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On the preference for the *sym–fac* isomer in the [Co(*N*,*N*′-bis(2-aminomethyl)amine)(2,2′-bipyridine)Cl]$^{2+}$ system

Zhu Tao [a], Qianjiang Zhu [a], W. Gregory Jackson [b,*], Zhong-Yuan Zhou [c], Xiang-Ge Zhou [c]

[a] *Department of Basic Courses, Institute of Applied Chemistry, Guizhou University, Guiyang 550025, People's Republic of China*
[b] *School of Chemistry, University College (UNSW), Australian Defence Force Academy, Canberra, ACT 2600, Australia*
[c] *The Chengdu Institute of Organic Chemistry, Chinese Academy of Science, Chengdu 610041, People's Republic of China*

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Abstract

The *sym–fac* isomer of [Co(bpma)(bipy)Cl]$^{2+}$ is the only one synthesised for this system where, in principle, four exist (bpma = *N*,*N*′-bis(2-aminomethyl)amine, bipy = 2,2′-bispyridine). This observation is supported by ab initio energy calculations which reveal this to be the most stable form, and the *unsym–fac* isomer the highest in energy. It is one of only two cobalt(III) complexes known that contain a single NH centre trans to Cl$^-$. The structure is deduced from the ^{13}C NMR spectrum and 2D NMR techniques and confirmed by the X-ray crystal structure determination. The agreement between the single crystal data and the calculated ab initio molecular parameters is excellent (within ±3%).

Keywords: *Sym–fac*-[Co(bpma)(bipy)Cl]$^{2+}$ isomer; Isomer preference; Cobalt(III) complexes; Crystal structures; Energy minimisation

1. Introduction

In recent years there has been considerable interest in the relative importance of various types of intermolecular interactions, such as hydrogen-bonding, van der Waals, π-stacking, and electrostatic interactions [1]. A so-called X–H···π interaction of a hydrogen atom with the π-system of an aromatic ring in either an intermolecular or an intramolecular fashion has gained attention in the literature. This is a consequence of their role in conformational or isomer preferences for organic compounds, proteins and metal ion complexes [2,3], supramolecular assemblies [4], host-guest interactions [5], and in crystal structure predictions and determinations in general [6,7]. However, the detail of such interactions is poorly understood. The Co(III) complex reported herein, prepared for other reasons, may involve such a X–H···π interaction.

Although a number of complexes of bpma have been reported [8–10], no pentaamine metal ion complexes are known. For bpma, there is the only one NH proton, the central sec-amine, and for the [Co(bpma)(bipy)Cl]$^{2+}$ system, there are four possible geometric isomers for which acidic NH can be cis or trans to the leaving group Cl$^-$ (Fig. 1). For the *sym–fac* isomer of [Co(bpma)(bipy)Cl]$^{2+}$, the NH is trans to the leaving group chloride, and such complexes are rare. If it could be synthesised, a study of its rate of base catalysed hydrolysis offered the prospect of testing the effectiveness of trans deprotonation in base catalysed hydrolysis, never before demonstrated unambiguously [11]. Further, the two mer isomers have configurations in which the single NH proton is cis to the leaving group (Fig. 1). Thus, collectively, these complexes offered the prospect of resolving the long standing problem of the relative effectiveness of *cis* versus *trans* deprotonation in base hydrolysis [11,12], provided we could synthesise them.

As for the isomer preferences in this system, the intramolecular C–H···π interactions of the H6 proton of bipy with the pyridyl of bpma in the complexes are

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* Corresponding author. Fax: +61-2-6268-8090
E-mail address: wgj@adfa.edu.au (W.G. Jackson).

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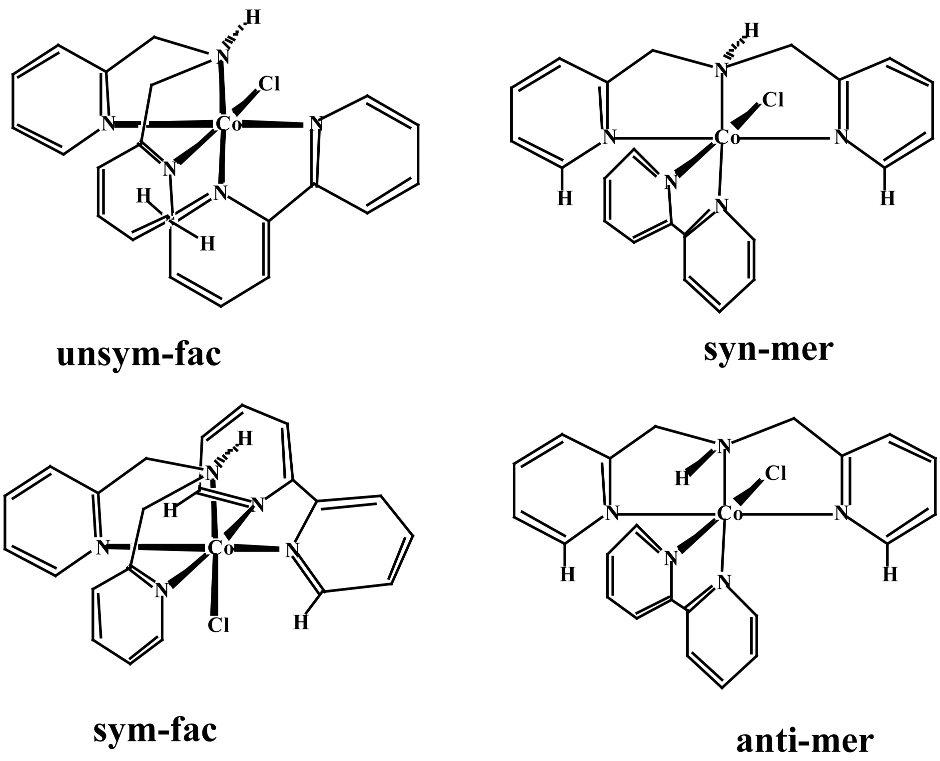

Fig. 1. The four geometric isomers for $[Co(bpma)(bipy)Cl]^{2+}$.

anticipated to involve either a stabilisation or destabilisation (attraction or repulsion), depending upon the position and charge of the groups involved, and we hoped to interpret the energies of the isomers in terms of such π-interactions. Ring current effects with resultant upfield or downfield C–H shifts in the ^1H NMR spectra were also anticipated.

2. Experimental

All chemicals were AnalaR or an equivalent grade. ^{13}C and H^1 NMR spectra were recorded on Varian XL-300 and Unity Plus 400 MHz instruments at 20 °C. Solvents used were D_2O with dioxane as the internal reference (^{13}C, δ 69.27 ppm relative to DSS), and Me_2SO-d_6 with the central peak of the CD_3 septet as the reference (^{13}C, δ 39.37 ppm relative to $SiMe_4$). ^1H NMR spectra reported for Me_2SO-d_6 are for the perchlorate salt; marked downfield shifts, especially for some NH protons, are observed for $ZnCl_4^{2-}$ salts in this solvent. The cation exchange medium used was Dowex 50 W × 2 (H^+ form, 200–400 mesh; Biorad).

2.1. Synthesis of salts of *sym–fac*-*[Co(bpma)(bipy)Cl]*$^{2+}$

The general procedures of Duffy et al. [13] and Gainsford and House [14] were followed on the same scale. An aqueous solution (50 ml) of *N*,*N′*-bis(2-aminomethyl)amine (bpma; 5.79 g, 290.1×10^{-3} mol; Aldrich) and an equimolar amount of 2,2′-bipyridine (bipy; 4.54 g, 291×10^{-3} mol; Aldrich) were added to a stirred solution of $Co(NO_3)_2 \cdot 6H_2O$ (7.5 g) 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 h; during this period a grey–brown precipitate formed. The suspension was left at 4 °C overnight and collected by filtration. The dark brown crystalline complex (peroxo-bis((bpma)(bipy)cobalt(III) species)) 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 washed (H_2O) and then eluted with 2–4 M HCl to yield a major red 2+ band, which was evaporated to dryness and crystallised from a minimum of water using a fifth volume of 'H_2ZnCl_4' (2 M $ZnCl_2$ in 5 M HCl) to yield the $ZnCl_4^{2-}$ salt. The perchlorate salt was crystallised from water–$HClO_4$.

3. Results and discussion

3.1. 1-D and 2-D NMR spectra

The two mer-isomers and the *sym–fac* isomer of $[Co(bpma)(bipy)Cl]^{2+}$ have a plane of symmetry while the *unsym–fac* species is asymmetric. Further, for the mer isomers, the two 'halves' of the bipy ligand are different, whereas they are symmetry related for the *sym–fac* isomer. Thus, for the 22 carbon atoms in the molecule, the number of lines expected in the 1-D ^{13}C NMR spectrum are 16 (6 × 2C, 10 × 1C), 11 (11 × 2C) or 22 (22 × 1C), respectively. The ^{13}C NMR spectrum (Fig. 2) reveals that there are 11 resonances, uniquely defining the isomer as the *sym–fac* form.

The proton numbering scheme for the complex is shown in Fig. 3. Assignment of the overlapping aromatic CH signals for the bpma and bipy rings is possible using the DQCOSY spectrum (Fig. 4(a)). The resonances at δ 7.56, 7.81, 8.54 and 8.95 ppm correspond to protons H6 (doublet), H5 (triplet), H4 (triplet) and H3 (doublet) on bipy; δ 9.27, 7.86, 8.26 and 7.84 ppm are for protons H6′(doublet), H5′(triplet), H4′(triplet) and H3′(doublet) on bpma. Which set of four signals belonged to which ring followed from the NOESY spectrum discussed ahead. The AB quartet comprising doublets centred at δ 4.48 and 4.64 ppm represents H2 and Hl. The broader singlet at δ 8.33 ppm is clearly the NH proton H0 (Fig. 4(b)), and this is correlated with one of the CH_2 protons at δ 4.64 ppm.

These assignments were assisted by the fact the inner aromatic C–H protons are triplets, while the outer protons are doublets in the 1D spectrum (Fig. 4(b)). In the NOESY spectrum (Fig. 4(c)), through-space correlations between H3′ on the bpma ring (δ 8.95 ppm) and H2 and H1 on bpma (δ 4.48/4.64 ppm) are expected, and indeed observed. Also H6 (δ 7.56 ppm) appears at highest field for the aromatic CH protons because it is shielded by the pyridyl of bpma (Fig. 3). The NMR spectra are thus totally consistent with a *sym–fac*-$[Co(bpma)(bipy)Cl]^{2+}$ complex.

3.2. X-ray crystal structure analysis

The structure was solved by Patterson methods (SHELXS-86) and refined using empirically corrected absorption data. Hydrogen atoms on the cation were confined to their calculated positions. The details of the data collection and crystallographic data are summarised in Table 1.

3.3. Computational method

Pre-optimised configurations of the [Co(bpma)-$(bipy)Cl]^{2+}$ 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.

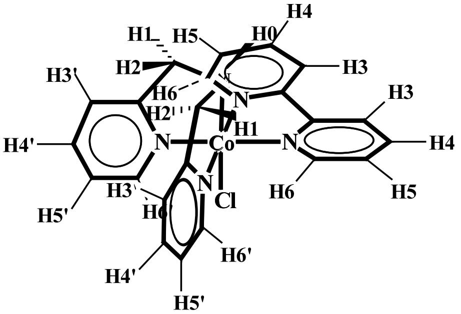

Fig. 3. The proton labelling scheme for the *sym–fac*-[Co(bpma)-$(bipy)Cl]^{2+}$ isomer.

3.4. Comparison of crystal and calculated structures

The final atomic coordinates of non-hydrogen atoms in these complexes are given in Table 2 and perspective views of the cations and unit cells in Fig. 5. Selected interatomic distances and angles with their e.s.d. are given in Tables 3 and 4. The calculated structural data and the errors between crystal and calculated data are also listed.

From Tables 3 and 4, it can be seen that bond lengths and bond angles differences between the experimental and calculated results are all less than 3%, with most of them less than 1%, the only anomaly being the Co1–N4 bond length (+3.5%).

It is concluded that crystal structure data can be satisfactorily reproduced by ab initio calculation, at least for this complex, but calculations on a number of related systems for which we have X-ray structural data are yielding results of comparable agreement.

3.5. Relative stability of the four $[Co(bpma)(bipy)Cl]^{2+}$ isomers

The relative stability of the isomers in the [Co(bpma)-$(bipy)Cl]^{2+}$ system has been modelled theoretically using the ab initio methods described herein and previously [15–17]. Table 5 shows the energy calculations for both the gas phase and also for the ions immersed in a solvent dielectric continuum. The first three rows show the primary energy data, and the last three the relative energies for the four isomers.

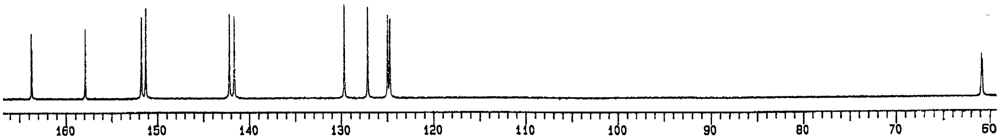

Fig. 2. The ^{13}C NMR spectrum of the *sym–fac*-$[Co(bpma)(bipy)Cl]^{2+}$ complex in 0.01 M DCl.

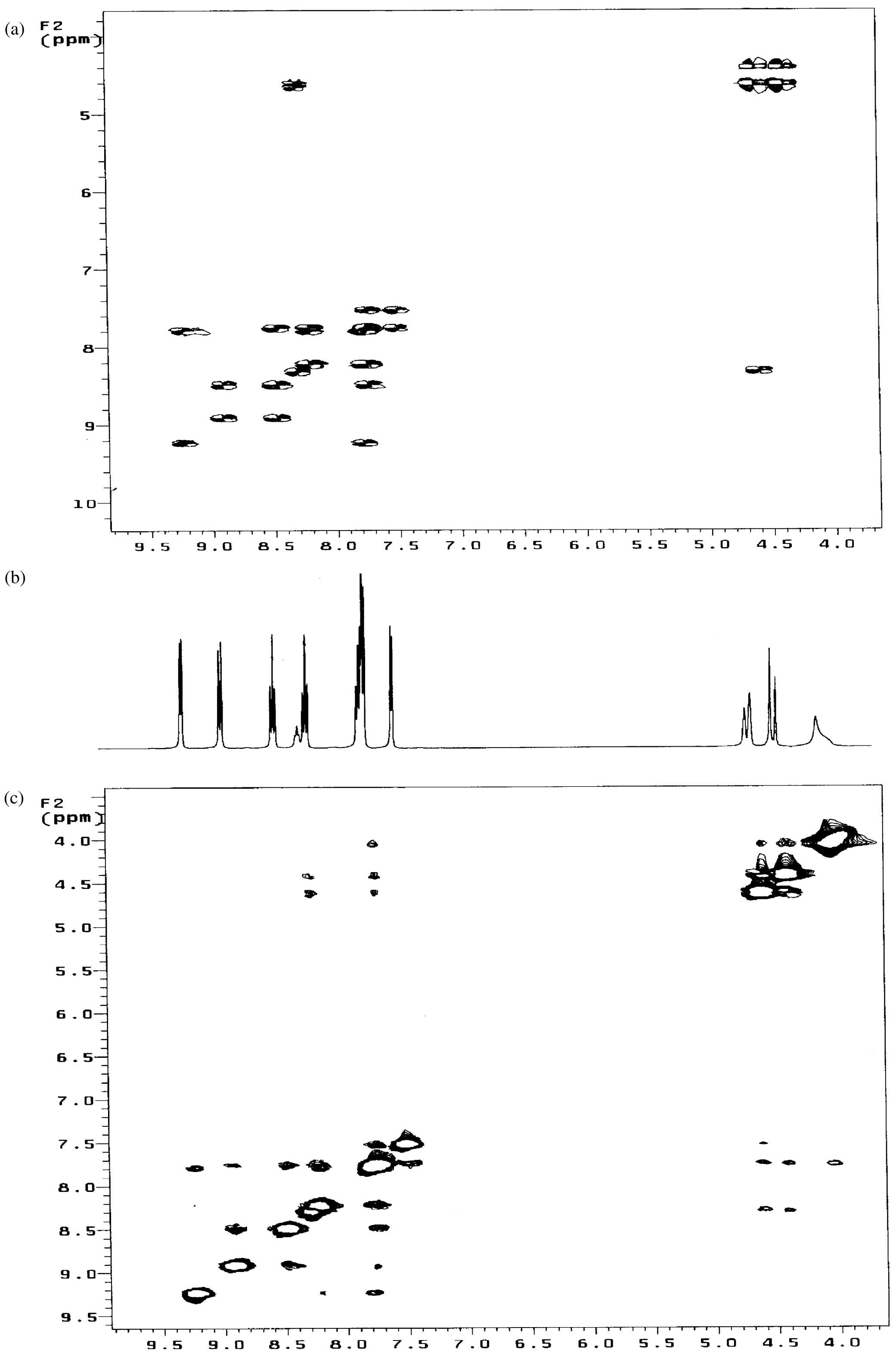

Fig. 4. (a) DQCOSY, (b) ^{1}H NMR and (c) NOESY spectra of *sym–fac*-[Co(bpma)(bipy)Cl](ClO$_4$)$_2$ in DMSO-d_6.

One can see immediately that in both the gas phase and in aqueous solution the energies of the other isomers are at least 20 kJ mol^{-1} higher than the *sym–fac* isomer. The last row indicates that aqueous solvation stabilises all four isomers, but since there is no great differences in solvation between the isomers the balance is not tipped. Indeed, the *sym–fac* isomer is even more stable relative to the other three in water.

Table 1
Crystal data and data collection details for *sym–fac*-[Co(bpma)(bipy)Cl]ZnCl$_4$

Formula	$C_{22}H_{21}N_5Cl_5ZnCo$
Formula weight	656.99
Crystal system	triclinic
Space group	$P\bar{1}$
a (nm)	0.8926(17)
b (nm)	1.2352(2)
c (nm)	1.3549(3)
α (°)	107.550(4)
β (°)	108.611(3)
γ (°)	92.584(4)
V (nm^3)	1.3331(4)
ρ_{cacl} (g cm^{-3})	1.637
Z	2
F(000)	660
μ (mm^{-1})	2.044
Scan technique	$\omega-2\theta$
Scan range (2θ°)	4.86–55.06
Number unique	8039
Number observed	6048
Number variables	308
R [a]	0.0469
R_w [b]	0.1277

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

It need be noted that the solvent correction is rather crude (inserting a gaseous cation into a solvent dielectric continuum), but the NH and Co–Cl groups likely to involve specific solvation effects are common to the four stereoisomers, while the aromatics tend to protect these groups from preferential solvation effects. The calculations tend to bear this out (Table 5).

A simple approach has been to observe the relative Σ (bond length deviations) and Σ (bond angle deviations) from their norms, with the smallest sums of deviations being optimal. Table 6 shows these data, and the same energy order for the four isomers emerges: *sym–fac* > *mer-exo* > *mer-endo* > *unsym–fac*. However, given the relatively small differences, this may well be fortuitous. We are presently testing this approach for a wide range of related systems.

Experimentally, the *sym–fac* complex was the only isomer to be synthesised or even observed, using a variety of synthetic techniques. This result is consistent with the calculations, although it cannot be regarded as firm proof that the other isomers are less stable, because even unstable isomers can be synthetically accessed by kinetic routes. It does strongly hint that this is so, however.

3.6. *C–H···π interactions*

In the NMR work, the shielding and deshielding phenomena were noted. The resonance of the proton H6 on the bipy shifts upfield from its normal position (~9 ppm) to 7.65 ppm, which is a significant shift. These phenomena involve well known ring current effects.

The exceptionally good agreement between the X-ray result and the ab initio calculations of course does not identify specific repulsions or attractions responsible for the relative energies for the four possible geometric isomers which also emerge from these calculations. In the literature [2–7], intramolecular C–H···π interactions of both stabilising and destabilising kinds have been discussed (these are distinct from π–π stacking interactions for extended arrays in crystals [1]). From Fig. 1, one can see that there are two stabilising interactions of H6 on the bipy with the π-aromatic ring on the bpma for the *sym–fac* form; the distance from the centre of the H6 on the pyridine ring of the

Table 2
Selected atomic coordinates and equivalent isotropic thermal parameters for *sym–fac*-[Co(bpma)(bipy)Cl]ZnCl$_4$

Atom	x	Y	z	U_{eq}	Atom	x	y	z	U_{eq}
Zn(1)	3836(1)	3010(1)	6497(1)	36(1)	C(6)	1366(2)	738(1)	3085(1)	36(1)
C1(2)	4943(1)	2533{1)	5119(1)	44(1)	C(7)	1873(2)	−146(2)	3438(2)	61(1)
C1(3)	2242(1)	4301(1)	6074(1)	56(1)	C(8)	2963(3)	−747(2)	3046(2)	77(1)
C1(4)	2522(1)	1439(1)	6531(1)	63(1)	C(9)	3484(2)	−433(2)	2311(2)	68(1)
C1(5)	5870(1)	3803(1)	8111(1)	67(1)	C(10)	2932(2)	458(2)	1985(1)	49(1)
Co(1)	1027(1)	2364(1)	2020(1)	28(1)	C(11)	1566(2)	1855(2)	−96(1)	53(1)
C1(1)	−1165(1)	1184(1)	744(1)	46(1)	C(12)	2445(3)	1957(2)	−732(2)	73(1)
N(1)	27(1)	2350(1)	3088(1)	29(1)	C(13)	3946(3)	2605(2)	−239(2)	85(1)
N(2)	1889(1)	1059(1)	2372{1)	35(1)	C(14)	4549(2)	3127(2)	882(2)	74(1)
N(3)	2148(2)	2361(1)	1011(1)	40(1)	C(15)	3623(2)	2974(2)	1502(2)	53(1)
N(4)	2895(1)	3412(1)	3152(1)	37(1)	C(16)	4237(2)	3392(2)	2726(2)	60(1)
N(5)	270(1)	3762(1)	1809(1)	33(1)	C(17)	2444(2)	4565(1)	3536(1)	46(1)
C(1)	−958(2)	3058(1)	3396(1)	38(1)	C(18)	1132(2)	4728(1)	2611(1)	39(1)
C(2)	−1744(2)	2886(2)	4071(1)	43(1)	C(19)	765(3)	5802(2)	2605(2)	60(1)
C(3)	−1561(2)	1965(2)	4429(1)	49(1)	C(20)	−519(3)	5876(2)	1738(2)	73(1)
C(4)	−522(2)	1241(1)	4127(1)	46(1)	C(21)	−1356(3)	4893(2)	914(2)	66(1)
C(5)	256(2)	1459(1)	3467(1)	33(1)	C(22)	−939(2)	3841(2)	955(1)	46(1)

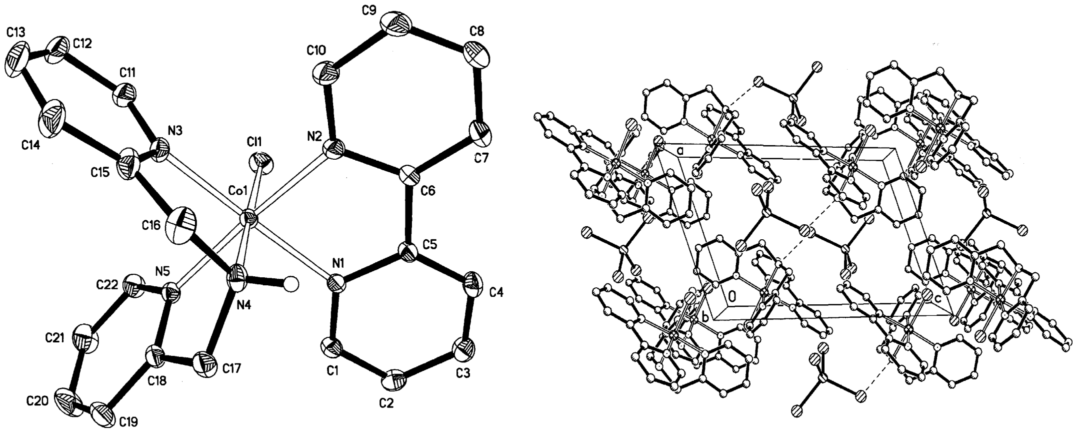

Fig. 5. The molecular cation and unit cell for *sym–fac*-[Co(bpma)(bipy)Cl]ZnCl$_4$.

Table 3
Selected experimental and calculated bond distances (nm) for *sym–fac*-[Co(bpma)(bipy)Cl]ZnCl$_4$

Atom–atom	Observed	Calculated	Error (%)	Atom–atom	Observed	Calculated	Error (%)
Co(1)–N(1)	0.19311(13)	0.19854	2.81	Co(1)–N(3)	0.19341(15)	0.19929	3.04
Co(1)–N(2)	0.19386(14)	0.19854	2.41	Co(1)–N(4)	0.1944b(11)	0.20115	3.47
Co(1)–N(5)	0.19490(13)	0.19928	2.25	Co(1)–C1(1)	0.22370(5)	0.22822	2.02
N(1)–C(1)	0.1339(2)	0.13417	0.20	N(1)–C(5)	0.1347(2)	0.13536	0.49
N(2)–C(10)	0.1354(2)	0.13417	0.91	N(2)–C(6)	0.1346(2)	0.13536	0.56
N(3)–C(15)	0.1341(2)	0.13504	0.70	N(3)–C(11)	0.13481(19)	0.13477	0.03
N(4)–C(17)	0.1483(2)	0.14977	0.99	N(4)–C(16)	0.1486(3)	0.14977	0.79
N(5)–C(22)	0.1338(2)	0.13478	0.73	N(5)–C(18)	0.13416(17)	0.13504	0.66
C(1)–C(2)	0.1375(3)	0.13877	0.92	C(2)–C(3)	0.1363(3)	0.13920	2.13
C(3)–C(4)	0.1387(3)	0.13953	0.60	C(4)–C(5)	0.1370(2)	0.13867	1.22
C(5)–C(6)	0.1473(2)	0.14782	0.35	C(6)–C(7)	0.1359(2)	0.13867	2.04
C(7)–C(8)	0.1393(3)	0.13953	0.17	C(8)–C(9)	0.1367(4)	0.13920	1.83
C(9)–C(10)	0.1361(3)	0.13877	1.96	C(11)–C(12)	0.1365(3)	0.13884	1.71
C(12)–C(13)	0.1375(3)	0.13933	1.33	C(13)–C(14)	0.1368(3)	0.13981	2.20
C(14)–C(15)	0.1396(3)	0.13839	0.87	C(15)–C(16)	0.1481(3)	0.15078	1.81
C(17)–C(18)	0.1490(2)	0.15078	1.19	C(18)–C(19)	0.1383(3)	0.13840	0.07
C(19)–C(20)	0.1384(3)	0.13981	1.02	C(20)–C(21)	0.1359(3)	0.13934	2.53
C(21)–C(22)	0.1380(3)	0.13884	0.61				

bipy to the plane of the pyridine of bpma is quite short, just 0.23 nm. In the *unsym–fac* isomer, two protons (one H6 on the bipy and one of the H6′ on the bpma) are so close as to cause severe steric strain. For the two mer configurations, although there are two C–H···π interactions, there are also two sets of repulsive interactions involving the pyridyl rings.

At present we cannot be certain of the specific origin of the stability of the *sym–fac* isomer relative to the other three. It may be the unique C–H···π interaction in this isomer, but until such time as the magnitude of the energy for this specific component can be calculated we cannot be certain, given the large number of other contributions to the total energy.

In summary, the isomer assignment for *sym–fac*-[Co(bpma)(bipy)Cl]$^{2+}$ through spectroscopic methods has been confirmed by the single crystal structural analysis. Theoretical calculations can reproduce experimental bond angles and bond length data, and they confirm that the *sym–fac* isomer is the most stable form in both the gas phase and aqueous solution by an appreciable margin.

4. Supplementary material

Complete crystallographic data for the structural analysis of the complex have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 183741. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 4
Selected observed and calculated bond angles (°) for *sym–fac*-[Co(bpma)(bipy)Cl]$ZnCl_4$

Atom–atom–atom	Observed	Calculated	Error (%)	Atom–atom–atom	Observed	Calculated	Error (%)
N(1)–Co(1)–N(3)	176.47(5)			N(1)–Co(1)–N(2)	83.04(5)	82.01	1.13
N(3)–Co(1)-N(2)	94.34(6)	94.93	0.63	N(1)–Co(1)–N(4)	91.94(5)	91.50	0.48
N(3)–Co(1)–N(4)	85.72(6)	83.77	2.28	N(2)–Co(1)–N(4)	91.00(5)	91.51	0.56
N(1}–Co(1)–N(5)	94.51(5)	94.94	0.45	N(3)–Co(1)–N(5)	87.90(6)	87.60	0.34
N(2)–Co(1)–N(5)	174.68(4)			N(4)–Co(1)–N(5)	84.35(5)	83.78	0.68
N(1)–Co(1)–C1(1)	86.71(3)	89.08	2.73	N(3)–Co(1)–C1(1)	95.67(4)	95.68	0.01
N(2)–Co(1)–C1(1)	89.74(4)	89.06	0.75	N(4)–Co(1)–C1(1)	178.37(4)		
N(5)–Co(1)–C1(1)	94.85(4)	95.68	0.88	C(1)–N(1)–C(5)	118.50(14)	119.72	1.03
C(1)–N(1)–Co(1)	126.88(11)	125.62	1.00	C(5)–N(1)–Co(1)	114.32(10)	114.25	0.06
C(10)–N(2)–C(6)	118.07(15)	119.72	1.40	C(10)–N(2)–Co(1)	127.44(13)	125.61	1.43
C(6)–N(2)–Co(1)	114.49(10)	114.25	0.21	C(15)–N(3)–C(11)	119.61(16)	119.75	0.12
C(15)–N(3)–Co(1)	113.78(11)	114.55	0.68	C(11)–N(3)–Co(1)	126.55(12)	125.47	0.86
C(17)–N(4)–C(16)	114.57(15)	114.72	0.13	C(17)–N(4)–Co(1)	109.13(9)	109.20	0.06
C(16)–N(4)–Co(1)	109.59(10)	109.19	0.37	C(22)–N(5)–C(18)	119.13(14)	119.75	0.52
C(22)–N(5)–Co(1)	127.23(10)	125.47	1.39	C(18)–N(5)–Co(1)	113.59(10)	114.55	0.85
N(1)–C(1)–C(2)	121.71(16)	122.10	0.32	C(3)–C(2)–C(1)	120.16(16)	118.57	1.32
C(2)–C(3)–C(4}	118.22(18)	119.23	0.86	C(5)–C(4)–C(3)	119.45(17)	119.15	0.25
N(1)–C(5)–C(4)	121.90(14)	121.18	0.59	N(1)–C(5)–C(6)	114.15(14)	114.66	0.45
C(4)–C(5)–C(6)	123.93(15)	124.10	0.14	N(2)–C(6)–C(7)	122.23(16)	121.18	0.86
N(2)–C(6)–C(5)	113.67(14)	114.66	0.87	C(7)–C(6)–C(5)	124.07(17)	124.10	0.02
C(6)–C(7)–C(8)	119.01(2)	119.15	0.04	C(9)–C(8)–C(7)	118.8(2)	119.23	0.36
C(8)–C(9)–C(10)	119.5(2)	118.57	0.78	N(2)–C(10)–C(9)	122.24(19)	122.11	0.11
N(3)–C(11)–C(12)	121.35(17)	121.55	0.16	C(13)–C(12)–C(11)	119.55(18)	118.94	0.51
C(12)–C(13)–C(14)	119.7(2)	119.23	0.39	C(13)–C(14)–C(15)	118.75(18)	118.76	0.01
N(3)–C(15)–C(14)	120.99(16)	121.77	0.64	N(3)–C(15)–C(16)	116.03(17)	115.62	0.35
C(14)–C(15)–C(16)	122.81(16)	122.55	0.21	N(4)–C(16)–C(15)	110.54(14)	110.25	0.26
N(4)–C(17)–C(18)	109.16(12)	110.26	1.01	N(5)–C(18)–C(19)	121.76(15)	121.77	0.01
N(5)–C(18)–C(17)	115.77(14)	115.63	0.12	C(19)–C(18)–C(17)	122.38(13)	122.54	0.13
C(18)–C(19)–C(20)	118.78(15)	118.76	0.02	C(21)–C(20)–C(19)	118.89(19)	119.23	0.29
C(20)–C(21)–C(22)	120.18(18)	118.94	1.03	N(5)–C(22)–C(21)	121.17(14)	121.55	0.31

Table 5
The energies of alternative isomers relative to the *sym–fac* isomer

	m1	m2	*sym–fac*	*Unsym–fac*
E a.u.(gas)	−1275.7083699	−1275.7037907	−1275.7137815	−1275.6812589
E a.u.(H_2O)	−1275.7124632	−1275.7081095	−1275.7200913	−1275.6850498
ΔEg kJ mol^{-1} (gas-H_2O)	10.74	11.33	16.55	9.94
ΔE kJ mol^{-1} (gas)	14.19	26.21	0.00	85.31
ΔE kJ mol^{-1} (H_2O)	20.01	31.43	0.00	91.91

Table 6
Distortion analysis for the four possible geometric isomers of $[Co(bpma)(bipy)Cl]^{2+}$ from ab initio calculations

	m1	m2	*sym–fac*	*unsym–fac*
Σ bonds	75.22	75.23	75.20	78.17
Σ deviation*	51.69	57.10	48.85	80.41
Σ deviation**	212.62	237.52	208.31	315.19

Σ deviation* is a sum of the absolute values of the deviations from idealised octahedral bond angles (90 and 180°). Σ deviation** is a sum of the deviations of all angles from the idealised octahedral or tetrahedral values.

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