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Synthesis, characterization and structural studies of mono- and polynuclear complexes of zinc(II) with 1,10-phenanthroline, 2,2′-bipyridine and 4,4′-bipyridine

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Abstract—Three complexes of the formula [Zn(2,2′-bipy)$(CCl_3CO_2)_2(H_2O)$] (**1**). [Zn (1,10-phen) $(CCl_3CO_2)_2(H_2O)$] (**1a**) and [Zn(μ-4,4′-bipy)(4,4′-bipy)$_2(CCl_3CO_2)_2(H_2O)_4]_n$ (**2**) have been synthesized and characterized by elemental analysis, IR spectra, thermal analysis and single-crystal X-ray diffraction for **1** and **2** and X-ray powder pattern for **1a**. The metal coordination in complex **1** is distorted trigonal bipyramidal with N(1), O(2) and O(5) defining the basal plane, O(3) and N(2) being in apical positions. The X-ray crystal structure of **2** reveals that the local coordination round the Zn^{II} ion is a distorted octahedron, in which $Zn(H_2O)_4$ coordination planes are bridged by 4,4′-bipyridine to form an infinite chain structure. Two 4,4′-bipyridine molecules and two trichloroacetate anions exist in the lattice linked by intermolecular hydrogen bonds to coordinated water molecule. Complexes **1** and **1a** have a similar pattern of bonding and showed identical TGA curve and almost similar X-ray powder diffractograms. © 1997 Elsevier Science Ltd

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Carboxylate anions have versatility which has wide application in the development of coordination chemistry. They are found in both low and high oxidation state environments in coordination compounds and bioinorganic systems and bond in a surprising number of different modes such as monodentate or bidentate to one metal ion, or acting as a bridging ligand to two metal ions or simply as an anion. They can thus play a key role in many biochemical systems involving mono- or polymetallic sites [1].

A major reason for the importance of zinc in enzyme chemistry is its ability to adopt coordination numbers of 4, 5 or 6 in its complexes and to change its coordination geometry comparatively easily [2].

In this paper we report the synthesis of three complexes of Zn^{II} with the anionic ligand trichloroacetate and neutral ligands 2,2′-bipyridine, 1,10-phenanthroline and 4,4′-bipyridine, of the formula [Zn (2,2′-bipy)$(CCl_3CO_2)_2(H_2O)$] (**1**), [Zn(1,10-phen) $(CCl_3CO_2)_2(H_2O)$] (**1a**) and [Zn(μ-4,4′-bipy) (4,4′-bipy)$_2(CCl_3CO_2)_2(H_2O)_4]_n$ (**2**). The ligands were chosen to distinguish that the zinc(II) ion forms a monomer or polymer on changing the ligand's position of nitrogen. From TGA curves it has been observed that **1**, **1a** and **2** under non-isothermal condition pass through unstable intermediates even at low rate of heating.

EXPERIMENTAL

Materials and methods

$Zn(CCl_3CO_2)_2$ was prepared according to the cited procedure [3]. 2,2′-Bipyridine (S.D. Fine Chemicals,

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Calcutta, India), 1,10-phenanthroline (BDH, India Limited) and 4,4′-bipyridine (Fluka Chemie, Switzerland) were used as received.

Synthesis of the complexes

$[Zn(2,2'\text{-bipy})(CCl_3CO_2)_2(H_2O)]$ (**1**). This complex was prepared by the addition of 2,2′-bipyridine (1.18 mmol) in 5 cm^3 of ethanol to a solution of zinc(II) trichloroacetate (1.17 mmol) dissolved in 20 cm^3 of water. The resulting mixture was stirred and kept at room temperature. Shiny colourless crystals appeared after 2 days, from which crystals suitable for X-ray analysis were separated. The rest were filtered, washed and dried in air. Found: C, 29.6; H, 1.6; N, 4.9. $C_{14}H_{10}Cl_6O_5N_2Zn$ requires: C, 29.8; H, 1.8; N, 4.9%.

$[Zn(1,10\text{-phen})(CCl_3CO_2)_2(H_2O)]$ (**1a**). The same procedure as complex **1** was adopted in this case. Colourless crystals appeared, which were filtered and dried. Found: C, 32.7; H, 1.4; N, 4.5. $C_{16}H_{10}O_5N_2Cl_6Zn$ requires: C, 32.6; H, 1.7; N, 4.8%.

$[Zn(\mu\text{-}4,4'\text{-bipy})(4,4'\text{-bipy})_2(CCl_3CO_2)_2(H_2O)_4]_n$ (**2**). The synthesis was carried out using the same procedure as in **1**. The resulting mixture was set aside at room temperature. After 2–3 days colourless crystals appeared, from which crystals suitable for X-ray analysis were separated. The rest were filtered and dried. Found: C, 43.6; H, 6.5; N, 9.0. $C_{34}H_{32}O_8N_6Cl_6Zn$ requires: C, 43.8; H, 6.9; N, 9.0%.

Physical measurements

The IR spectra were recorded on a Perkin–Elmer model 595 spectrophotometer in KBr as a medium. A Perkin–Elmer 240C elemental analyser was used to collect microanalytical data (C, H, N). Thermal investigation (TGA) was carried out on a Shimadzu TGA-50 thermal analyser under a dynamic nitrogen environment.

X-ray data collection and structure refinement

X-ray powder patterns were recorded on a Philips XRD diffractometer (PW 1710) operating at 40 KV and 20 mA with the θ range 4–70°.

The determination of unit-cell and single-crystal data collection were carried out with Mo-K_α radiation ($\lambda = 0.71069$ Å) on an Enraf–Nonius CAD-4 four-circle diffractometer equipped with a graphite crystal monochromator at 293 K. Crystallographic data for complexes **1** and **2** are given in Table 1. Lattice constants were determined by least-squares refinement of angular settings of 25 reflections. Intensity data were collected by the ω–2θ scan technique and corrected for Lorentz–polarization and absorption factors. The absorption correction was applied for complex **1** based on the empirical ψ scan method [4], but not for **2**. Scattering factors were taken from Cromer and Waber [5]. The goodness-of-fit was 0.98 for **1** and 0.95

Table 1. Crystallographic and structure solution data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{14}H_{10}Cl_6N_2O_5Zn$	$C_{34}H_{32}Cl_6N_6O_8Zn$
Crystal colour	Colourless	Colourless
Crystal symmetry	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Mol. wt ($g\ mol^{-1}$)	564.3	930.8
a (Å)	9.440(1)	8.808(1)
b (Å)	11.340(1)	8.810(1)
c (Å)	11.691(3)	12.751(5)
α (°)	115.57(1)	82.27(1)
β (°)	107.29(1)	86.07(2)
γ (°)	96.26(1)	79.47(1)
V (Å^3)	1036.2	963.0
Z	2	1
$F(000)$ (e)	560	474
D_{calc} ($g\ cm^{-3}$)	1.81	1.6
Crystal size (mm)	0.21 × 0.49 × 0.42	0.42 × 0.42 × 0.14
T (K)	293	293
μ (cm^{-1})	20.22	11.28
No. of reflections measured	5411	4614
Criterion for observed data	$I > 2\sigma(I)$	$I > 2\sigma(I)$
No. of observed data	4162	3804
R^a	0.034	0.042
wR^{2b}	0.114	0.115

[a] $R = (\Sigma \| F_o| - |F_c \|)/\Sigma | F_o |$, with $F = 0.0$ if $F^2 < 0.0$.

[b] $wR^2 = [\Sigma[w(F_o^2 - F_o^2)^2]/\Sigma[(F_o^2)]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + aP^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

for **2** and the maximum residual on the final difference map was 0.65 for **1** and 0.82 e $Å^{-3}$ for **2**. All computations were carried out on a DEC ALPHA computer using SHELXS-86 [6], SHELXL-93 [7], PATSEE [8] and ORTEP [9] programs.

Additional material are available from the Cambridge Crystallographic Data Centre comprising of atom coordinates thermal parameters and remaining bond lengths and angles.

RESULTS AND DISCUSSIONS

IR spectra

The broad absorption band for ν(HOH) at 3040–3290 cm^{-1} indicates the presence of a water molecule as well as hydrogen bonding in **1**.

The bands appearing at 3050–3060 (s, br) and at 1560, 1590, 770 cm^{-1} are apparently the characteristic absorptions of 2,2′-bipyridine present in **1**.

Carboxylate groups can coordinate to metals in a number of ways. IR spectroscopy is a useful tool in diagnosing the nature of carboxylate coordination. The separation between $\gamma_{as}(CO_2^-)$ and $\gamma_s(CO_2^-)$ when significantly less than in the free carboxylate anion is indicative of a bidentate bridging or chelating carboxylate group and separation more than the free anionic value is indicative of a unidentate ligand [10]. The bands at $\gamma_{as}(CO_2^-)$ at 1660 cm^{-1} and $\gamma_s(CO_2^-)$ at 1330 cm^{-1}, respectively, 330 cm^{-1} separation ($\Delta\nu$ value), is significantly higher than the value of $\Delta\nu$ for free $CCl_3CO_2^-$, indicating that the carboxylate group is coordinating with Zn in a monodentate fashion [10], which is unambiguously confirmed by the crystal structure of **1**.

Strong broad bands at 3400 and 3040 cm^{-1} indicate the presence of γ(OH) and γ(NH) in **1a**. The difference between $\gamma_{as}(CO_2^-)$ at 1680 cm^{-1} and $\gamma_s(CO_2^-)$ at 1340 cm^{-1} is 340 cm^{-1} ($\Delta\gamma$), which indicates that the carboxylate group is acting as a monodentate ligand [10]. The bands at 1585, 1520, 1430, 1145, 1100, 865, 840, 750, 720, 550, 470, 410, 375 and 320 cm^{-1} are the characteristic absorptions of 1,10-phenanthroline present in **1a**.

The presence of water molecules in **2** was confirmed by IR spectral bands at 3200 cm^{-1} (s, br) [γ(HOH)] and at 1650 cm^{-1}(s) [δ(HOH)]. The broad and strong absorption band at 3200 cm^{-1} is perhaps attributable to $\gamma(O—H\cdots X)$ (X is an electronegative nitrogen atom or oxygen atom), indicating the presence of hydrogen bonds in the complex. The appearance of γ(Zn—O) at 470 cm^{-1} and $\rho_w(H_2O)$ at 570 cm^{-1} indicate the presence of coordinated water molecules. The presence of bands at 1596, 1540, 1406, 1220, 1069, 809 and 620 cm^{-1} indicate that some 4,4′-bipyridine exists as non-coordinated molecules [11,12]. The γ(C=O) band at 1680 cm^{-1} indicates the presence of the free trichloroacetate anion [13].

Thermal analysis

The complex **1** is stable up to approximately 55°C. The mass loss in TGA curve (Fig. 1) corresponds to the release of one coordinated water molecule followed by one molecule of 2,2′-bipyridine.

Complex **1a** starts decomposition at approximately 50°C with the release of one coordinated water molecule followed by the loss of one molecule of 1,10-phenanthroline (Fig. 1).

Complex **2** is stable up to 60°C and then its decomposition starts. The loss in the temperature range 60–105°C corresponds exactly to the release of four coordinated water molecules. Soon after, the loss of 4,4′-bipyridine molecule starts. Loss at low temperature indicate that they are non-coordinated. At still higher temperature the loss of bridged 4,4′-bipyridine molecule [14] starts without any distinguishable step (Fig. 1).

Description of structure

The crystal structure of **1** is shown in Fig. 2. Selected bond distances and bond angles are listed in Table 2. It crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. The coordination geometry around the Zn^{II} ion can be considered as distorted trigonal bipyramidal with N(1), O(2) and O(5) in equatorial sites and O(3) and N(2) in axial sites. The

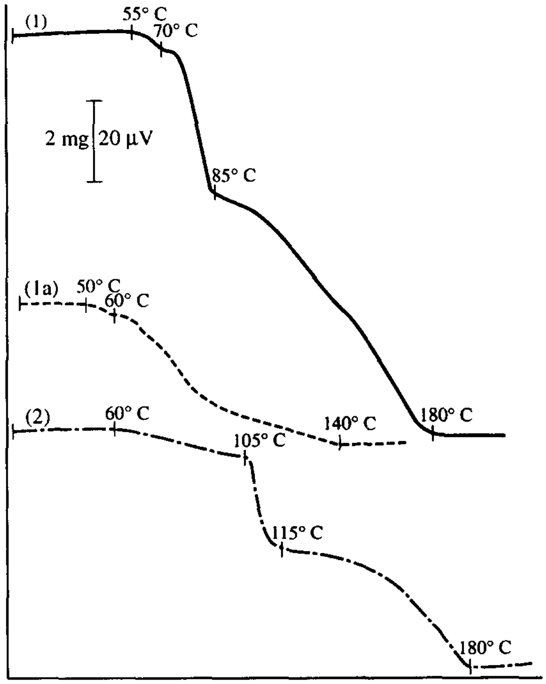

Fig. 1. TGA curves for complexes **1** (—) (weight taken = 11.75 mg), **1a** (- - -) (weight taken = 10.42 mg) and **2** (–·–·–) (weight taken = 9.175 mg). Heating rate is 3°C min^{-1} in each run.

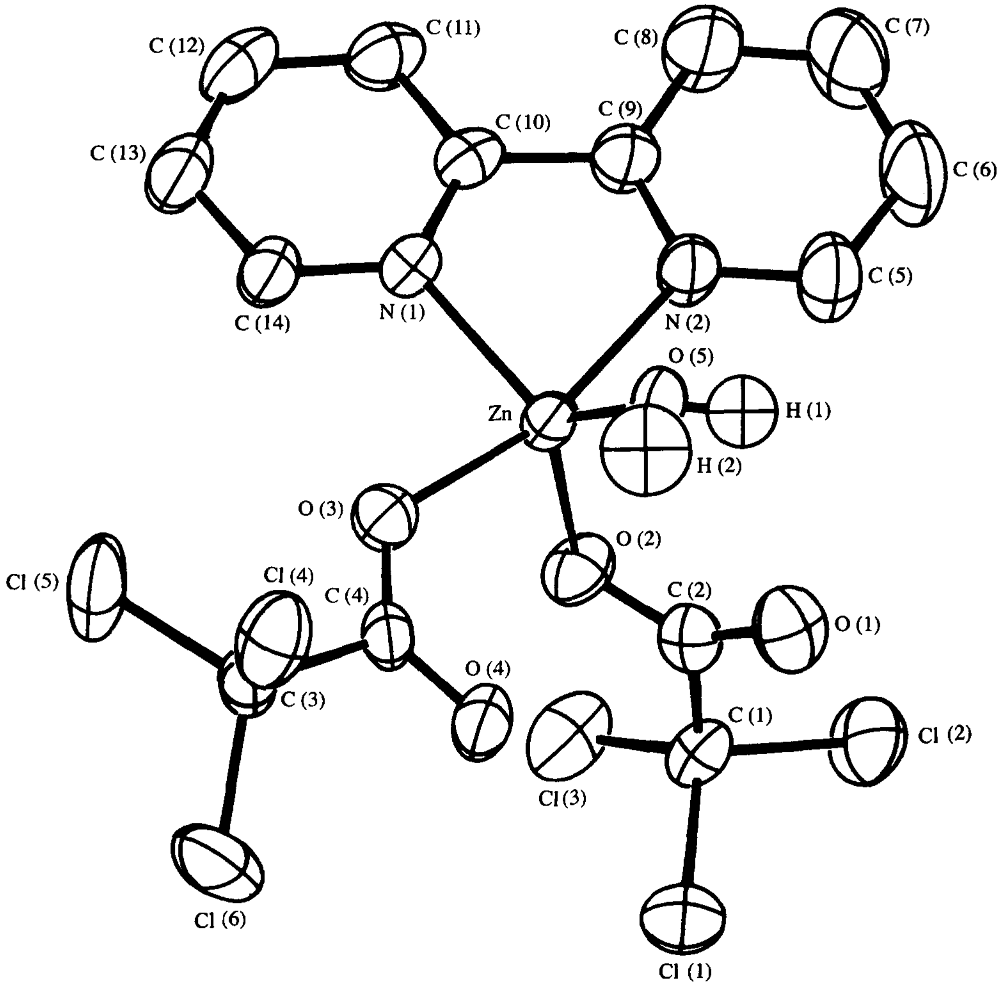

Fig. 2. ORTEP view of [Zn(2,2′-bipy)$(CCl_3CO_2)_2(H_2O)$] (**1**).

Table 2. Selected bond distances (Å) and angles (°) for **1**

Zn—O(2)	1.993(2)	Zn—O(3)	2.051(2)
Zn—O(5)	2.003(2)	Zn—N(1)	2.086(2)
Zn—N(2)	2.151(2)	O(3)—C(4)	1.243(3)
O(2)—C(2)	1.255(4)	O(5)—H(1)	0.82(4)
O(5)—H(2)	0.76(6)		
O(1)- - -O(5)	2.715(3)	O(4)- - -O(5)	2.650(3)

N(2)—Zn—N(1)	77.2(1)	N(2)—Zn—O(5)	90.2(1)
N(2)—Zn—O(3)	165.2(1)	N(2)—Zn—O(2)	94.3(1)
N(1)—Zn—O(5)	123.5(1)	N(1)—Zn—O(3)	90.2(1)
N(1)—Zn—O(2)	111.3(1)	O(5)—Zn—O(3)	90.3(1)
O(5)—Zn—O(2)	124.6(1)	O(3)—Zn—O(2)	97.5(1)
C(2)—O(2)—Zn	119.3(2)	C(4)—O(3)—Zn	126.2(2)
C(1)—C(2)—O(1)	116.5(3)	C(1)—C(2)—O(2)	114.8(2)
C(3)—C(4)—O(4)	114.9(3)	C(3)—C(4)—O(3)	115.0(3)

Zn^{II} atom deviates only 0.1(3) Å from the equatorial plane and the axial bonds are longer than the equatorial ones [1.993(2)–2.086(2) Å] as has been suggested for trigonal bipyramidal coordination [15]. The compound is not polymeric, but the presence of intermolecular hydrogen bond between the O atom of H_2O coordinated with Zn^{II} and a carboxyl O atom is indicated by the distances O(1)···O(5) and O(4)···O(5), which are 2.715(3) and 2.650(3) Å, respectively (Fig. 3). The carboxyl C—O bond lengths and C—C—O angles of both monodentate trichloroacetate groups are significantly different and indicate the double-bond character for the non-bonded carboxyl oxygen atom.

X-ray powder diffraction patterns of complexes **1** and **1a** were recorded and found to have similar pattern of bonding [16–19]. The *d* and I/I_0 values are more or less same and are enlisted in Table 3. Slight differences in d values of both complexes may be due to the difference in the structure of the organic ligands.

The crystal structure of **2** is shown in Fig. 4. Selected bond distances and angles are listed in Table 4. It crystallizes in the triclinic space group $P\bar{1}$ with one formula unit per unit cell. Each repeat unit of the complex consists of $Zn(H_2O)_4$, one bridging 4,4′-bipyridine along with two non-coordinated 4,4′-bipyridine molecules and two trichloroacetate anions. The $Zn(H_2O)_4$ planar units are bridged by 4,4′-bipyridine in a nearly linear fashion forming a polymeric chain in the crystal. The local coordination geometry around the Zn^{II} ion lying on a crystallographic inversion centre is distorted octahedron. The coordinated water molecules are hydrogen bonded to the N atoms of the non-coordinated 4,4′-bipyridines as well as to the O atoms of the non-coordinated trichloroacetate anions. The distances N—O and O—O are less than 3 Å, implying the presence of hydrogen bonds, since

Table 3. Representative peaks of powder diffraction patterns of complexes **1** and **1a**

No.	**1** *d* value in (Å)	I/I_{max}	*d* value (Å)	**1a** I/I_{max}
1	9.21	10	9.21	16
2	6.73	30	6.97	100
3	6.36	16	6.09	19
4	5.94	32	5.83	59
5	5.32	100	5.05	41
6	4.38	13	4.39	69
7	4.13	19	4.17	18
8	3.93	26	3.97	34
9	3.87	18	3.87	31
10	3.74	8	3.77	67
11	3.51	10	3.53	17
12	3.24	19	3.20	55
13	3.17	9	3.16	30
14	3.07	93	3.09	25
15	2.94	15	2.93	28
16	2.74	14	2.75	33
17	2.63	14	2.66	29
18	2.58	69	2.52	23
19	2.35	31	2.38	8
20	2.06	6	2.08	13
21	2.02	18	2.02	9
22	2.00	14	1.99	13
23	1.94	5	1.92	12
24	1.82	17	1.84	8
25	1.59	3	1.60	5

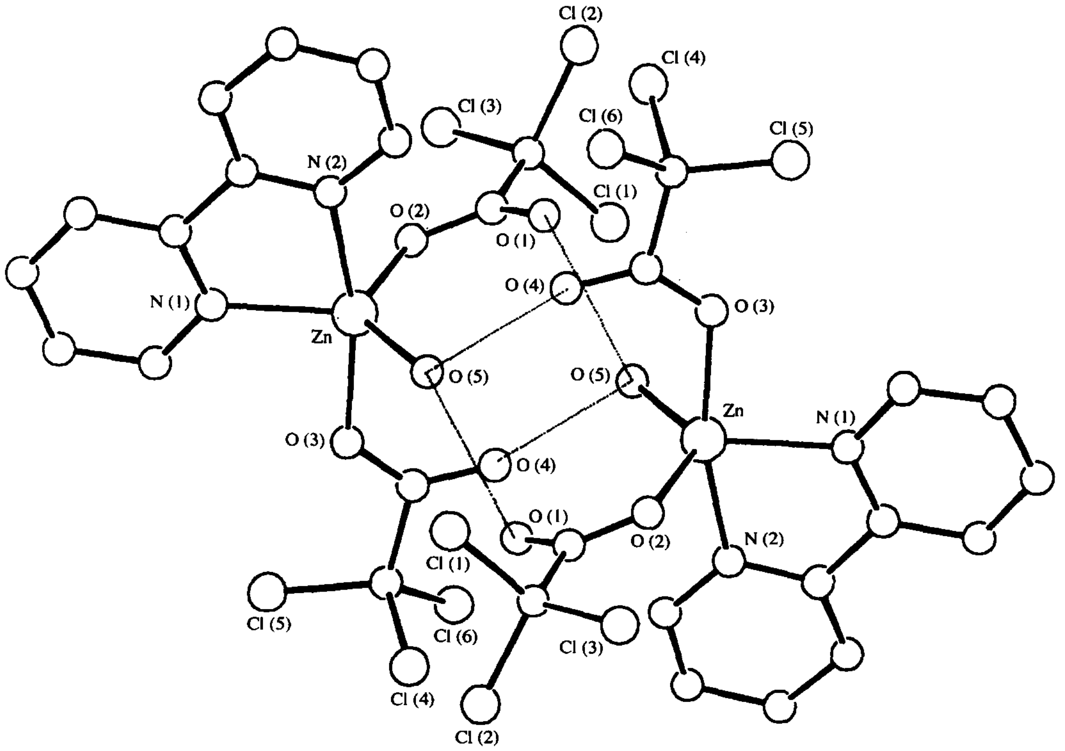

Fig. 3. A perspective view of the unit cell of **1**, hydrogen-bonding interactions shown by broken lines.

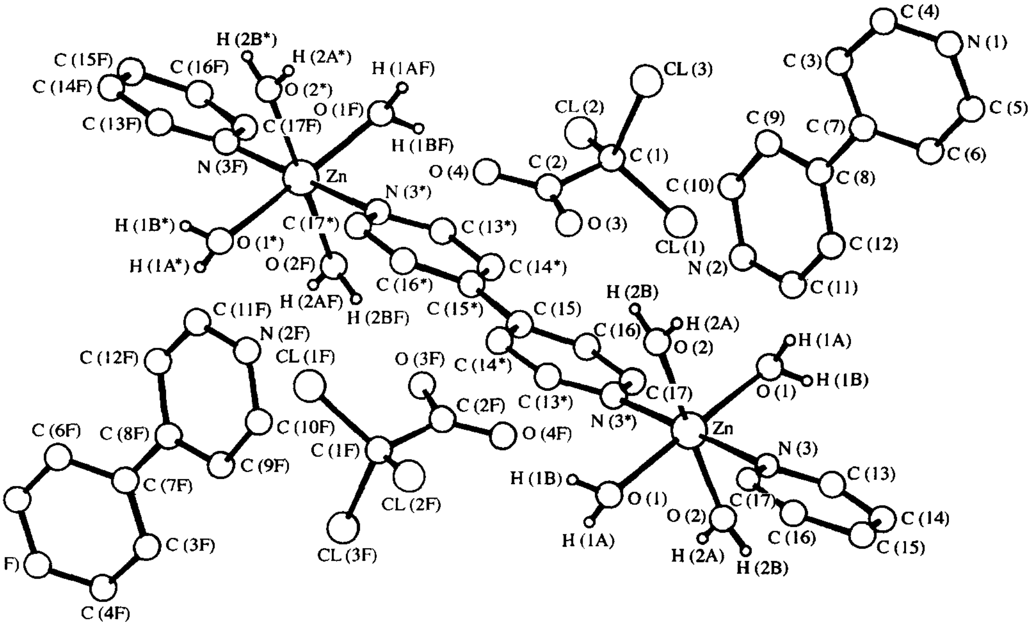

Fig. 4. ORTEP view of $[Zn(\mu\text{-}4,4'\text{-bipy})(4,4'\text{-bipy})_2(CCl_3CO_2)_2(H_2O)_4]_n$ (**2**), showing a segment of one infinite chain.

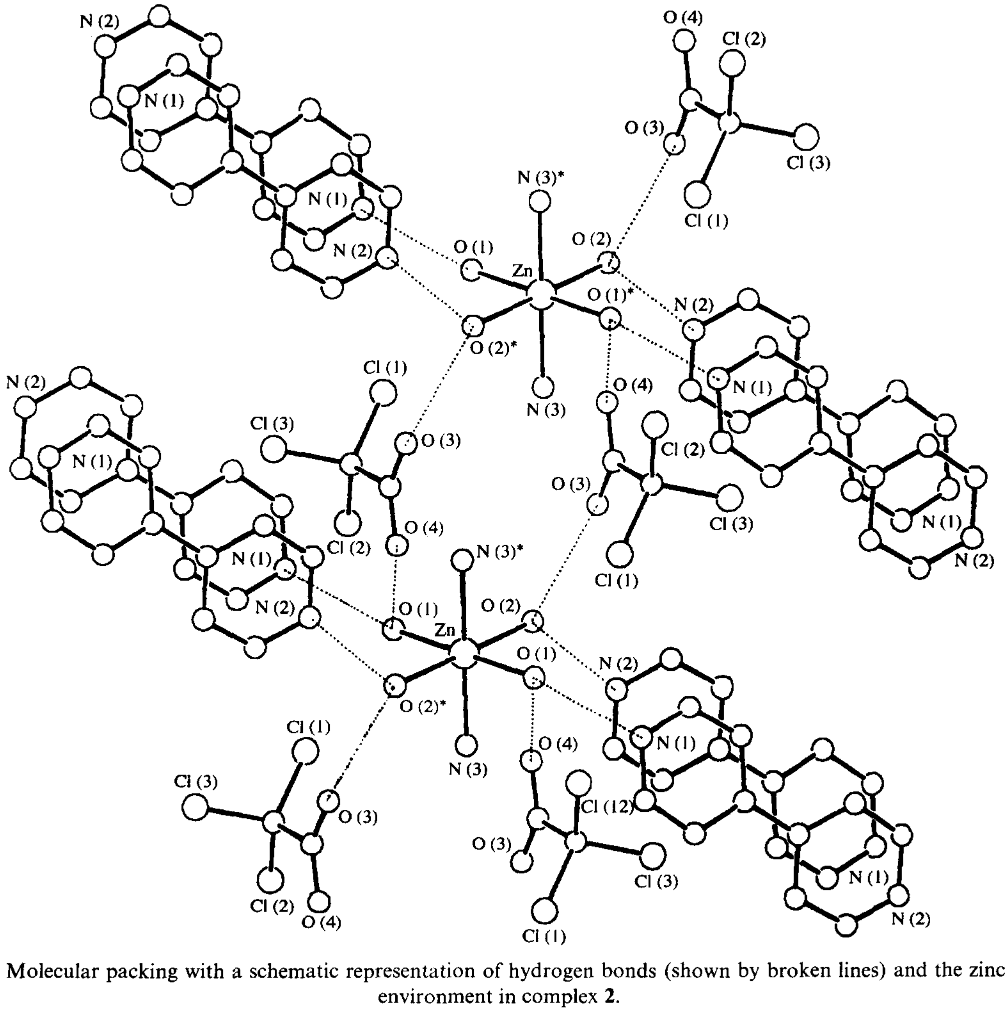

Fig. 5. Molecular packing with a schematic representation of hydrogen bonds (shown by broken lines) and the zinc atom environment in complex **2**.

Table 4. Selected bond distances (Å) and angles (°) for **2**

Zn—O(1)	2.112(2)	Zn—O(2)	2.172(2)
Zn—N(3)	2.109(2)		
O(1)···N(1)	2.788(3)	O(1)···N(3)	2.998(2)
O(1)···O(4)	2.702(3)	O(2)···O(3)	2.830(3)
N(3)—Zn—O(2)	90.8(1)	N(3)—Zn—O(1)	89.5(1)
O(2)—Zn—O(1)	87.7(1)		

their distances are less than the sum of van der Waals radii of nitrogen atom (1.55 Å) and oxygen atoms (1.5 Å) [20] (Fig. 5).

The Zn—O bond distances indicate that it has slightly tetragonally distorted octahedral geometry although it is involved in the polymeric chain. In the complex, packing is determined by a network of hydrogen bonds involving water molecules, coordinated and non-coordinated carboxyl oxygens and bipyridyl N atoms.

Nearly identical X-ray powder pattern of complexes **1** and **1a** indicate that they might have a similar pattern of bonding [16–19]. Complex **2** has octahedral coordination geometry around the Zn^{II} ion. Complexes having same ligands and trifluoroacetates of other metal ion(s) are still under investigation.

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