Co-ordination of Alkali Metals by Open-chain Polyethers in Transition Metal Complexes. Part 4.‡ Variation in Alkali-metal Ion Selectivity in Cobalt and Zinc Complexes of 1-(*o*-Carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethane (HL) and the *X*-Ray and Molecular Structure § of [Zn(NH₄L₂)₂]

David L. Hughes *† and Jonathan N. Wingfield
Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts AL5 2JQ

The syntheses of complexes of the title ligand $[Zn(ML_2)_2]$ (M = K, Rb, or NH₄) are described. The *X*-ray structure of $[Zn(NH_4L_2)_2]$ is compared with those of $[Co(ML_2)_2]$ (M = K or Rb), and the importance of the hydrogen-bonded dimer L_2 in the chemistry of HL is discussed. Subtle changes in M′ of $[M'(ML_2)_2]$ give large changes in the selective binding of the alkali metal M. Crystals of $[Zn(NH_4L_2)_2]$ are orthorhombic, space group *Pncb*, with $a = 14.046(7)$, $b = 14.577(5)$, $c = 16.691(11)$ Å, and $Z = 2$. The structure was refined to $R = 0.071$ for 1 595 reflections.

In recent papers, we have reported the chemistry of 1-(*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethane (HL)[1] (see Figure 1 of ref. 2) and discussed its ability to form hydrogen-bonded dimer pairs. These units are the building blocks of the acid salt KHL_2,[3] which is a step polymer; in the presence of cobalt(II) and M⁺ (M = K or Rb) ions, two such pairs generate discrete molecules of $[Co(ML_2)_2]$.[2,4] The dimer pairs are also found in the pseudo-cubane structure of NaL.[5]

The ready formation of the complex $[Co(KL_2)_2]$ from cobalt acetate hexahydrate, HL, and potassium bromide in ethanol, and the absence of any evidence for the production of the analogous sodium complex[4] has led to the idea that a range of transition-metal open-chain polyether complexes could be used selectively to complex alkali metal ions. Further work[6] has shown that, whereas potassium ions may be extracted as $[Co(KL_2)_2]$ into a methylene chloride solution of HL, no such extraction occurs for sodium or ammonium ions, and hence the same range of complexes may also be considered as highly selective ion-transport reagents.

In an attempt to vary the selectivities of the complexes, we have been studying alternatives to cobalt(II) for holding the open-chain polyethers in suitable positions for binding other cations. In this paper, we describe the chemistry of zinc in this role and report the crystal structure of $[Zn(NH_4L_2)_2]$.

Results

The reactions of zinc acetate and HL with potassium bromide or rubidium bromide give colourless crystalline products which have i.r. spectra very similar to those of $[Co(KL_2)_2]$ and $[Co(RbL_2)_2]$, and whose elemental analyses agree well with the formulations $[Zn(KL_2)_2]$ and $[Zn(RbL_2)_2]$. This is not unexpected, since zinc(II) prefers tetrahedral co-ordination, is an 'intermediate acid' like cobalt(II) on the Pearson scale of 'Hard and Soft Acids',[7] and is of comparable size to cobalt(II) (both having an ionic radius of 0.74 Å on the Pauling scale). It was therefore very surprising that the reaction of zinc acetate with HL and ammonium iodide in ethanol produced a colourless crystalline complex, whereas the analogous reaction with
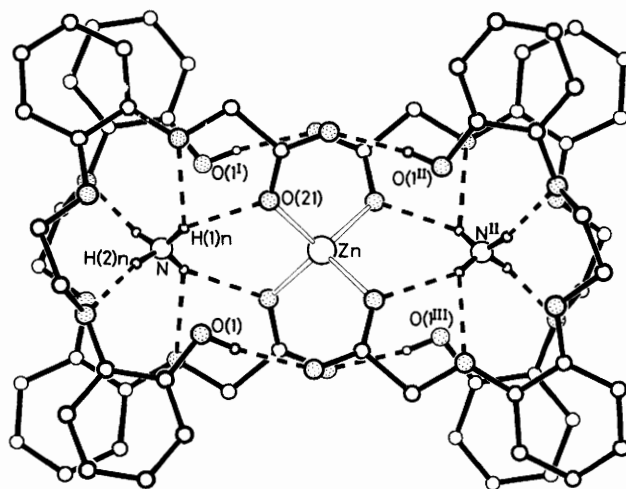
Figure 1. View of the complex molecule $[Zn(NH_4L_2)_2]$. Hydrogen bonds are represented by dashed lines. Roman superscripts represent positions related by symmetry to the atoms (with no superscript) at (x, y, z) of Table 3: I $-x$, $\frac{1}{2}-y$, z; II $-x$, y, $\frac{1}{2}-z$; III x, $\frac{1}{2}-y$, $\frac{1}{2}-z$. Ligand atoms are numbered as in Figure 1 of ref. 2

cobalt(II) not only gave no complex product, but also showed neither colour change to the characteristic blue of tetrahedral cobalt, nor any extraction of a complex into methylene chloride. Elemental analysis suggested that the zinc complex was $[Zn(NH_4L_2)_2]\cdot 2C_2H_5OH$, and a suitable crystal was selected for *X*-ray crystallographic study.

Description of the Structure.—The complex molecule $[Zn(NH_4L_2)_2]$ has a structure very similar to those of $[Co(ML_2)_2]$ (M = K or Rb).[2,4] In the Co complexes, a linear three-metal group M •••Co••• M is sandwiched by two approximately parallel ligand sheets; each sheet comprises an almost planar hydrogen-bonded L_2 dimer pair, the same as in the sodium salt NaL (where, however, the coplanarity has been lost) and similar to that found in the acid salt, KHL_2. In the zinc complex, the alkali-metal cation is replaced by the ammonium ion, but the view of the molecule normal to the ligand sheet planes (Figure 1) is very similar to those of the cobalt complexes.[2,4] The dimensions about the central metal ion, Co or Zn, are virtually identical in the three complexes (Table 1, and Table 2 of ref. 2). Examination of the torsion angles in the ligands L [Table 1(*c*), and Table 3 of ref. 2] shows the zinc

Table 1. Molecular dimensions with e.s.d.s in parentheses

(a) Bond lengths (Å)

Zn–O(21)	1.948(3)	O(1)–C(2)	1.356(6)	C(9)–C(10)	1.482(8)	C(17)–O(18)	1.365(6)
Zn···N	3.690(8)	C(2)–C(3)	1.366(7)	C(10)–O(11)	1.417(6)	O(18)–C(19)	1.416(6)
N···O(1)	2.916(5)	C(2)–C(7)	1.385(7)	O(11)–C(12)	1.360(6)	C(19)–C(20)	1.516(7)
N···O(8)	2.944(6)	C(3)–C(4)	1.379(8)	C(12)–C(13)	1.401(8)	C(20)–O(21)	1.267(6)
N···O(11)	2.976(6)	C(4)–C(5)	1.358(8)	C(12)–C(17)	1.382(7)	C(20)–O(22)	1.228(6)
N···O(18)	3.003(4)	C(5)–C(6)	1.388(8)	C(13)–C(14)	1.396(9)	O(1)s–C(2)s	1.434(19)
N···O(21)	2.904(7)	C(6)–C(7)	1.382(8)	C(14)–C(15)	1.364(8)	C(2)s–C(3)s	1.503(19)
N–H(1)n	0.839(25)	C(7)–O(8)	1.388(6)	C(15)–C(16)	1.379(8)	O(4)s–C(5)s	1.431(20)
N–H(2)n	0.863(26)	O(8)–C(9)	1.427(6)	C(16)–C(17)	1.398(7)	C(5)s–C(6)s	1.501(20)
O(1)–H(1)	0.849(28)						

(b) Valence angles (°)

O(21)–Zn–O(21ⁱ)	102.7(1)	C(4)–C(5)–C(6)	119.9(6)	C(13)–C(14)–C(15)	121.2(7)
O(21)–Zn–O(21ⁱⁱ)	118.3(1)	C(5)–C(6)–C(7)	119.5(6)	C(14)–C(15)–C(16)	120.4(6)
O(21)–Zn–O(21ⁱⁱⁱ)	107.8(1)	C(2)–C(7)–C(6)	120.5(5)	C(15)–C(16)–C(17)	119.7(6)
H(1)n–N–H(1ⁱ)n	102.4(46)	C(2)–C(7)–O(8)	119.7(5)	C(12)–C(17)–C(16)	120.0(5)
H(1)n–N–H(2)n	109.9(48)	C(6)–C(7)–O(8)	119.8(5)	C(12)–C(17)–O(18)	115.0(5)
H(1)n–N–H(2ⁱ)n	120.0(51)	C(7)–O(8)–C(9)	115.1(4)	C(16)–C(17)–O(18)	125.0(5)
H(2)n–N–H(2ⁱ)n	95.6(47)	O(8)–C(9)–C(10)	109.5(5)	C(17)–O(18)–C(19)	117.9(4)
H(1)–O(1)–C(2)	105.3(49)	C(9)–C(10)–O(11)	108.7(5)	O(18)–C(19)–C(20)	108.8(4)
O(1)–C(2)–C(3)	123.4(5)	C(10)–O(11)–C(12)	118.9(4)	C(19)–C(20)–O(21)	116.8(5)
O(1)–C(2)–C(7)	118.0(5)	O(11)–C(12)–C(13)	124.2(5)	C(19)–C(20)–O(22)	116.6(5)
C(3)–C(2)–C(7)	118.6(5)	O(11)–C(12)–C(17)	115.7(5)	O(21)–C(20)–O(22)	126.5(5)
C(2)–C(3)–C(4)	121.4(6)	C(13)–C(12)–C(17)	120.1(5)	O(1)s–C(2)s–C(3)s	110.0(19)
C(3)–C(4)–C(5)	120.1(6)	C(12)–C(13)–C(14)	118.5(6)	O(4)s–C(5)s–C(6)s	110.1(20)

(c) Selected torsion angles (°)

H(1)–O(1)–C(2)–C(7)	−169(4)	C(9)–C(10)–O(11)–C(12)	−172.6(5)	C(17)–O(18)–C(19)–C(20)	−178.1(4)
O(1)–C(2)–C(7)–O(8)	2.6(8)	C(10)–O(11)–C(12)–C(17)	176.7(5)	O(18)–C(19)–C(20)–O(21)	21.7(6)
C(2)–C(7)–O(8)–C(9)	−107.8(6)	O(11)–C(12)–C(17)–O(18)	1.5(7)	O(18)–C(19)–C(20)–O(22)	−161.3(5)
C(7)–O(8)–C(9)–C(10)	−178.6(4)	C(12)–C(17)–O(18)–C(19)	−168.9(5)	C(19)–C(20)–O(21)–Zn	146.5(4)
O(8)–C(9)–C(10)–O(11)	−65.5(6)				

Table 2. Hydrogen-bonding distances (Å) and angles (°) with e.s.d.s in parentheses *

	D···A	D–H	H···A	D–H···A
O(1)–H(1)···O(22ⁱⁱ)	2.726(6)	0.85(3)	1.88(4)	171(6)
N–H(1)n···O(18)	3.003(4)	0.84(3)	2.35(5)	135(4)
N–H(1)n···O(21)	2.904(7)	0.84(3)	2.13(5)	153(4)
N–H(2)n···O(8)	2.944(6)	0.86(3)	2.09(5)	169(5)
O(1)s···O(22ⁱⁱ)	3.08(3)			

* D is the donor atom in the hydrogen bond, *viz.* N or O; A is the acceptor O atom.

complex to resemble [Co(RbL₂)₂]; this similarity is extended in the Co···Rb *versus* Zn···N distances, and also in the O···O hydrogen-bond dimensions (Table 2), which are all slightly longer than in the Co–K complex. The most striking visual difference in these complexes are in the views along the line of the three 'metal' centres, Figure 2; the irregularities and slight deviations from coplanarity in the ligand sheets in the cobalt complexes are developed in the zinc complex (where the symmetry simplifies the view) into a 'twist' in the sheet.

It was noted in ref. 2 that molecules of the two cobalt complexes packed in almost identical sheets, forming the *a–b* plane in the potassium case and the *b–c* plane in the rubidium complex. The *b–c* plane of the zinc complex, shown in Figure 3, is virtually identical to those sheets. It is in the stacking of the sheets that we note distinctions in these crystals. In both cobalt complexes the adjacent sheets make good contacts, and the bulky phenyl rings of one sheet interlock either into the spaces (level with the cobalt atoms) of the complex molecules of the adjoining sheet, or into the gaps between the complex molecules. Hence, looking perpendicularly onto the sheets (as in
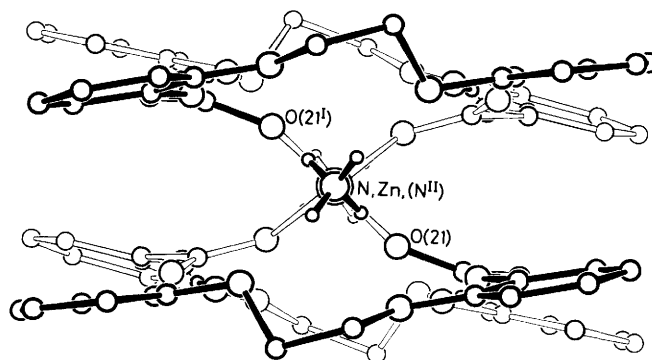
Figure 2. The complex molecule [Zn(NH₄L₂)₂] viewed along the N···Zn···Nᴵᴵ direction. The ligands with 'filled' bonds are the pair closer to the viewer. Hydrogen bonds have been omitted. This projection is similar to those of Figure 4 of ref. 2

Figure 3), one sheet is displaced about one quarter of the length (and about half the height) of a complex molecule from its neighbour. As we noted previously, the displacements (vertical in the arrangement of Figure 3) progress + − + − +*etc.* in successive sheets in the potassium complex, but + + + + +*etc.* in the rubidium crystal;² the horizontal displacement of the sheets in both crystals is + + + + +. We suggest that 'mistakes' in the crystal growing process might easily happen, and a displacement in the wrong direction would account for the preponderance of twinned crystals in both samples.

In the zinc sample, twinned crystals were not apparent. The sheets of packed molecules (Figure 3) line up with
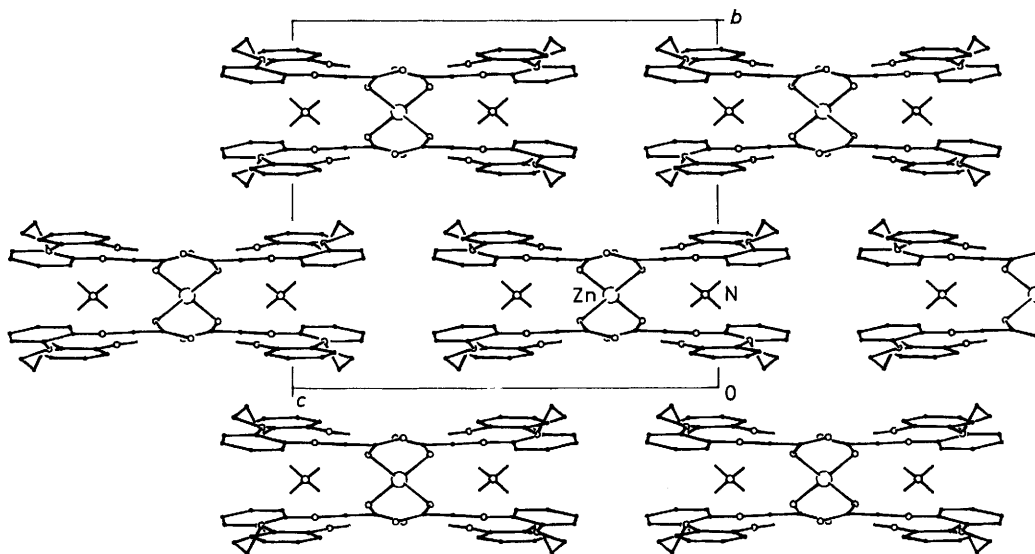
Figure 3. One sheet of $[Zn(NH_4L_2)_2]$ molecules, normal to the a axis. This view of the molecules compares with those of Figure 3 of ref. 2, and the packing arrangement within this sheet is common to the three complexes $[Co(KL_2)_2]$, $[Co(RbL_2)_2]$, and $[Zn(NH_4L_2)_2]$

no displacement between adjacent layers; thus, the only contacts between adjacent layers are edge-to-edge, phenyl-ring $\cdots$ phenyl-ring interactions. The gaps level with the Zn atoms of adjacent molecules contain the solvent molecules; the cavity associated with each complex molecule holds two solvent molecules, disordered over eight possible sites (some combinations of which, of course, are not possible). In one of the two unique sites, the ethanol O atom, O(1)s, hydrogen-bonds with the carbonyl oxygen of an L ligand (Table 2). Hydrogen bonding between the two solvent molecules is also feasible in several of the possible combinations.

Discussion

The structure of $[Zn(NH_4L_2)_2]$ shows many features common with those in $[Co(KL_2)_2]$ and $[Co(RbL_2)_2]$. For example, two strong phenolic to carbonyl hydrogen bonds joining two ligands L into a dimer unit are present in all three structures. Two such dimer units are held in position by tetrahedral co-ordination of the cobalt(II) or zinc(II) from the four carboxyl oxygens, one from each L, and this arrangement of ligands is such that two further cations (K^+, Rb^+, NH_4^+) are encapsulated to give a discrete molecular entity. The hydrogen-bonded dimer unit is an essential determinant of the chemistry of HL, also being present in the structures of NaL and KHL$_2$.

Co-ordination of alkali-metal ions by oxygen atoms of polyethers is by ion-dipole interaction, and there is no directionality of bonding except that imposed by packing of the oxygens round the spherical cation. The interaction of ammonium ions, however, is by hydrogen bonding from the positively charged hydrogen atoms of the ammonium ion to the oxygens of the polyether. Directionality of bonding is therefore imposed in this case, although the possibility of bifurcated hydrogen bonding allows some flexibility in the co-ordinated geometries adopted. The $[Zn(NH_4L_2)_2]$ structure shows the effect of directionality in the modification of the basic geometry adopted for spherical cations, as in $[Co(KL_2)_2]$ and $[Co(RbL_2)_2]$. The carboxyl oxygens of L, which are held in place by tetrahedral co-ordination to zinc(II), are, nevertheless, the most negatively charged oxygens of the ligands and, therefore, are expected to form the strongest bonds with the hydrogens of the ammonium ions. Since these oxygens are fixed, it is not possible to have a configuration where each of these

oxygens has a hydrogen atom from an ammonium ion pointing directly towards it. A compromise is found where two symmetry-related hydrogen atoms of the ammonium ion each form a bifurcated hydrogen bond involving the carboxyl oxygen O(21) and carboxymethoxy oxygen O(18) of one L ligand. The other two symmetry-related hydrogen atoms of the ammonium ion each point directly to the O(8) oxygen of symmetry-related ligands, giving a strong hydrogen bond (Figure 1). This hydrogen-bonding arrangement imparts a twist in the L_2 dimer unit so that the two monomer L units are each rotated by *ca.* 10° from the dimer mean plane; this differs from the almost planar configurations in $[Co(KL_2)_2]$ and $[Co(RbL_2)_2]$.

The comparison of $[Zn(NH_4L_2)_2]$, $[Co(KL_2)_2]$, and $[Co(RbL_2)_2]$ gives no explanation of the ease of formation of $[Zn(NH_4L_2)_2]$ against the failure to form the ammonium-cobalt analogue. The size and steric requirements of cobalt and zinc are very similar, and therefore, it is noteworthy that small differences in the two ions (perhaps in their electronegativities) bring about large changes in selectivity properties. It should, therefore, be possible, with small modifications of the central metal and/or the ligand system, to tailor-make complexes for selection of any required ion. Further investigations into this area will be highly rewarding.

The substitution of the alkali-metal ions or ammonium ion by a soft acid such as thallium has been attempted. However, co-ordination of thallium with the hard base oxygen does not appear to be sufficiently strong to form the analogous $[Zn(TlL_2)_2]$ or $[Co(TlL_2)_2]$, and only TlL has so far been isolated from their attempted syntheses. For these softer metals, it may be necessary to change the donor atoms of the ligands from oxygen to perhaps sulphur.

Experimental

Preparation of $[Zn(KL_2)_2]$.—(a) Zinc acetate dihydrate (0.11 g, 0.5 mmol) was dissolved in hot ethanol (30 cm³). The ligand HL (0.304 g, 1 mmol) and KL (0.342, 1 mmol) were added and the mixture refluxed for 16 h. A white precipitate was formed, which, after allowing the solution to cool to room temperature, was collected on a sinter, washed successively with small amounts of alcohol, water, and alcohol, and dried *in vacuo.* Yield 0.52 g, 77%; m.p. 247—252 °C.

(b) Zinc acetate dihydrate (0.11 g, 0.5 mmol) was dissolved in hot ethanol (30 cm³) and HL (0.304 g, 1 mmol) added. Reflux produced a clear solution. Finely ground potassium iodide (0.166 g, 1 mmol) was added and immediate reaction occurred, giving a white precipitate. Reflux was continued for 3 h, after which the precipitate was collected on a sinter, washed successively with alcohol, water, then alcohol, and dried in vacuo. Yield 0.33 g, 97%.

The i.r. spectra of the products obtained in (a) and (b) were identical (Found C, 56.7; H, 4.60. $C_{64}H_{60}K_2O_{24}Zn$ requires C, 56.65; H, 4.45%).

Preparation of [Zn(RbL₂)₂].—Zinc acetate dihydrate (0.11 g, 0.5 mmol) and HL (0.304 g, 1 mmol) were heated together in refluxing ethanol (30 cm³) to give a clear solution. Finely ground rubidium bromide (0.165 g, 1 mmol) was added and immediate reaction occurred; colourless crystals were deposited. These were collected on a sinter, washed successively with small amounts of alcohol, water, then alcohol, and dried in vacuo. Yield 0.26 g, 71.5%; m.p. 205—206 °C (Found: C, 52.6; H, 4.40. $C_{64}H_{60}O_{24}Rb_2Zn$ requires C, 53.05; H, 4.15%).

Preparation of [Zn(NH₄L₂)₂].—Zinc acetate dihydrate (0.11 g, 0.5 mmol) was dissolved in hot ethanol (30 cm³), and HL (0.304 g, 1 mmol) added. Ammonium iodide (0.145 g, 1 mmol), dissolved in hot ethanol (15 cm³), was added to give a clear solution. This was refluxed for 1 h; standing at room temperature produced colourless crystals. Recrystallisation from ethanol gave crystals suitable for X-ray analysis. Yield 0.24 g, 68%; m.p. 142—144 °C (goes opaque at ca. 115 °C) (Found: C, 57.95; H, 5.60; N, 2.00. $C_{68}H_{80}N_2O_{26}Zn$ requires C, 58.05; H, 5.75; N, 2.00%).

Attempted Preparation of [Co(NH₄L₂)₂].—Cobalt acetate tetrahydrate (0.125 g, 0.5 mmol) was dissolved in hot ethanol (50 cm³) and HL (0.304 g, 1 mmol) added. The hot pink-mauve solution was filtered, and the filtrate treated with ammonium iodide (0.145 g, 1 mmol) dissolved in hot ethanol (10 cm³) and refluxed for 2 h. No colour change was observed, and no precipitate was deposited on standing at room temperature. Potassium iodide (0.166 g, 1 mmol) in hot ethanol (20 cm³) was added and, during further reflux, the solution became dark blue. This solution was concentrated to 20 cm³ and, on standing at room temperature, blue crystals of [Co(KL₂)₂] were deposited. Yield 0.16 g, 47%; m.p. 243—245 °C.

Attempted Preparation of [Zn(TlL₂)₂].—Zinc acetate dihydrate (0.11 g, 0.5 mmol) dissolved in hot ethanol (30 cm³) was treated with HL (0.304 g, 1 mmol) to give a clear solution. Thallium(I) formate (0.248 g, 1 mmol) dissolved in hot ethanol (20 cm³) was added, and the mixture refluxed for 1 h to give a clear solution. Standing at room temperature gave a white solid which was collected on a sinter and washed successively with small quantities of water and ethanol. Yield 0.3 g, 59%; m.p. 190—192 °C. The i.r. spectrum of this product was identical with that of an authentic specimen of TlL·H₂O (m.p. 192 °C) (Found: C, 36.45; H, 3.40. $C_{16}H_{17}O_7Tl$ requires C, 36.55; H, 3.25%).

Crystal Structure Analysis.—Crystals are thick, clear, colourless plates with approximately rectangular faces. A small block-shaped crystal, ca. 0.2 × 0.15 × 0.12 mm, was mounted on a glass fibre and, after preliminary photographic examination (which suggested a monoclinic system), the crystal was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated Mo-K_α radiation), for determination of accurate cell parameters and measurement of diffraction intensities.

Table 3. Final atomic fractional co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Zn	0	2 500	2 500
N	0	2 500	289(5)
H(1)n	−345(36)	2 198(34)	604(26)
H(2)n	256(42)	2 138(35)	−58(28)
O(1)	1 410(3)	1 180(3)	851(2)
H(1)	1 644(47)	1 250(49)	1 316(23)
C(2)	2 168(4)	1 057(4)	360(3)
C(3)	3 074(4)	921(4)	632(4)
C(4)	3 824(4)	800(4)	110(4)
C(5)	3 673(5)	826(4)	−693(4)
C(6)	2 760(4)	961(4)	−988(4)
C(7)	2 013(4)	1 082(4)	−459(3)
O(8)	1 107(2)	1 266(2)	−750(2)
C(9)	625(4)	499(4)	−1 094(4)
C(10)	−317(4)	795(4)	−1 398(3)
O(11)	−887(2)	1 068(3)	−739(2)
C(12)	−1 820(4)	1 267(4)	−866(3)
C(13)	−2 254(4)	1 279(4)	−1 622(4)
C(14)	−3 221(5)	1 492(5)	−1 670(4)
C(15)	−3 741(4)	1 679(4)	−999(4)
C(16)	−3 316(4)	1 668(4)	−255(4)
C(17)	−2 343(4)	1 480(3)	−190(3)
O(18)	−1 840(2)	1 480(3)	510(2)
C(19)	−2 355(4)	1 529(4)	1 238(3)
C(20)	−1 656(4)	1 552(4)	1 929(3)
O(21)	−817(2)	1 814(2)	1 771(2)
O(22)	−1 972(3)	1 352(3)	2 593(2)

Solvent molecule 1: site occupancy 26.5%

O(1)s	4 125(18)	1 757(17)	2 397(15)
C(2)s	4 685(49)	1 141(40)	2 874(25)
C(3)s	5 454(34)	717(43)	2 370(40)

Solvent molecule 2: site occupancy 23.5%

O(4)s	4 841(23)	1 812(24)	3 308(21)
C(5)s	4 587(41)	1 181(49)	2 687(50)
C(6)s	5 343(45)	461(35)	2 599(46)

Crystal data.—$C_{64}H_{68}N_2O_{24}Zn\cdot2C_2H_6O$, $M = 1\,406.8$, orthorhombic, space group Pncb [symmetry positions: $\pm(x, y, z; -x, \frac{1}{2}-y, z; -x, y, \frac{1}{2}-z; x, \frac{1}{2}-y, \frac{1}{2}-z)$; equivalent to Pban, no. 50], $a = 14.046(7)$, $b = 14.577(5)$, $c = 16.691(11)$ Å, $U = 3\,417.4(29)$ Å³, $Z = 2$, $D_c = 1.367$ g cm⁻³, $F(000) = 1\,480$, $\mu(Mo-K_\alpha) = 4.5$ cm⁻¹, $\lambda(Mo-K_{\bar{\alpha}}) = 0.710\,69$ Å.

Intensities of reflections with indices hkl and $hk\bar{l}$ were measured and, after correction for Lorenz-polarisation effects, were averaged. Bayesian methods were applied to assure no negative net intensities.[8] 1 595 Unique reflections with $\theta_{max.} = 20°$ were entered into the SHELX system.[9]

In the space group Pncb, with eight equivalent general positions, and with an estimated 'reasonable' density, it was deduced, assuming a molecular structure analogous to that of [Co(KL₂)₂],[4] that the zinc atom must occupy a site of four-fold symmetry and was therefore located at $(0, \frac{1}{4}, \frac{1}{4})$ with 222 symmetry, the point of intersection of three two-fold symmetry axes. An electron-density map phased solely by the zinc atom contained much pseudo-symmetry, but the next map, phased by the zinc atom and an oxygen atom in a general position (a major peak in the first map), showed most of the molecular structure. The remainder of the non-hydrogen atoms, including the solvent molecules, were located in difference maps. Positions of most of the hydrogen atoms were calculated with idealised geometries; the phenolic and ammonium H atoms were identified in difference maps and refined with constrained O–H and N–H bond lengths and H–N–H angle.

There is one independent ligand L in the complex molecule; the others are related to it by the two-fold symmetry axes. Similarly, the two ammonium N atoms in the molecule lie on a two-fold axis and are related to each other by the two other symmetry axes.

The solvent molecule (one-half of C_2H_5OH per ligand L) is disordered, approximately equally, over two overlapping sites; the six sites for C and O atoms have been refined, with constraints on the C–C and C–O bond lengths, and the C–C–O angle. The site occupancies for the difference molecules have also been refined, one arrangement showing 26.5% occupancy, the other 23.5%.

Scattering factors were taken from ref. 10. The Zn, N, and O atoms (except in the solvent molecules) were allowed aniso-tropic thermal parameters; all C atoms and the solvent atoms were refined isotropically. The temperature factors of the hydrogen atoms in idealised positions were set to 'ride' on those of their neighbouring C atoms, but those of the phenolic and ammonium groups were refined independently and satisfactorily.

Refinement, by full-matrix least-squares methods, converged with $R = 0.071$ and $R' = 0.078$ for all 1 595 reflections; a weighting scheme set at $w = [\sigma(F)^2 + 0.003\ F^2]^{-1}$ gave a satisfactory variance analysis.

Atomic parameters are listed in Table 3, molecular di-mensions in Table 1, and hydrogen-bond dimensions in Table 2.

In addition to the SHELX system, the principal computer programs used in this structure analysis included the CAD4 data-processing program,[11] GEOM for molecular geometry calculations and preparation of tables,[12] and ORTEP for the diagrams.[13]

References
1 D. G. Parsons, M. R. Truter, and J. N. Wingfield, *Inorg. Chim. Acta,* 1981, **51**, 93.
2 D. L. Hughes and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.,* 1983, 915.
3 D. L. Hughes and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.,* 1984, 1187.
4 D. L. Hughes and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.,* 1982, 1239.
5 D. L. Hughes and J. N. Wingfield, *J. Chem. Soc., Chem. Commun.,* 1984, 408.
6 J. N. Wingfield, unpublished work.
7 R. G. Pearson, *Chem. Br.,* 1984, **3**, (3), 103.
8 S. French and K. Wilson, *Acta Crystallogr., Sect. A.,* 1978, **34**, 517.
9 G. M. Sheldrick, SHELX-76, A program for crystal structure determination, University of Cambridge, 1976.
10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.
11 CAD4 processing program, from M. B. Hursthouse, Queen Mary College, London, 1976.
12 J. D. Owen, GEOM, Suite of crystallographic programs for the Prime computer, Rothamsted Experimental Station, Harpenden, 1981.
13 C. K. Johnson, ORTEP-II, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, U.S.A., revised 1971.