–C(21)	118.7(10)	118.9107	0.18
N(1)–C(17)–C(15)	122.3(9)	121.7462	0.45
N(3)–C(18)–C(4)	110.7(7)	109.6079	0.99
C(4)–C(19)–C(20)	119.6(8)	118.9178	0.57
C(19)–C(20)–C(12)	119.3(9)	119.1175	0.15
C(16)–C(21)–C(15)	119.6(9)	119.1502	0.38
N(3)–C(31)–C(3)	110.6(8)	112.6942	1.89

been isolated, a fact supported by the energy calculations (f3′ has the highest energy in both the pema and ptma systems).

Differences become apparent in a comparison for the f3 and f2′ forms. Both are stabilized by a specific C–H$\cdots\pi$ aromatic interaction; however, they are observed in the 2,2-tri but not the 2,3-tri ligand system. The calculated energies support the experimental observations, but it is not immediately obvious why these two isomers are sufficiently unstable in the 2,3-tri system to be unobserved. Models suggest that a stabilizing π interaction is still likely if the chair conformation is adopted for the 6-membered ring component of facially bound ptma. However, an energy shift of just 10 kJ mol^{-1} is sufficient to move a 50:50 isomer I:II distribution to 2:98, i.e., experimentally difficult to detect, and for water, we note that the f2′ and f3 isomers are computed to be less stable than the m3 isomer by 10 and 18 kJ mol^{-1}, respectively.

3.6. Summary and conclusions

The two [Co(ptma)(ampy)C1]$^{2+}$ isomeric structures assigned spectroscopically have been confirmed by the single crystal structural analysis reported herein. Further, there is good agreement between the X-ray structural parameters and those calculated through the ab initio methods. At present we cannot be certain of the specific origin of the preferred stability of the two isomers. The answer awaits further work with 6-membered ring systems, and the explicit calculation of the energy for the unique C–H$\cdots\pi$ interaction that presently is difficult given the large number of other contributions to the total energy.

4. Supplementary material

Figs. 8S and 10S, unit cell diagrams available from the authors (W.G.J.). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 209675 (m3) and 209676 (m4). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge,

Table 6
Computed relative energies of alternative isomers [Co(ptma)(amp)Cl]$^{2+}$ system

Isomer	E (a.u.$_{(\mathrm{gas})}$)	E (a.u.$_{(\mathrm{H_2O})}$)	ΔE (kJ mol$^{-1}_{(\mathrm{gas-H_2O})}$)	E (kJ mol$^{-1}_{(\mathrm{gas})}$)	E (kJ mol$^{-1}_{(\mathrm{H_2O})}$)
f1	−1011.84176	−1011.845462	9.8	32.8	33.6
f1′	−1011.84213	−1011.845615	9.2	31.8	33.2
f2	−1011.84756	−1011.850766	8.5	17.5	19.6
f2′	−1011.85093	−1011.854004	8.1	8.6	11.1
f3	−1011.84848	−1011.850894	6.4	15.1	19.3
f3′	−1011.83702	−1011.840711	9.8	45.3	46.2
m1	−1011.84564	−1011.848082	6.5	22.6	26.7
m2	−1011.84443	−1011.847308	7.6	25.8	28.8
m3	−1011.85238	−1011.857842	14.4	4.7	0.9
m4	−1011.85418	−1011.858187	10.6	0.0	0.0

CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit~ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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