

# Synthesis of Open-Chain Schiff-Base Ligand 1,3-Di(pyridine-2-carboxaldimino)propane Incorporating Nitrogen-Donor Atoms and Crystal Structures of Its Co<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> Complexes

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The synthesis and structures of 1,3-di(pyridine-2-carboxaldimino)propane (C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>, **1**) and its cobalt(II) perchlorate (C<sub>15</sub>H<sub>20</sub>Cl<sub>2</sub>CoN<sub>4</sub>O<sub>10</sub>, **2**), copper(II) perchlorate (C<sub>15</sub>H<sub>16</sub>Cl<sub>2</sub>CuN<sub>4</sub>O<sub>8</sub>, **3**) and zinc(II) perchlorate (C<sub>15</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>8</sub>Zn, **4**) complexes are described. Compound **1** was characterized by <sup>1</sup>H-, <sup>13</sup>C NMR and mass spectrometry. The structures of the metal complexes were determined by X-ray structure analysis. Crystal data: **2**: triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 8.076(2) Å, *b* = 10.129(2) Å, *c* = 13.849(5) Å,  $\alpha$  = 80.11(2)°,  $\beta$  = 83.69(3)°,  $\gamma$  = 80.46(2)°, *V* = 1100.3(5) Å<sup>3</sup>, *Z* = 2; **3**: monoclinic, space group *P*2<sub>1</sub>/*c* (No. 14), *a* = 14.419(3) Å, *b* = 7.118(3) Å, *c* = 19.704(3) Å,  $\beta$  = 110.34(1)°, *V* = 1896.2(9) Å<sup>3</sup>, *Z* = 4; **4**: triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 8.748(2) Å, *b* = 9.169(2) Å, *c* = 25.081(6) Å,  $\alpha$  = 82.13(2)°,  $\beta$  = 83.10(2)°,  $\gamma$  = 75.56(2)°, *V* = 1922.1(8) Å<sup>3</sup>, *Z* = 4.

There is a growing interest in finding alternative approaches for building new inexpensive and easy-to-prepare supramolecular systems. Hannon and co-workers have described a simple and inexpensive way to prepare imine-based macrocyclic complexes that have a triple-helical structure.<sup>1</sup> The Schiff-base ligands have generally been synthesised, as their metal complexes, through the (2+2) condensation using metals as template devices.<sup>2</sup> The reactions conducted in the absence of metal ions usually afford mainly oligomeric or polymeric products. On the other hand, using template effects, it is often very difficult to remove the template from the macrocycle or sometimes even impossible. As an alternative approach we used 1,3-diaminopropane as a flexible spacer in our ligand system enabling the four metal binding sites to coordinate to a single metal centre. We herein report a simple non-template procedure for the synthesis of open-chain Schiff-base ligand derived from 2-pyridylcarbaldehyde and 1,3-diaminopropane, preparation of Co<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> complexes and the definitive characterization of these complexes by X-ray diffraction.

## Experimental

**Reagents.** All the starting reagents were Merck analytical grade reagents. 2-Pyridylcarbaldehyde and 1,3-diamino-

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propane and the metal salts were used as supplied commercially without further purification. The <sup>1</sup>H- and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX500 FT NMR spectrometer. All chemical shifts are relative to the internal tetramethylsilane. The mass spectrum was run on a VG AutoSpec HRMS spectrometer.

**Preparation of L<sup>1</sup> (1).** 7.9 mmol of 1,3-diaminopropane was dissolved in 30 cm<sup>3</sup> of methanol by refluxing and to this solution 2-pyridylcarbaldehyde (15 mmol in 30 cm<sup>3</sup> of MeOH) was slowly added. The mixture was refluxed for 3 h. The reaction yielded a yellowish mainly oily product. Yield 92%. The nature of this ligand was deduced via <sup>1</sup>H, <sup>13</sup>C NMR and mass spectrum because all attempts to crystallize it failed. <sup>1</sup>H NMR (MeOH, TMS):  $\delta$  = 2.16 (qv), 3.81 (dt, CH<sub>2</sub>), 7.31–7.48 (m, Ar-H), 7.88 (dt, Ar-H), 8.01 (d, Ar-H), 8.41 (s, CH=N), 8.58–8.61 (m, Ar-H). <sup>13</sup>C NMR (MeOH, TMS):  $\delta$  = 32.59, 59.81, 122.72, 126.54, 138.60, 150.26, 155.23, 163.50. The mass spectra showed a strong peak for [L<sup>1</sup>]<sup>+</sup> at *m/e* 252: no peaks were observed at higher *m/e*.

**Preparation of CoL<sup>1</sup> (ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (2).** 4 mmol of 1,3-diaminopropane was dissolved in 30 cm<sup>3</sup> of methanol by refluxing. 8 mmol of 2-pyridylcarbaldehyde was dissolved in 30 cm<sup>3</sup> of methanol and added to the hot solution. The mixture was refluxed for 15 min and then a meth-

anodic solution of cobalt(II) perchlorate was slowly added (4 mmol in 50 cm<sup>3</sup> MeOH). The solution was refluxed for 3 h. The clear solution was allowed to stand at room temperature overnight, when suitable crystals for X-ray work were formed. Yield 46%.

*Preparation of CuL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (3).* The copper(II) complex was obtained by similar procedure to the above and a methanolic solution of copper(II) perchlorate (4 mmol in 50 cm<sup>3</sup> MeOH) was used. The mixture was refluxed for 3 h. The clear solution was allowed to stand at room temperature overnight, when blue crystals appeared. Yield 42%. Recrystallation from acetonitrile afforded better crystals.

*Preparation of ZnL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (4).* The zinc(II) complex was obtained by similar procedure to that above except that the reaction in acetonitrile took place and zinc(II) perchlorate solution (4 mmol in 50 cm<sup>3</sup> CH<sub>3</sub>CN) was used. The solution was allowed to stand overnight during which time colourless crystals of the product formed. Yield 38%.

*Crystal structure determinations and refinements.* Suitable single crystals were selected and mounted on top of a glass fibre and crystal data were collected with an Enraf-Nonius CAD4 single crystal diffractometer. Data were collected at 180 K with graphite monochromatized Mo-K $\alpha$  radiation [ $\lambda(\text{MoK}\alpha)=0.7107 \text{ \AA}$ ] and  $\omega/2\theta$  scan mode. A summary of X-ray data collection parameters and structural refinement results are given in Table 1. The cell parameters were determined by automatic centering of 25 reflections and refined by the least-squares method. During data collection an intensity check was made every 60 min with two or three reflections. Reflections were measured in the range  $2^\circ \leq \theta \leq 25^\circ$  and were assumed as observed by applying the conditions  $I \geq 2\sigma(I)$ . The intensity data obtained were corrected for linear decay as well as Lorentz and polarization effects. The empirical absorption corrections ( $\psi$ -scan) were applied to the data with minimum and maximum correction coefficients (correction coefficients: **2** 0.7810, 0.9989; **3** 0.8920, 0.9978; **4** 0.9498, 0.9998), respectively. The atomic scattering factors and anomalous dispersion factors were taken from Ref. 3. The structures were solved

Table 1. Crystal data of compounds CoL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (**2**), CuL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (**3**) and ZnL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (**4**).

	<b>2</b>	<b>3</b>	<b>4</b>
Chemical formula	C <sub>15</sub> H <sub>20</sub> Cl <sub>2</sub> CoN <sub>4</sub> O <sub>10</sub>	C <sub>15</sub> H <sub>16</sub> Cl <sub>2</sub> CuN <sub>4</sub> O <sub>8</sub>	C <sub>15</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>8</sub> Zn
Formula weight	546.18	514.76	516.59
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
Wavelength, MoK $\alpha$ / $\text{\AA}$	0.7107	0.7107	0.7107
<i>a</i> / $\text{\AA}$	8.076(2)	14.419(3)	8.748(2)
<i>b</i> / $\text{\AA}$	10.129(2)	7.118(3)	9.169(2)
<i>c</i> / $\text{\AA}$	13.894(5)	19.704(3)	25.081(6)
$\alpha$ / $^\circ$	80.11(2)	90	82.13(2)
$\beta$ / $^\circ$	83.69(3)	110.34(1)	83.10(2)
$\gamma$ / $^\circ$	80.46(2)	90	75.56(2)
<i>V</i>	1100.3(5)	1896.2(9)	1922.1(8)
<i>Z</i>	2	4	4
<i>T</i> /K	180(2)	180(2)	180(2)
<i>F</i> (000)	558	1044	1048
$\mu$ /mm <sup>-1</sup>	1.082	1.489	1.610
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.649	1.803	1.785
$\theta$ <sub>min</sub> / $\theta$ <sub>max</sub> / $^\circ$	2.06/25.13	2.20/25.00	2.31/24.97
Crystal size/mm	0.3 × 0.2 × 0.2	0.9 × 0.3 × 0.2	0.5 × 0.4 × 0.4
Reflections collected	4192	3336	7229
Independent reflections	3893	3336	6742
Refinement method on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3892/57/300	3335/21/271	6739/99/527
Goodness-of-fit on <i>F</i> <sup>2</sup> ( <i>S</i> )	1.028	1.062	1.016
Weighting scheme ( <i>w</i> <sup>-1</sup> )	$[\delta^2(F_o^2) + (0.1660P)^2 + 6.18P]$ ; $P = (F_o^2 + 2F_c^2)/3$	$[\delta^2(F_o^2) + (0.0897P)^2 + 1.52P]$ ; $P = (F_o^2 + 2F_c^2)/3$	$[\delta^2(F_o^2) + (0.0352P)^2 + 9.75P]$ ; $P = (F_o^2 + 2F_c^2)/3$
Final <i>R</i> -indices [ <i>F</i> > 4 $\delta$ ( <i>F</i> )]	<i>R</i> <sub>1</sub> = 0.0831 <i>wR</i> <sub>2</sub> = 0.2189	<i>R</i> <sub>1</sub> = 0.0378 <i>wR</i> <sub>2</sub> = 0.1156	<i>R</i> <sub>1</sub> = 0.0453 <i>wR</i> <sub>2</sub> = 0.1028
<i>R</i> -indices (all data)	<i>R</i> <sub>1</sub> = 0.1325 <i>wR</i> <sub>2</sub> = 0.2769	<i>R</i> <sub>1</sub> = 0.0471 <i>wR</i> <sub>2</sub> = 0.1244	<i>R</i> <sub>1</sub> = 0.0574 <i>wR</i> <sub>2</sub> = 0.1113
Extinction coefficient	None	None	0.0067(8)
Diff. Four. $\Delta\rho$ <sub>max</sub> /e $\text{\AA}$ <sup>-3</sup>	1.233	1.023	2.255 (near Cl2)
Diff. Four. $\Delta\rho$ <sub>min</sub> /e $\text{\AA}$ <sup>-3</sup>	-1.659	-0.466	-2.137

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ with } F > 4\sigma(F), \text{ function minimized is } wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]}{[\sum [w(F_o^2)]]}^{0.5},$$

$$S = \frac{[\sum [w(F_o^2 - F_c^2)^2]}{(n - p)]^{0.5}}.$$

by direct methods using the SHELX-86 program<sup>4</sup> and refined by the full-matrix least-squares method on  $F_o^2$  using SHELXL-93.<sup>5</sup> All non-disordered non-H atoms were refined anisotropically. The disordered oxygen atoms of the perchlorate anions in compounds **2** and **4** were located from the  $\Delta F$  map and then refined isotropically with site occupation factors of 0.4 and using geometrical restraints to prevent anomalous bond distances inside the perchlorate tetrahedra. In compound **2** disordered carbon atom, C(9), was located from the  $\Delta F$  map and then refined with the occupancy 0.5. The hydrogen atoms were calculated to their ideal positions (C–H distance 0.93 Å for aromatic CH and 0.97 Å for CH<sub>2</sub>). All hydrogen atoms were refined as riding atoms with  $U = 1.2U(C)$  or  $U = 1.5U(O)$ . After the final refinement cycle the refinement converged to  $R_1 = 0.0831$  (compound **2**),  $R_1 = 0.0378$  (compound **3**),  $R_1 = 0.0453$  (compound **4**). The final atomic coordinates and equivalent isotropic

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{CoL}^1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (**2**).

Atom	x	y	z	$U(\text{eq})^a$
Co(1)	2191(1)	4631(1)	2619(1)	32(1)
O(1)	1050(10)	4692(8)	1327(5)	49(2)
O(2)	3451(10)	4736(7)	3829(5)	51(2)
N(1)	1957(9)	6801(6)	2293(5)	35(2)
N(2)	-160(9)	5236(7)	3332(5)	40(2)
N(3)	2075(9)	2576(7)	3147(5)	37(2)
N(4)	4439(8)	3626(7)	1930(5)	34(2)
C(2)	3006(11)	7578(9)	1759(7)	41(2)
C(3)	2636(12)	8998(9)	1546(7)	45(2)
C(4)	1099(13)	9607(9)	1956(7)	50(2)
C(5)	26(12)	8799(9)	2529(7)	47(2)
C(6)	479(10)	7414(8)	2665(6)	35(2)
C(7)	-628(11)	6508(9)	3222(7)	43(2)
C(8)	-1272(13)	4317(10)	3893(8)	53(2)
C(9A)	-220(27)	3131(19)	4446(14)	52(5) <sup>b</sup>
C(9B)	-921(24)	2838(18)	3609(15)	48(4) <sup>b</sup>
C(10)	702(13)	2083(9)	3836(7)	49(2)
C(11)	3338(11)	1757(8)	2899(6)	37(2)
C(12)	4658(10)	2270(8)	2192(6)	31(2)
C(13)	5983(11)	1411(8)	1816(6)	39(2)
C(14)	7138(10)	1951(9)	1106(7)	41(2)
C(15)	6928(11)	3347(9)	833(7)	45(2)
C(16)	5605(11)	4146(8)	1244(6)	39(2)
Cl(1)	-4706(3)	1973(2)	5621(2)	41(1)
O(11)	-4723(12)	2263(8)	4594(6)	87(3)
O(12)	-5888(10)	1111(8)	6027(9)	103(4)
O(13)	-3065(9)	1388(8)	5862(6)	67(2)
O(14)	-5192(10)	3232(7)	6001(7)	76(2)
Cl(2)	2171(3)	2342(2)	-453(2)	41(1)
O(21)	1995(11)	13506(9)	-1160(7)	86(3)
O(22)	3680(20)	12404(17)	-10(12)	92(4)
O(23)	2029(27)	11134(14)	-726(13)	98(4)
O(24)	952(22)	12529(18)	354(10)	93(4)
O(22')	2449(32)	12469(22)	484(11)	92(4) <sup>c</sup>
O(23')	3249(30)	11283(18)	-827(17)	98(4) <sup>c</sup>
O(24')	639(25)	11741(22)	-379(16)	93(4) <sup>c</sup>

<sup>a</sup> $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>b</sup>Site occupation factors for C(9A) and C(9B) are 0.5. <sup>c</sup>Site occupation factors for disordered oxygen atoms are 0.4.

thermal parameters for non-H atoms are given in Tables 2–4, while selected bond distances and angles are listed in Tables 5 and 6. Tables of anisotropic thermal parameters, coordinates of calculated hydrogen atoms and listings of observed and calculated structure factors are available from the authors on request. The molecules are shown in Figs. 1–3. Figure 4 shows the formation of hydrogen bonding in compound **2**. The plots were generated with the program DIAMOND<sup>6</sup> except for Fig. 4, which was drawn using SCHAKAL92,<sup>7</sup> and structures in figures were drawn using the 50% probability level.

## Results and discussion

**Structure of  $\text{CoL}^1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (**2**).** Figure 1 shows a perspective drawing of structure **2** with the atom labelling. In Fig. 1 the disordered uncoordinated perchlorate groups and the alternative position of the carbon atom C(9) are omitted for clarity. The cobalt atom is six-coordinated, with the ligand acting as a tetradentate ligand. The two pyridyl nitrogens and two Schiff-base nitrogens lie at the corners of the base of a distorted square bipyramid, and two water molecules occupy the apical sites. Inspection of the Co–N bond distances shows that the bonds to the imino nitrogens N(2) and

**Table 3.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{CuL}^1(\text{ClO}_4)_2$  (**3**).

Atom	x	y	z	$U(\text{eq})^a$
Cu(1)	7363(1)	2292(1)	4619(1)	20(1)
N(1)	6182(2)	2689(3)	3693(1)	20(1)
N(2)	6308(2)	2220(3)	5044(1)	22(1)
N(3)	8435(2)	2623(3)	5576(2)	24(1)
N(4)	8532(2)	2027(4)	4287(2)	24(1)
C(2)	6136(2)	3054(4)	3020(2)	26(1)
C(3)	5243(3)	3232(5)	2450(2)	32(1)
C(4)	4369(3)	3046(5)	2574(2)	31(1)
C(5)	4405(3)	2748(4)	3281(2)	30(1)
C(6)	5316(2)	2568(4)	3820(2)	22(1)
C(7)	5440(2)	2334(4)	4589(2)	23(1)
C(8)	6488(2)	2095(5)	5820(2)	27(1)
C(9)	7298(2)	3456(5)	6237(2)	29(1)
C(10)	8317(3)	2840(5)	6288(2)	35(1)
C(11)	9281(2)	2837(4)	5526(2)	27(1)
C(12)	9380(2)	2486(4)	4820(2)	23(1)
C(13)	10294(3)	2496(4)	4739(2)	33(1)
C(14)	10321(3)	1994(5)	4053(2)	37(1)
C(15)	9462(2)	1469(5)	3518(2)	36(1)
C(16)	8582(2)	1492(5)	3657(2)	29(1)
Cl(1)	6848(1)	-2602(1)	4637(1)	23(1)
O(11)	7102(2)	-1065(3)	4266(2)	47(1)
O(12)	6959(2)	-2056(4)	5365(2)	47(1)
O(13)	5844(2)	-3147(4)	4262(2)	49(1)
O(14)	7486(2)	-4162(3)	4654(1)	36(1)
Cl(2)	8337(1)	6430(1)	2672(1)	27(1)
O(21)	9264(2)	5946(5)	2616(2)	63(1)
O(22)	8449(2)	6453(6)	3421(2)	67(1)
O(23)	8017(3)	8230(5)	2378(2)	79(1)
O(24)	7603(2)	5050(4)	2311(1)	39(1)

<sup>a</sup> $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 4. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{ZnL}^1(\text{ClO}_4)_2$  (**4**).

Atom	x	y	z	$U(\text{eq})^a$
Zn(1)	6342(1)	6807(1)	3506(1)	24(1)
N(1A)	6831(9)	7641(8)	4191(3)	24(2)
N(2A)	8493(9)	7458(8)	3217(3)	25(2)
N(3A)	6281(9)	6116(8)	2743(3)	23(2)
N(4A)	4370(8)	5832(8)	3656(3)	22(2)
C(2A)	5984(12)	7822(11)	4665(4)	29(2)
C(3A)	6507(13)	8354(11)	5088(4)	34(2)
C(4A)	7960(13)	8703(12)	5017(4)	37(2)
C(5A)	8860(12)	8522(12)	4528(4)	35(2)
C(6A)	8257(10)	7999(10)	4124(4)	25(2)
C(7A)	9125(11)	7854(10)	3585(4)	28(2)
C(8A)	9324(12)	7381(11)	2671(4)	31(2)
C(9A)	9044(11)	6106(11)	2395(4)	30(2)
C(10A)	7357(11)	6330(12)	2256(4)	30(2)
C(11A)	5212(11)	5422(10)	2732(4)	25(2)
C(12A)	4123(10)	5235(10)	3218(4)	22(2)
C(13A)	2921(12)	4498(11)	3221(4)	32(2)
C(14A)	1919(12)	4381(12)	3686(4)	35(2)
C(15A)	2147(11)	4995(11)	4134(4)	29(2)
C(16A)	3402(11)	5704(10)	4103(4)	25(2)
Zn(2)	6527(1)	1871(1)	1270(1)	24(1)
N(1B)	7287(8)	1823(8)	2045(3)	22(2)
N(2B)	8570(9)	2701(9)	1070(3)	25(2)
N(3B)	6046(9)	2266(9)	451(3)	26(2)
N(4B)	4622(8)	854(8)	1306(3)	22(2)
C(2B)	6596(11)	1492(10)	2536(4)	26(2)
C(3B)	7329(12)	1406(11)	3004(4)	29(2)
C(4B)	8833(12)	1648(11)	2966(4)	30(2)
C(5B)	9554(11)	2022(11)	2460(4)	28(2)
C(6B)	8739(10)	2122(10)	2011(4)	22(2)
C(7B)	9362(10)	2651(10)	1463(4)	26(2)
C(8B)	9119(12)	3295(13)	523(4)	36(2)
C(9B)	7734(13)	4114(12)	202(4)	35(2)
C(10B)	6882(12)	3058(13)	5(4)	35(2)
C(11B)	4832(11)	1835(10)	371(4)	27(2)
C(12B)	4054(10)	986(10)	820(4)	23(2)
C(13B)	2852(11)	318(11)	742(4)	30(2)
C(14B)	2227(12)	-520(12)	1177(4)	35(2)
C(15B)	2803(12)	-654(11)	1672(4)	32(2)
C(16B)	4000(11)	58(10)	1720(4)	27(2)
Cl(1)	3172(3)	9649(2)	3331(1)	27(1)
O(11A)	4879(8)	9108(8)	3245(3)	37(2)
O(12A)	2780(9)	11219(8)	3142(4)	50(2)
O(13A)	2454(9)	8834(9)	3022(3)	45(2)
O(14A)	2672(11)	9355(10)	3888(3)	56(2)
Cl(2)	7829(3)	3517(3)	4276(1)	37(1)
O(21A)	7880(8)	4430(7)	3760(3)	30(2)
O(22A)	8711(21)	2035(18)	4244(7)	62(4)
O(23A)	6332(19)	3787(19)	4555(7)	64(3)
O(24A)	8763(19)	4186(18)	4615(6)	61(3)
O(22')	9243(29)	2299(26)	4273(10)	62(4) <sup>b</sup>
O(23')	6585(27)	2644(25)	4182(9)	64(3) <sup>b</sup>
O(24')	6937(28)	4332(27)	4673(8)	61(3) <sup>b</sup>
Cl(2)	8355(3)	-1543(3)	872(1)	27(1)
O(21B)	8034(8)	-632(7)	1316(2)	28(1)
O(22B)	9433(10)	-2926(9)	1022(3)	48(2)
O(23B)	9048(11)	-705(10)	423(3)	54(2)
O(24B)	6904(9)	-1787(10)	751(3)	50(2)
Cl(1)	3279(2)	4509(2)	1541(1)	24(1)
O(11B)	4994(7)	4175(8)	1405(3)	34(2)
O(12B)	2522(9)	4356(8)	1095(3)	39(2)
O(13B)	2781(9)	6001(8)	1678(3)	43(2)
O(14B)	2942(10)	3450(8)	1990(3)	43(2)

<sup>a</sup>  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>b</sup> Site occupation factors for disordered oxygen atoms are 0.4.

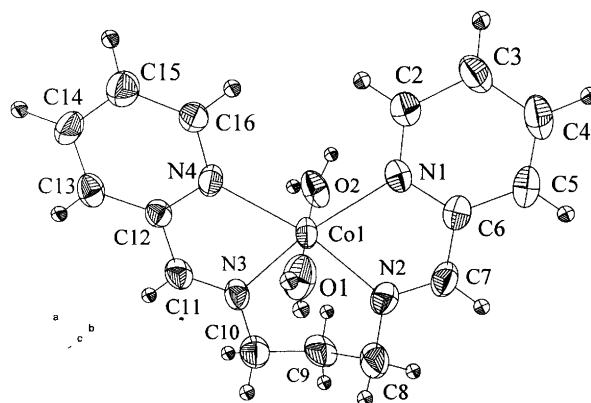


Fig. 1. View of  $\text{CoL}^1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (**2**) with the atom labels. The two uncoordinated disordered perchlorate groups and the alternative position of the carbon atom are omitted for clarity.

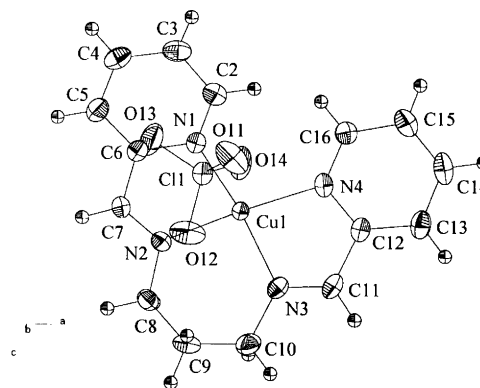


Fig. 2. View of  $\text{CuL}^1(\text{ClO}_4)_2$  (**3**) with the atom labels, where one of the two perchlorate groups is forming [4+2] coordination. The other uncoordinated perchlorate group is omitted for clarity.

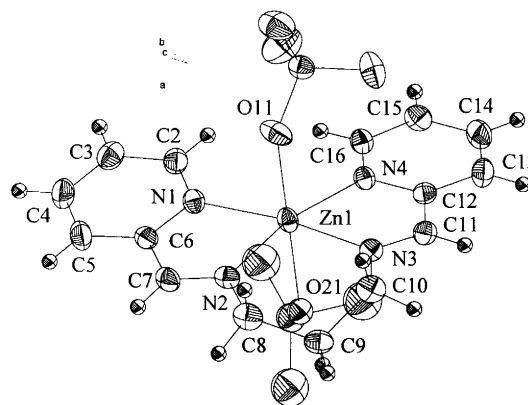
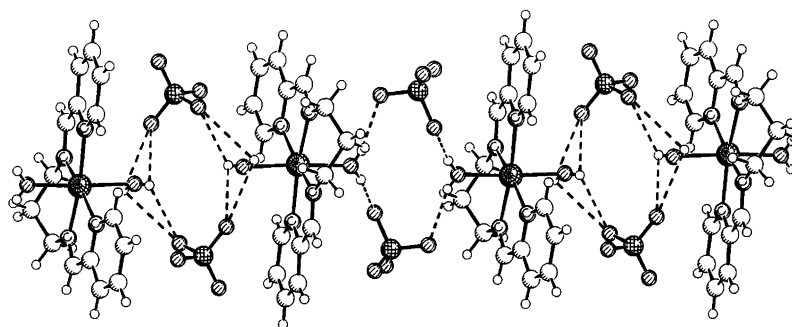


Fig. 3. View of  $\text{ZnL}^1(\text{ClO}_4)_2$  (**4**) showing the molecule A with the atom labels. The disordered part of the perchlorate group is omitted for clarity.

$\text{N}(3)$  [ $\text{Co}(1)\text{-N}(2)=2.091(7)$   $\text{\AA}$  and  $\text{Co}(1)\text{-N}(3)=2.099(7)$   $\text{\AA}$ ] are slightly shorter than the bonds to the pyridyl nitrogens  $\text{N}(1)$  and  $\text{N}(4)$  [ $\text{Co}(1)\text{-N}(1)=2.148(7)$   $\text{\AA}$  and  $\text{Co}(1)\text{-N}(4)=2.142(6)$   $\text{\AA}$ ]. The  $\text{Co}(1)\text{-N}(2)$  and  $\text{Co}(1)\text{-N}(3)$  bond lengths are reduced

Table 5. Selected bond lengths (Å) for 2–4.

<b>[CoL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O (2)</b>					
Co(1)–O(2)	2.084(7)	N(4)–C(12)	1.346(10)	The uncoordinated perchlorates:	
Co(1)–N(2)	2.091(7)	N(4)–C(16)	1.367(10)	Cl(1)–O(12)	1.407(8)
Co(1)–O(1)	2.093(7)	C(2)–C(3)	1.406(12)	Cl(1)–O(11)	1.408(8)
Co(1)–N(3)	2.099(7)	C(4)–C(5)	1.383(14)	Cl(1)–O(13)	1.411(7)
Co(1)–N(4)	2.142(6)	C(6)–C(7)	1.455(12)	Cl(1)–O(14)	1.442(7)
Co(1)–N(1)	2.148(7)	C(8)–C(9A)	1.50(2)	Cl(2)–O(23)	1.368(14)
N(1)–C(2)	1.330(11)	C(8)–C(9B)	1.59(2)	Cl(2)–O(21)	1.397(9)
N(1)–C(6)	1.344(11)	C(9A)–C(10)	1.52(2)	Cl(2)–O(24)	1.425(14)
N(2)–C(7)	1.269(11)	C(9B)–C(10)	1.44(2)	Cl(2)–O(22)	1.439(13)
N(2)–C(8)	1.468(12)	C(13)–C(14)	1.386(12)	The disordered part:	
N(3)–C(11)	1.260(11)	C(15)–C(16)	1.364(12)	Cl(2)–O(22')	1.38(2)
N(3)–C(10)	1.477(11)			Cl(2)–O(23')	1.40(2)
				Cl(2)–O(24')	1.45(2)
<b>CuL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (3)</b>					
Cu(1)–N(2)	1.976(3)	N(4)–C(16)	1.324(4)	The uncoordinated perchlorates:	
Cu(1)–N(3)	1.994(3)	N(4)–C(16)	1.346(4)	Cl(1)–O(13)	1.430(3)
Cu(1)–N(4)	2.017(2)	C(2)–C(3)	1.390(5)	Cl(1)–O(11)	1.433(2)
Cu(1)–N(1)	2.038(3)	C(4)–C(5)	1.391(5)	Cl(1)–O(14)	1.435(2)
N(1)–C(2)	1.329(4)	C(6)–C(7)	1.471(4)	Cl(1)–O(12)	1.439(3)
N(1)–C(6)	1.359(4)	C(8)–C(9)	1.521(5)	Cl(2)–O(23)	1.416(3)
N(2)–C(7)	1.264(4)	C(9)–C(10)	1.503(5)	Cl(2)–O(21)	1.421(3)
N(2)–C(8)	1.461(4)	C(13)–C(14)	1.411(6)	Cl(2)–O(22)	1.427(3)
N(3)–C(11)	1.267(4)	C(15)–C(16)	1.388(5)	Cl(2)–O(24)	1.438(2)
N(3)–C(10)	1.479(4)				
<b>ZnL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (4)</b>					
Averaged bond lengths:					
Zn–N(1)	2.112	C(4)–C(5)	1.384	Cl(2)–O(22B)	1.414(8)
Zn–N(4)	2.114	C(6)–C(7)	1.476	Cl(2)–O(24B)	1.417(7)
Zn–N(3)	2.109	C(8)–C(9)	1.518	Cl(2)–O(23B)	1.433(8)
Zn–N(2)	2.113	C(9)–C(10)	1.518	Cl(2)–O(21B)	1.441(6)
Zn–O(11)	2.241	C(13)–C(14)	1.381	Cl(1)–O(13B)	1.405(7)
Zn–O(21)	2.325	C(15)–C(16)	1.394	Cl(1)–O(12B)	1.406(7)
N(1)–C(2)	1.333	The coordinated perchlorates:		Cl(1)–O(14B)	1.437(7)
N(1)–C(6)	1.354	Cl(1)–O(12A)	1.421(7)	Cl(1)–O(11B)	1.462(7)
N(2)–C(7)	1.265	Cl(1)–O(14A)	1.423(8)	The disordered part of molecule A:	
N(2)–C(8)	1.473	Cl(1)–O(13A)	1.437(7)	Cl(2)–O(24')	1.37(2)
N(3)–C(11)	1.333	Cl(1)–O(11A)	1.452(7)	Cl(2)–O(22')	1.45(2)
N(3)–C(10)	1.471	Cl(2)–O(23A)	1.39(2)	Cl(2)–O(23')	1.56(2)
N(4)–C(16)	1.330	Cl(2)–O(22A)	1.39(2)		
N(4)–C(12)	1.351	Cl(2)–O(21A)	1.443(7)		
C(2)–C(3)	1.392	Cl(2)–O(24A)	1.52(2)		

Fig. 4. The formation of hydrogen bonding in direction [101] in CoL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O (3).

relative to the other Co–N bond distances in order to reduce the angular strain at these centres [C(6)–C(7)–N(2) 119.8(8)° and C(12)–C(11)–N(3) 119.0(7)°]. All internal angles at C and N are close to

the regular tetrahedral value.<sup>8</sup> The angles and bond distances subtended by the chelate rings at the metal ion are similar and compare well with the values found in analogous compounds.<sup>9,10</sup> The uncoordinated disordered

Table 6. Selected bond angles (°) for 2–4.

<b>CoL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O (2)</b>					
O(2)–Co(1)–N(2)	92.3(3)	C(2)–N(1)–Co(1)	129.6(6)	C(8)–C(9A)–C(10)	115.5(14)
O(2)–Co(1)–O(1)	174.1(3)	C(6)–N(1)–Co(1)	112.3(5)	C(10)–C(9B)–C(8)	114.7(13)
N(2)–Co(1)–O(1)	90.1(3)	C(7)–N(2)–Co(1)	114.6(6)	C(9B)–C(10)–N(3)	111.8(11)
O(2)–Co(1)–N(3)	89.4(3)	C(8)–N(2)–Co(1)	125.3(6)	N(3)–C(10)–C(9A)	113.4(10)
N(2)–Co(1)–N(3)	92.1(3)	C(11)–N(3)–Co(1)	115.6(6)	N(3)–C(11)–C(12)	119.0(7)
O(1)–Co(1)–N(3)	95.9(3)	C(10)–N(3)–Co(1)	124.0(5)	N(4)–C(12)–C(13)	123.6(7)
O(2)–Co(1)–N(4)	91.2(3)	C(12)–N(4)–Co(1)	113.4(5)	N(4)–C(12)–C(11)	114.6(7)
N(2)–Co(1)–N(4)	168.6(3)	C(16)–N(4)–Co(1)	129.8(5)	C(12)–C(13)–C(14)	119.1(8)
O(1)–Co(1)–N(4)	87.5(3)	N(1)–C(2)–C(3)	123.6(8)	C(16)–C(15)–C(14)	120.4(8)
N(3)–Co(1)–N(4)	77.1(3)	C(5)–C(4)–C(3)	119.3(8)	C(15)–C(16)–N(4)	122.4(8)
O(2)–Co(1)–N(1)	87.6(3)	N(1)–C(6)–C(5)	122.8(8)		
N(2)–Co(1)–N(1)	77.8(3)	N(1)–C(6)–C(7)	115.3(7)		
O(1)–Co(1)–N(1)	87.6(3)	N(2)–C(7)–C(6)	119.8(8)		
N(3)–Co(1)–N(1)	169.4(3)	N(2)–C(8)–C(9A)	109.0(10)		
N(4)–Co(1)–N(1)	113.1(3)	N(2)–C(8)–C(9B)	113.7(10)		
<b>CuL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (3)</b>					
N(2)–Cu(1)–N(3)	93.42(11)	C(11)–N(3)–Cu(1)	113.1(2)	C(10)–C(9)–C(8)	113.6(3)
N(2)–Cu(1)–N(4)	171.11(10)	C(10)–N(3)–Cu(1)	127.1(2)	N(3)–C(10)–C(9)	113.5(3)
N(3)–Cu(1)–N(4)	81.80(11)	C(16)–N(4)–Cu(1)	130.9(2)	N(3)–C(11)–C(12)	117.8(3)
N(2)–Cu(1)–N(1)	81.73(11)	C(12)–N(4)–Cu(1)	111.0(2)	N(4)–C(12)–C(13)	123.7(3)
N(3)–Cu(1)–N(1)	164.32(10)	N(1)–C(2)–C(3)	122.3(3)	N(4)–C(12)–C(11)	114.8(3)
N(4)–Cu(1)–N(1)	104.80(11)	C(3)–C(4)–C(5)	118.5(3)	C(12)–C(13)–C(14)	117.0(3)
C(2)–N(1)–Cu(1)	131.0(2)	N(1)–C(6)–C(5)	122.8(3)	C(14)–C(15)–C(16)	119.2(3)
C(6)–N(1)–Cu(1)	111.2(2)	N(1)–C(6)–C(7)	113.9(3)	N(4)–C(16)–C(15)	122.7(3)
C(7)–N(2)–Cu(1)	114.5(2)	N(2)–C(7)–C(6)	118.4(3)		
C(8)–N(2)–Cu(1)	24.2(2)	N(2)–C(8)–C(9)	110.5(3)		
<b>ZnL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (4)</b>					
N(1A)–Zn(1)–N(4A)	112.7(3)	N(3A)–Zn(1)–O(21A)	88.7(3)	N(2A)–C(7A)–C(6A)	119.4(8)
N(1A)–Zn(1)–N(3A)	167.9(3)	C(2A)–N(1A)–Zn(1)	130.0(6)	N(2A)–C(8A)–C(9A)	112.3(7)
N(4A)–Zn(1)–N(3A)	79.4(3)	C(6A)–N(1A)–Zn(1)	112.2(6)	C(10A)–C(9A)–C(8A)	114.4(8)
N(1A)–Zn(1)–N(2A)	79.0(3)	C(7A)–N(2A)–Zn(1)	112.6(6)	N(3A)–C(10A)–C(9A)	111.5(8)
N(4A)–Zn(1)–N(2A)	167.1(3)	C(8A)–N(2A)–Zn(1)	127.7(6)	N(3A)–C(11A)–C(12A)	119.7(8)
N(3A)–Zn(1)–N(2A)	88.9(3)	C(11A)–N(3A)–Zn(1)	113.1(6)	N(4A)–C(12A)–C(13A)	122.7(8)
N(1A)–Zn(1)–O(11A)	89.4(3)	C(10A)–N(3A)–Zn(1)	126.7(6)	N(4A)–C(12A)–C(11A)	115.9(8)
N(4A)–Zn(1)–O(11A)	93.4(3)	C(16A)–N(4A)–Zn(1)	130.3(6)	C(14A)–C(13A)–C(12A)	118.8(9)
N(3A)–Zn(1)–O(11A)	90.5(3)	C(12A)–N(4A)–Zn(1)	111.8(6)	C(14A)–C(15A)–C(16A)	118.7(9)
N(2A)–Zn(1)–O(11A)	92.1(3)	O(11A)–Zn(1)–O(21A)	178.9(3)	N(4A)–C(16A)–C(15A)	122.7(8)
N(1A)–Zn(1)–O(21A)	91.3(3)	N(1A)–C(2A)–C(3A)	122.9(9)		
N(4A)–Zn(1)–O(21A)	87.1(3)	C(3A)–C(4A)–C(5A)	119.2(9)		
N(2A)–Zn(1)–O(21A)	87.2(3)	N(1A)–C(6A)–C(7A)	116.1(8)		

perchlorate group possesses electron density ca. 1.13 Å<sup>3</sup> from the metal in a position approximately *trans* to the oxygen O(2). All four N–Co(1)–O(2)(H<sub>2</sub>O) angles are in the range of 87–92°, suggesting that a lone pair is stereochemically active in the other axial position and that its presence may be the cause of the perchlorate ion disorder. The disorder of the carbon atom C(9) is due to the flexible carbon chain C(8)–C(9)–C(10), which can have two alternative positions. The macrocycle is nearly planar, because the deviation of Co from the least-squares plane N(1)–N(2)–N(3)–N(4) is 0.002(4) Å. In this structure molecules form long chains which are joined together by hydrogen bonds formed between the coordinated water molecules and perchlorate groups in the direction [101]. This is illustrated in Fig. 4.

*Structure of CuL<sup>1</sup>(ClO<sub>4</sub>)<sub>2</sub> (3).* Figure 2 shows the molecular structure of compound 3 with atom labelling. The

coordination around the copper atom can be described as [4+2] coordination. The coordination mainly resembles square planar, but there is an obvious, but weak interaction between copper and the two oxygens of one perchlorate group. The copper atom is coordinated to the four nitrogen atoms, with the shortest bonds being to the Schiff-base nitrogens [Cu(1)–N(2) = 1.976(3) Å, Cu–N(3) = 1.994(3) Å]. The shorter Cu–N–(Schiff-base) bond distances reduce the angular strain at the Cu–N(Schiff-base) centres [C(6)–C(7)–N(2) 118.4(3)° and C(12)–C(11)–N(3) 117.8(3)°]. The Cu–N(Schiff-base) and Cu–N(pyridyl) distances are comparable with those in analogous complexes.<sup>11–13</sup> The perchlorate is not directly coordinated to the copper atom, but the Cu(1)···O(11) and Cu(1)···O(14) distances are 2.48 and 2.53 Å, respectively, and both bond lengths are within the range of 2.52(2)–2.883(2) Å reported<sup>14</sup> for a variety of copper(II) complexes con-

taining coordinated perchlorate groups.<sup>15</sup> The macrocycle is quite planar, because the deviation of Cu from the least-squares plane N(1)–N(2)–N(3)–N(4) is  $-0.069(1)$  Å.

*Structure of  $ZnL^1(ClO_4)_2$  (4).* The asymmetric unit contains two nearly identical molecules A and B of which molecule A is shown in Fig. 3 to illustrate the molecular structure of compound 4 with atom labelling. In Fig. 3 the disordered part of the perchlorate [O(22'), O(23') and O(24')] in molecule A is omitted for clarity. The zinc atom is six-coordinated to two Schiff-base and two pyridyl nitrogen atoms, which form the base of the square bipyramid and to two oxygen atoms of the perchlorate groups, which occupy the apical sites. The distances between the zinc and the four nitrogen atoms of the macrocycle differ slightly, but mainly the Zn–N bond lengths appear unremarkable and with the other bond distances and angles are in good agreement with the literature.<sup>16,17</sup> The maximum electron density of  $2.255 \text{ e } \text{Å}^{-3}$  near Cl(2) may be due to the measuring temperature of 180 K, because of the slow thermal motion, and that is the cause of the severe disorder in this particular perchlorate group. The electron density present around the Cl(2) resembles a donut, and the perchlorate tetrahedrons cannot be modelled so that they would retain their tetrahedral nature and would be chemically reasonable. The macrocycle is quite planar, because the deviation of Zn from the least-squares plane N(1)–N(2)–N(3)–N(4) is  $0.05(4)^\circ$ . The two coordinated perchlorates form an angle of  $178.9(3)^\circ$  with the zinc atom.

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