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The chemistry of $[Co(triamine)(diamine)Cl]^{2+}$ complexes: the single crystal X-ray structures of five $[Co(dien)(ibn)Cl]ZnCl_4$ isomers

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Abstract

Of the seven isomeric forms possible for $[Co(dien)(ibn)Cl]^{2+}$ system, the structures of three mer- and two fac-isomers have been determined by single crystal X-ray diffraction. The structural work corroborates the detailed 2D NMR study reported elsewhere.

Keywords: X-ray structures; Cobalt(III) complexes; Diethylenetriamnine; Isobutylenediamine

1. Introduction

Amine complexes of cobalt(III) invariably undergo base catalysed substitution reactions in water, and the source of the catalysis is deprotonation of a bound amine or an α-pyridyl methylene group. Most of the studies of this reaction have centred on tetraamine and pentaaminecobalt(III) species [1–4], usually for chloride as a leaving group. House has provided an immense amount of kinetic data on these systems [5–13], while Tobe has provided a detailed consideration of the important factors in the mechanism [14,15]. Sargeson, Jackson, Buckingham and Marty and co-workers 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 as cited [16] are cited [17–25].

We have been engaged in a systematic attack on the remaining problems, and as part of this approach we have synthesised a large number of new $[Co(pentaamine)X]^{2+}$ and $[Co(triamine)(diamine)X]^{2+}$ complexes. The latter have mostly involved unsymmetrical diamines such as ibn and ampy, and such systems comprise seven isomeric forms (excluding catoptric forms), the synthesis of which have been described recently [26–28]. Part of that research required unambiguous structural assignments using largely 2D NMR spectroscopic methods. This paper describes the single crystal X-ray structures of five of the seven isomers (m1, m2, m3, f1 and f2; Fig. 1) for $[Co(dien)(ibn)Cl]ZnCl_4$ which substantiate the results of these studies, and which provide further structural detail.

2. Experimental

2.1. Synthesis and separation of the $[Co(dien)(ibn)Cl]^{2+}$ isomers

Details have appeared recently [26]. Each of the isomers was characterised as chloride, perchlorate and tetrachlorozincate salts; the latter two salts were obtained from concentrated solutions of the chlorides using one-fifth volume of the appropriate precipitant (70% $HClO_4$ or 2 M 'H_2ZnCl_4' (2 M $ZnCl_2$ in 5 M HCl)). *Anal.* Calc. for $[Co(dien)(ibn)Cl]ZnCl_4$: C, 19.49; H, 5.11; N, 14.21. Fd: C, 19.33; H, 4.83; N, 14.08% (m3).

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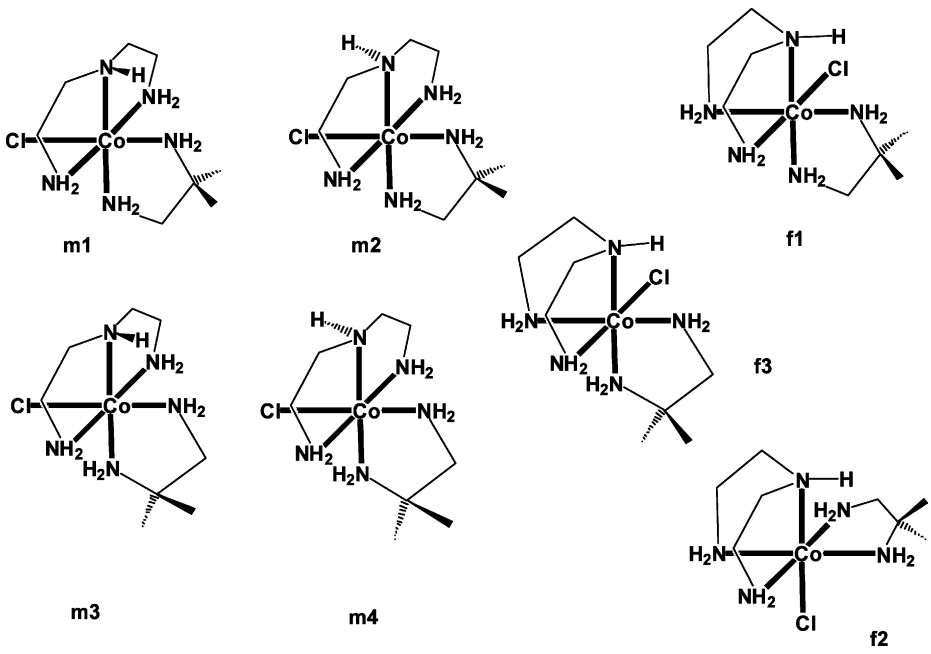

Fig. 1. The seven geometric isomers for $[Co(dien)(ibn)Cl]^{2+}$.

2.2. X-ray crystal structure analysis

Single crystals of the m1, m2, m3, f1 and f2 isomers suitable for X-ray crystal structural determinations were obtained by gradually adding 'H_2ZnCl_4' (2 M $ZnCl_2$ in 5 M HCl)) to an aqueous solution of the chloride salts at room temperature. Crystals of the four mer-isomers are red–pink and air stable. Diffraction data were obtained at ambient temperature on a Rigaku AFC-5 automated four-circle diffractometer (for $f1 \cdot ZnCl_4 \cdot H_2O$ and $f2 \cdot ZnCl_4 \cdot H_2O$) and a Bruker P4 X-ray four-circle diffractometer (for $m1 \cdot ZnCl_4$, $m2 \cdot ZnCl_4$ and $m3 \cdot ZnCl_4$) using Mo Kα radiation. The details of the data collection and crystallographic data are summarised in Table 1.

Table 1
Crystal data and data collection details for m1-, m2-, m3-, f1- and f2- $[Co(dien)(ibn)Cl]ZnCl_4 \cdot n H_2O$

Isomer	m1	m2	m3	f1	f2
Formula	$C_8H_{25}N_5Cl_5ZnCo$	$C_8H_{25}N_5Cl_5ZnCo$	$C_8H_{25}N_5Cl_5ZnCo$	$C_8H_{27}N_5OCl_5ZnCo$	$C_8H_{27}N_5OCl_5ZnCo$
Formula weight	492.88	492.88	492.88	510.91	510.91
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	8.077(2)	9.0661(13)	9.893(4)	11.746(2)	8.229(2)
b (Å)	15.517(4)	9.3410(14)	11.235(5)	13.800(2)	11.936(3)
c (Å)	15.296(4)	11.6228(18)	17.604(7)	12.761(6)	20.340(5)
α (°)		104.209(3)			
β (°)	98.272(5)	96.722(3)	102.814(8)	109.320(20)	98.230(20)
γ (°)		103.237(3)			
V (Å^3)	1897.2	913.0(2)	1908.0(13)	1952.0(1)	1977.2(8)
D_{calc} (g cm^{-3})	1.726	1.793	1.716	1.738	1.716
Z	4	2	4	4	4
$F(0\,0\,0)$	1000	500	1000	1040.00	1040.00
μ (cm^{-1})	28.39	29.5	28.23	27.66	27.31
Scan technique	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan range 2θ (°)	5–50	4.66–55.08	4.34–55.18	6–50	6–50
No. unique reflections	7702	6028	6155	3259	3456
No. observed reflections	4346	4140	4387	3078	3190
No. variables	241	233	236	191	190
R [a]	0.0416	0.0342	0.0418	0.054	0.031
R_w [b]	0.1359	0.0914	0.0993	0.072	0.038

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

The structures were solved by direct methods (SHELXS-97) for m1, m2 and m3 which yielded the positions of most 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 structural analysis. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located using difference Fourier syntheses and refined by Fourier and least-square methods (SHELXL-97). The structures of the salts of the f1 and f2 isomers were solved by direct methods (SHELXS-86). The Fourier methods located all the non-hydrogen atoms, and these were refined using isotropic and subsequently anisotropic thermal parameters. The hydrogen atoms were introduced in their calculated positions. At the final stage, full-matrix least-squares methods were carried out and the weighting scheme $1/\sigma^2$ was adopted. The final atomic coordinates of non-hydrogen atoms are given in supplementary material (Section 4).

3. Results and discussion

3.1. X-ray crystallography

X-ray crystal structure analysis was once the only definitive method to determine the isomer configurations in systems where structural differences are subtle. The 2D NMR techniques seemed successful in achieving this end [27], but to substantiate this claim, we undertook the crystal structural analysis of several of the isomers. All five reported herein support the topological assignments deduced from an analysis of the 2D NMR spectra.

Not all crystallised suitably, but crystals of the m1, m2, m3, f1 and f3 complexes as the tetrachlorozincate salts diffracted well. Perspective views (ORTEP diagrams) and unit cells for the five structures are shown in Figs. 2–11.

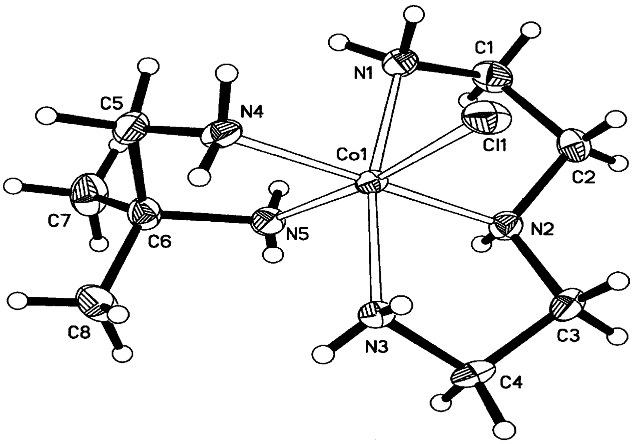

Fig. 2. Molecular cation (m1).

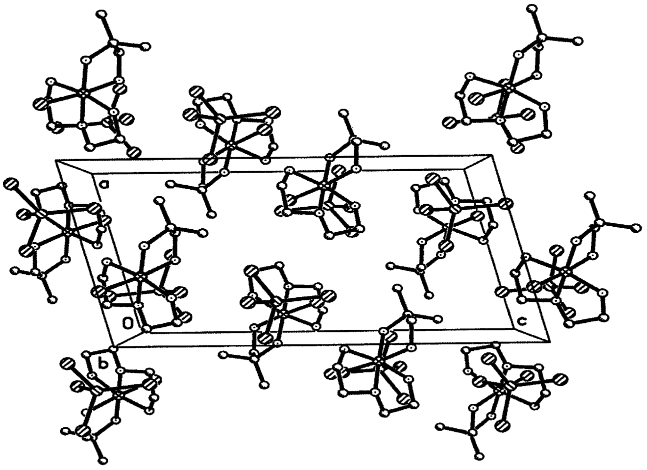

Fig. 3. The unit cell (m1·$ZnCl_4$).

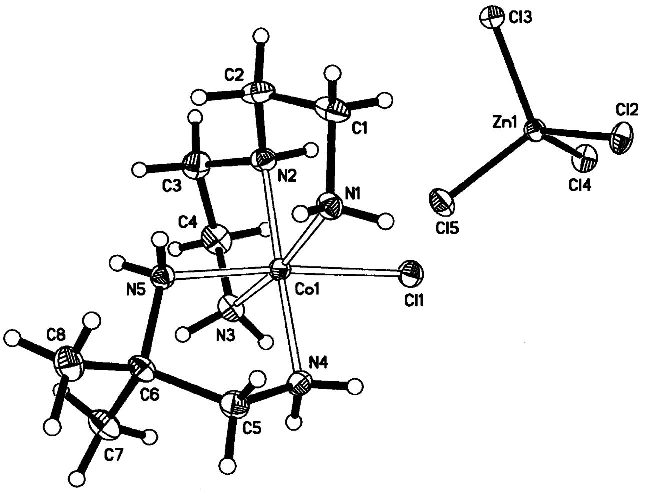

Fig. 4. Molecular cation (m2) and $ZnCl_4^{2-}$ anion.

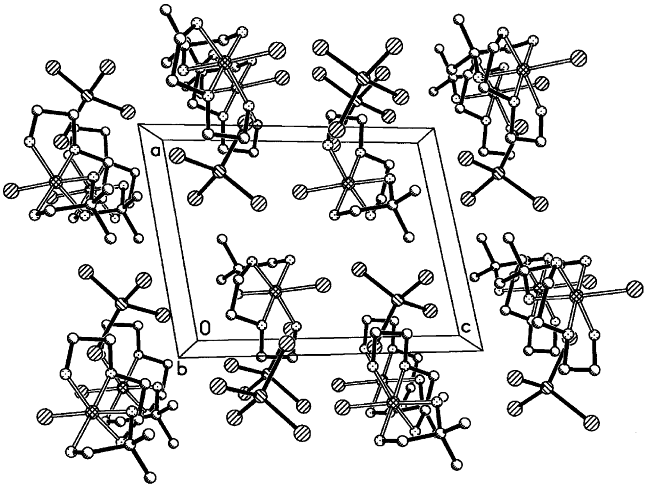

Fig. 5. The unit cell (m2·$ZnCl_4$).

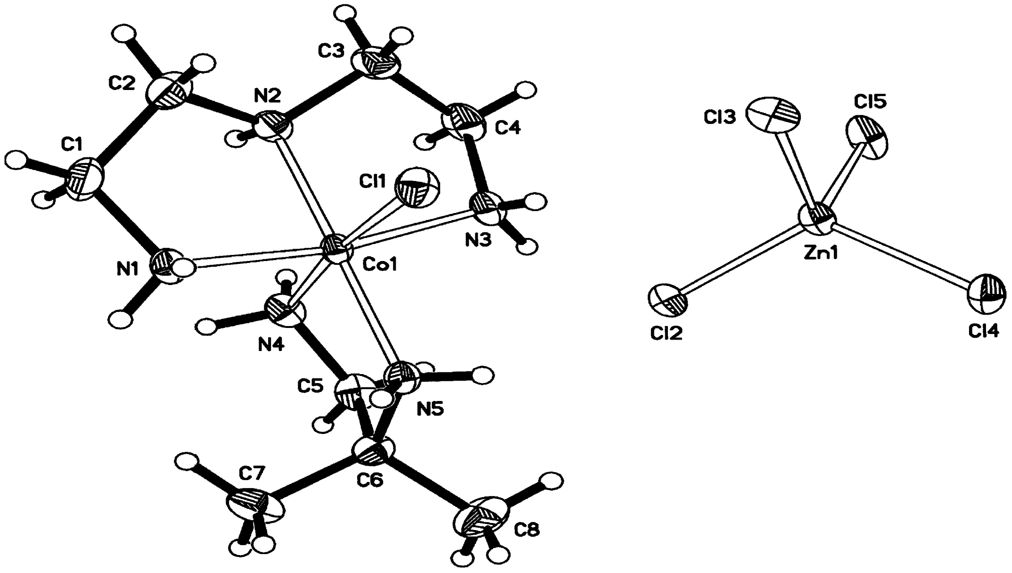

Fig. 6. Molecular cation (m3) and $ZnCl_4^{2-}$ anion.

Selected interatomic distances and angles with their estimated standard deviations are given in Tables 2 and 3.

The Co–Cl bond length has been considered to be related to the substitutional reactivity of a complex and some controversy has arisen. We have found no obvious link. The distances 2.261–2.278 Å (Table 2) are within the normal range, as reference to House's compilation [29] indicates.

If we consider the distortions for the different isomers, for both bond lengths and bond angles, some interesting results emerge. We adopt in the first instance a very simple approach. The sum of deviations (absolute value) of the eight N–Co–N bond angles from the ideal octahedral angle are listed in Table 3. The two anti-mer isomers are about the same, but the value for the syn isomer (m2) is less. The values for the two fac isomers are however significantly less. This picture is not very different if the distortions for the four NCoCl angles are also included, although the relativity amongst the mer isomers is affected. These results could be construed to indicate why the fac isomers are more stable than the mer, but it would be a gross over-simplification. Certainly, the anti-mer isomers are more stable than the syn, almost universally so in such systems, and these data do not corroborate this fact. A similar calculation for all the tetrahedral bond angle distortions leads to a similar conclusion only in so far as the fac isomers are more stable than mer. Again one sees an anomaly in the relative distortions for the corresponding syn/anti pair, and for the m1/m3 comparison (the latter isomers are in almost equal abundance under equilibrium conditions). In summary, it seems this simple minded picture is inadequate, and more sophisticated ab initio calculations have been undertaken for these and related systems, with an attempt to include the important role of solvent.

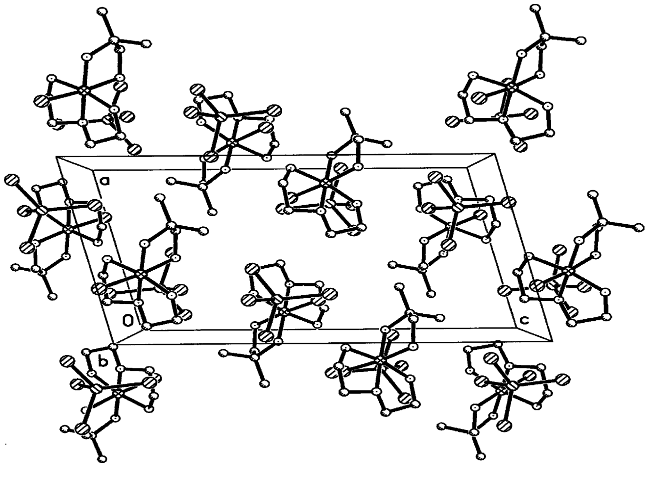

Fig. 7. The unit cell ($m3 \cdot ZnCl_4$).

3.2. Description of the structures

We currently have structural data for five of the seven isomers, and indeed, additional and independent structural data for the m1, f1 (two repeat structures) and m3 isomers. It suffices to say that the repeat structures show remarkably good agreement in all aspects of the structure–cell parameters, and bond length and angle data.

For the mer isomers, all the structural determinations reveal the 'flat' dien configuration to be meso, i.e. adjacent λ and δ five-membered ring conformations,

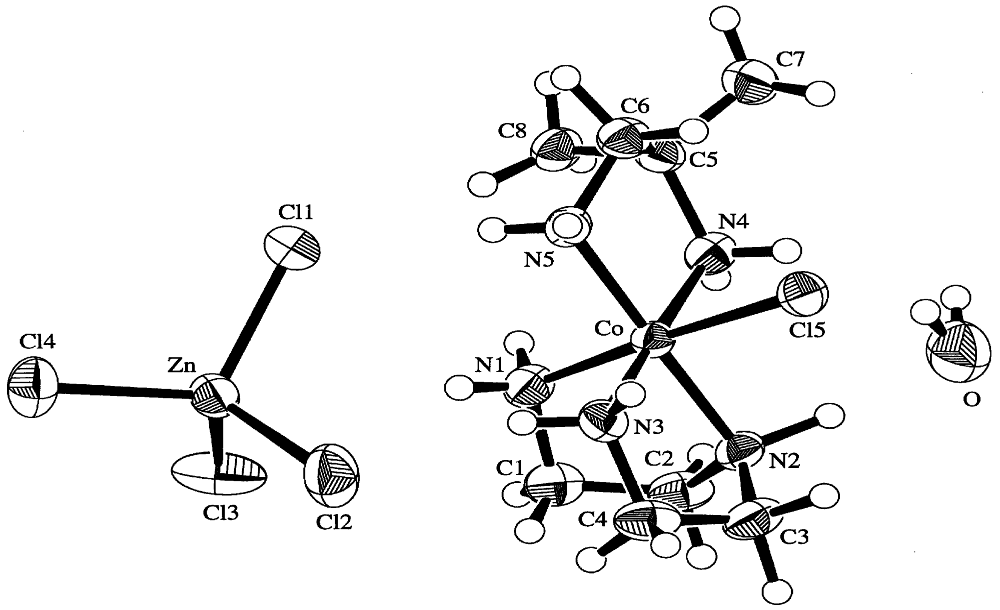

Fig. 8. Molecular cation (f1), $ZnCl_4^{2-}$ anion and lattice H_2O.

and this is usual. It represents the least strained configuration for such linearly coupled 5-membered rings. The additional ibn chelate adopts the expected λ or δ gauche configuration, with one methyl substituent axial and the other equatorial. Overall, the alternative configurations for the mer complexes are equal in energy and enantiomeric, and thus it occasions no surprise that most of the mer complexes crystallise as racemates, appropriately labelled mer–meso-λ and mer–meso-δ.

For the two facial isomers, f1 and f2, the dien configurations are also meso (λ and δ for the joined 5-membered chelates), and this also seems to be the norm. The ibn ligand also adopts the two δ and λ gauche configurations, as it does in the mer isomers, and solid state racemates are observed in the crystal for each isomeric complex.

The m1 isomer was a compound found to be dimorphic. Two structures were determined, one a racemate in the space group $P2_1/c$, and a chiral form $P1$. They were stoichiometrically identical, and the two forms were no doubt obtained at different temperatures, although we do not know the transition temperature. The analogy to Pasteur's active and racemic tartaric acids is a particularly instructive one to recall.

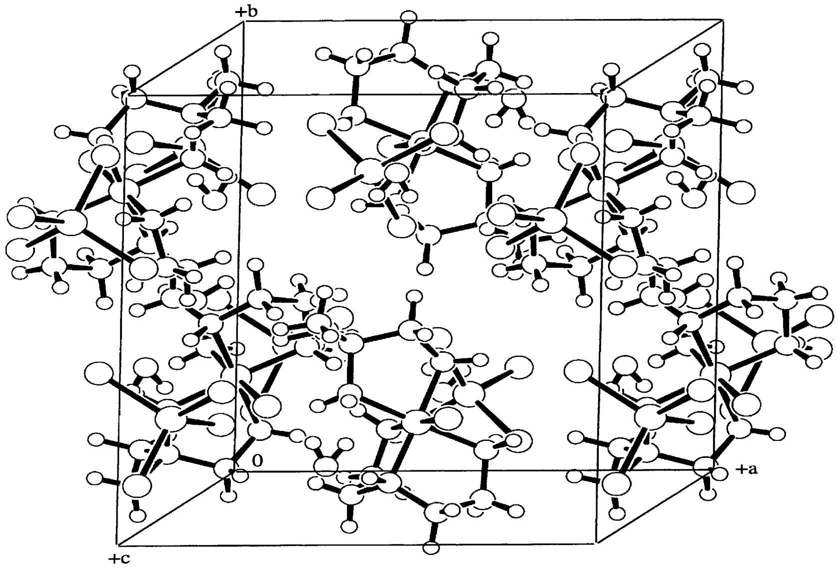

Fig. 9. The unit cell (f1·$ZnCl_4$·H_2O).

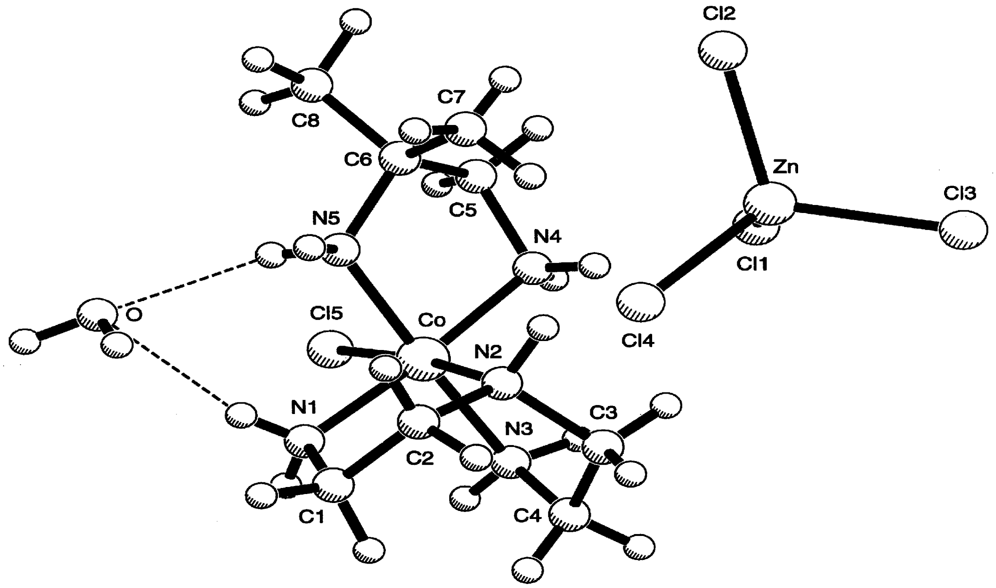

Fig. 10. Molecular cation (f2), $ZnCl_4^{2-}$ anion and lattice H_2O.

The chiral form for the m1 isomer contains two different molecules in the unit cell. Curiously, the dien is meso (achiral) in both, and the ibn configurations are essentially enantiomeric. However, clearly the two component structures of the unit cell cannot be enantiomeric; the two molecules in the unit cell differ subtly in several respects, which an inspection of the tabulated bond length and angle data reveal (Section 4).

4. Supplementary material

Crystallographic data for the structural analysis of the m1-, m2-, m3-, f1- and f2-[Co(dien)(ibn)Cl]$ZnCl_4 \cdot nH_2O$ complexes have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 186170 and 183868–183871, respectively. Data for a set of duplicate (and independent) structures are also deposited, CCDC Nos. 183867 and 186171–186173 (ml-, 2 × f1- and m3-isomers, respectively). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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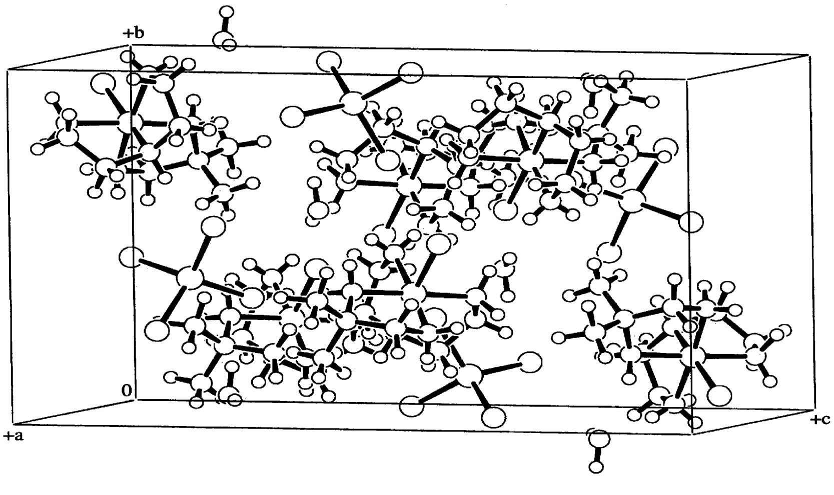

Fig. 11. The unit cell (f2·$ZnCl_4 \cdot H_2O$).

Table 2
Selected bond distances (Å) for m1-, m2-, m3-, f1- and f2-[Co(dien)(ibn)Cl]ZnCl$_4$·nH$_2$O

	m1	m2	m3	f1	f2
Co(1)–Cl(1)	2.2609(6)	2.2683(6)	2.2679(9)	2.268(2)	2.278(1)
Co(1)–N(1)	1.9820(15)	1.9702(16)	1.959(2)	1.963(5)	1.946(3)
Co(1)–N(2)	1.9510(13)	1.9392(16)	1.942(2)	1.964(5)	1.958(3)
Co(1)–N(3)	1.9714(14)	1.9753(16)	1.963(2)	1.947(6)	1.956(3)
Co(1)–N(4)	1.9609(14)	1.9701(15)	1.9588(19)	1.948(6)	1.961(3)
Co(1)–N(5)	1.9692(14)	1.9438(16)	1.9461(19)	1.956(5)	1.962(3)
Σ bonds	12.0954	12.0669	12.0368	12.046	12.061
N(1)–C(1)	1.493(2)	1.502(3)	1.491(3)	1.492(8)	1.494(6)
N(2)–C(2)	1.484(2)	1.482(2)	1.476(3)	1.493(7)	1.492(5)
N(2)–C(3)	1.485(2)	1.482(3)	1.487(3)	1.485(8)	1.511(5)
N(3)–C(4)	1.493(2)	1.493(3)	1.487(3)	1.486(8)	1.469(5)
N(4)–C(5)	1.466(2)	1.487(2)	1.484(3)	1.514(8)	1.502(5)
N(5)–C(6)	1.510(2)	1.518(2)	1.496(3)	1.487(9)	1.510(5)
C(1)–C(2)	1.509(3)	1.497(4)	1.500(4)	1.50(1)	1.504(6)
C(3)–C(4)	1.496(2)	1.511(3)	1.496(4)	1.50(1)	1.502(6)
C(5)–C(6)	1.524(3)	1.509(3)	1.524(4)	1.51(1)	1.524(6)
C(6)–C(7)	1.542(3)	1.527(3)	1.526(4)	1.53(1)	1.509(6)
C(6)–C(8)	1.507(3)	1.523(2)	1.527(4)	1.524(8)	1.515(6)
Σ bonds	28.604	28.598	28.531	28.567	28.593

Table 3
Selected bond angles (°) for m1-, m2-, m3-, f1- and f2-[Co(dien)(ibn)Cl]ZnCl$_4$·nH$_2$O

Atom-atom-atom	m1	m2	m3	f1	f2
N(1)–Co(1)–C1(1)	87.39(4)	89.31(5)	87.45(6)	176.6(2)	89.6(1)
N(2)–Co(1)–C1(1)	93.09(4)	89.39(5)	93.47(6)	90.4(1)	173.4(1)
N(3)–Co(1)–C1(1)	87.52(4)	90.67(5)	88.27(6)	87.7(1)	89.9(1)
N(4)–Co(1)–C1(1)	88.72(5)	89.79(5)	88.81(6)	88.2(1)	89.5(1)
N(5)–Co(1)–C1(1)	172.15(4)	173.84(5)	172.82(6)	89.4(1)	89.8(1)
N(1)–Co(1)–N(2)	84.81(6)	85.63(7)	85.12(9)	86.2(2)	85.7(1)
N(1)–Co(1)–N(3)	168.30(6)	170.07(7)	169.28(8)	91.6(2)	92.4(1)
N(1)–Co(1)–N(4)	94.33(6)	92.80(7)	93.54(9)	92.6(2)	175.1(1)
N(1)–Co(1)–N(5)	91.74(6)	90.11(6)	95.42(8)	94.0(2)	90.7(1)
N(2)–Co(1)–N(3)	84.95(6)	84.44(7)	85.33(9)	86.7(2)	85.6(1)
N(2)–Co(1)–N(4)	177.96(6)	178.23(7)	177.68(8)	94.1(2)	95.5(1)
N(2)–Co(1)–N(5)	94.60(6)	96.69(6)	93.71(8)	178.6(2)	95.0(1)
N(3)–Co(1)–N(4)	96.08(6)	97.14(7)	91.94(9)	175.8(2)	92.4(1)
N(3)–Co(1)–N(5)	94.71(6)	90.95(7)	94.32(8)	94.6(2)	176.9(1)
N(4)–Co(1)–N(5)	83.57(6)	84.11(6)	84.01(8)	84.5(2)	84.5(1)
Σ distortion [a]	38.13	33.51	38.57	29.5	30.2
C(1)–N(1)–Co(1)	110.51(11)	109.11(13)	110.02(15)	110.6(4)	113.0(3)
C(2)–N(2)–Co(1)	109.44(11)	108.88(12)	108.98(15)	108.6(4)	109.5(2)
C(3)–N(2)–Co(1)	109.08(10)	109.89(13)	108.98(16)	108.1(4)	109.2(2)
C(4)–N(3)–Co(1)	110.54(10)	110.22(13)	109.85(16)	111.8(4)	111.8(2)
C(5)–N(4)–Co(1)	111.08(10)	111.13(11)	109.24(15)	113.5(4)	109.5(2)
C(6)–N(5)–Co(1)	113.28(10)	112.56(11)	115.15(14)	109.9(4)	114.3(2)
N(1)–C(1)–C(2)	107.96(14)	108.59(17)	108.3(2)	107.5(5)	108.2(4)
N(2)–C(2)–C(1)	106.30(14)	105.63(16)	105.4(2)	109.6(5)	110.1(3)
N(2)–C(3)–C(4)	106.65(14)	104.40(17)	106.0(2)	110.8(5)	108.5(3)
N(3)–C(4)–C(3)	107.97(14)	108.21(16)	107.2(2)	109.0(6)	107.9(3)
N(4)–C(5)–C(6)	108.52(14)	108.14(16)	109.21(19)	106.3(5)	109.0(3)
N(5)–C(6)–C(5)	104.44(13)	105.06(15)	104.80(18)	108.5(5)	105.8(3)
N(5)–C(6)–C(7)	108.72(14)	110.05(16)	110.2(2)	109.4(4)	108.8(4)
N(5)–C(6)–C(8)	110.77(15)	109.60(14)	109.5(2)	108.4(5)	108.9(4)
C(2)–N(2)–C(3)	117.13(13)	118.16(16)	118.50(19)	114.6(5)	113.6(3)
C(5)–C(6)–C(7)	110.66(16)	111.20(16)	110.6(2)	111.4(5)	112.8(4)
C(5)–C(6)–C(8)	111.82(15)	111.53(17)	110.5(2)	110.8(6)	110.1(4)
C(7)–C(6)–C(8)	110.25(16)	109.33(17)	111.0(2)	110.2(5)	110.4(4)
Σ distortion [b]	106.14	90.54	100.84	72.0	75.9

[a] Sum of the deviations (absolute values) from the idealised N–Co–N octahedral bond angle of 90°.

[b] Sum of the deviations (absolute values) from of the idealised tetrahedral bond angle of 109°28′.

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