Metal–Phenoxyalkanoic Acid Interactions. Part 28.[1] Crystal and Molecular Structures of the Sodium, Ammonium, and Magnesium Complexes of (*o*-Phenylenedioxy)diacetic Acid†

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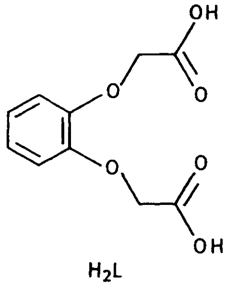
The crystal structures of three compounds involving (*o*-phenylenedioxy)diacetic acid (H_2L) and sodium, ammonium, and magnesium ions have been determined by *X*-ray diffraction. $[\{Na_4L_2(H_2O)_8\}_n]$ (**5**) is triclinic, with $a = 7.206(1)$, $b = 14.306(5)$, $c = 14.545(4)$ Å, $\alpha = 101.86(2)$, $\beta = 92.19(2)$, $\gamma = 90.32(2)°$, $Z = 2$, and space group $P\bar{1}$. Ionic $[NH_4]_2[L]$ (**6**) is orthorhombic, with $a = 11.833(3)$, $b = 9.199(2)$, $c = 10.932(1)$ Å, $Z = 4$, and space group *Pbcn*. $[MgL(H_2O)_3]\cdot 4H_2O$ (**7**) is monoclinic, with $a = 29.17(1)$, $b = 6.758(2)$, $c = 17.347(8)$ Å, $\beta = 108.99(3)°$, $Z = 8$, and space group *C*2/*c*. (**5**), (**6**), and (**7**) were refined to residuals 0.044, 0.033, and 0.071 for 3 034, 1 024, and 1 448 observed reflections respectively. Complex (**5**) has a polymeric structure comprising four independent and different sodium centres, one five-, two six-, and one seven-co-ordinate. Each planar L^{2-} ligand is bonded to a sodium ion *via* its four 'inner' oxygen donor atoms, with two waters in the axial sites of a pentagonal bipyramid. However, in one case the fifth pentagonal planar site is occupied by a bridging water molecule while for the other there is no water in this site. One of the axial waters in each also forms bridges to the third and fourth sodiums, together with a carboxyl oxygen of each acid ligand. The co-ordination about these two sodium ions is completed by the remaining water ligands, including two which bridge the centres and another which forms a polymer link. Stereochemistry is distorted octahedral in one, distorted square pyramidal in the other, with a Na–O range and mean of 2.304(2)—2.693(4) Å and 2.420(2) Å respectively. In contrast, complex (**6**) is discretely ionic with the ammonium ion located outside the ionophore cavity of L^{2-} but hydrogen bonded to the carboxylate oxygens (2.89—3.13 Å). Complex (**7**) is isostructural and isomorphous with the zinc(II) and cobalt(II) complexes of L^{2-}. It is monomeric with pentagonal-bipyramidal stereochemistry about Mg, comprising unequal bonds to the four 'inner' oxygens of the ligand [Mg–O(ether) (mean) 2.417(5) Å, Mg–O(carboxylate) (mean) 2.126(5) Å] and three to water molecules [two axial, 2.048(6) Å (mean); one equatorial, 2.052(5) Å].

Unlike the substituted monocarboxylic acids such as (2,4-dichlorophenoxy)acetic acid and (2,4,5-trichlorophenoxy)acetic acid, the bifunctional phenoxyalkanoic acid (*o*-phenylenedioxy)diacetic acid (H_2L) shows no herbicidal activity. However, it does possess the ability to form chelate complexes. In this respect, it is analogous to the complexone ethylenediaminetetra-acetic acid but stability constants with divalent metal ions are considerably smaller.[2] This may be attributed to the lack of flexibility in the two oxyacetate side chains which, without exception, remain essentially coplanar with the benzene ring in all known complexes.[3–6] The tendency is for the quadridentate ligand system involving the 'inner' four oxygens to force a stereochemistry upon the metal ion, based on a pentagonal plane.



H_2L

In the case of the complex adduct $K(HL)(H_2L)$, the co-ordination about K is pentagonal antiprismatic,[3] while the stereochemistry about La in the complex $Na[LaL_2(H_2O)_2]$, is best described as *s*-capped square antiprismatic.[4] On the other hand, lithium forms centrosymmetric dimers with tetrahedral bis-$[Li(H_2O)_2]^+$-bridged $[LiL(H_2O)]^-$ centres, (**1**). These centres have distorted square-pyramidal geometry with a water in the axial position and bridges through both carboxylate oxygens.[5] The divalent metal ions Ca and Mn give isomorphous complexes $[\{ML(H_2O)_2\}_n]\cdot nH_2O$ (**2**) with an additional water in the second axial position of a pentagonal bipyramid and a single bridge through a carboxyl group.[6] In contrast, $[ZnL(H_2O)_3]\cdot 3.5H_2O$ (and its Co^{II} isomorph), (**3**), are monomeric with the bridging position of the Ca or Mn in the Type 2 polymer replaced by a water ligand.[6] Nickel(II) alone gives a monomeric complex $[Ni(HL)_2(H_2O)_4]\cdot H_2O$ (**4**) in which the ligand is monoprotonated and unidentate.[6]

This work reports the interaction of Na^+, $NH_4{}^+$, and Mg^{2+} ions with H_2L and the crystal structures of the products

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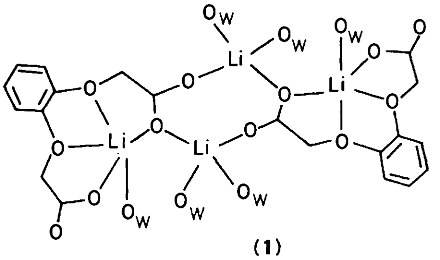
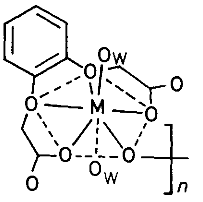
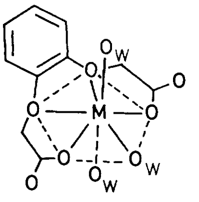
† *Supplementary data available* (No. SUP 56717, 5 pp.): infrared spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



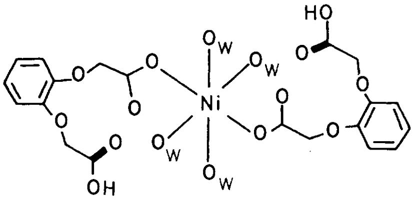
(1)



(2) M = Ca or Mn



(3) M = Co or Zn



(4)

[$\{Na_4L_2(H_2O)_8\}_n$] (**5**), [$NH_4]_2[L$] (**6**), and [$MgL(H_2O)_3$]·$4H_2O$ (**7**).

Experimental

Preparation of Complexes.—Both [$\{Na_4L_2(H_2O)_8\}_n$] (**5**) and [$NH_4]_2[L$] (**6**) were prepared by titrating to the phenolphthalein end point, 50% aqueous ethanolic solutions of (*o*-phenylenedioxy)diacetic acid (H_2L) with either 1 mol dm^{-3} NaOH or 1 mol dm^{-3} ammonia solutions. Complex [MgL($H_2O)_3$]·$4H_2O$ (**7**) was prepared by mixing at *ca.* 80 °C an aqueous ethanolic solution of H_2L with an excess of magnesium carbonate.[7] The unreacted excess was filtered off and colourless prismatic crystals were obtained after partial room temperature evaporation of the filtrate. Complex (**5**) was found to lose crystallinity and to degenerate over several weeks to a white powder, presumably due to loss of water. [Analysis: Found for (**5**): C, 34.0; H, 4.7. Calc. for $C_{20}H_{32}Na_4O_{20}$: C, 35.1; H, 4.7%. Found for (**6**): 46.2; H, 6.3; N, 10.7. Calc. for $C_{10}H_{16}N_2O_6$: C, 46.1, H, 6.2; N, 10.8%. Found for (**7**): C, 32.0; H, 5.6. Calc. for $C_{10}H_{22}MgO_{13}$: C, 32.1; H, 5.9%.]

Infrared spectra were recorded on a Jasco IR-810 spectrophotometer as Nujol mulls on KBr discs.

Crystal-structure Determinations.—Single-crystal *X*-ray preliminaries were completed on an Enraf-Nonius Weissenberg goniometer using nickel-filtered Cu-K_α radiation. Unique intensity data sets were collected on a Nicolet *R*3*m* four-circle diffractometer at 20 °C using graphite-monochromated Mo-K_α radiation and were corrected for Lorentz and polarization effects but not for absorption.

Crystal data for (**5**). $C_{20}H_{32}Na_4O_{20}$, M = 684.4, triclinic, a = 7.206(1), b = 14.306(5), c = 14.545(4) Å, α = 101.86(2), β = 92.19(2), γ = 90.32(2)°, U = 1 466.2(6) Å^3, D_m = 1.55, D_c = 1.549 g cm^{-3}, Z = 2, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 2.0 cm^{-1}, F(000) = 712, space group $P\bar{1}$ (C_i^1, no. 2), T = 293 K.

Crystal data for (**6**). $C_{10}H_{16}N_2O_6$, M = 260.2, orthorhombic, a = 11.833(3), b = 9.199(2), c = 10.932(1) Å, U = 1 190.0(5) Å^3, D_m = 1.46, D_c = 1.452 g cm^{-3}, Z = 4, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 1.3 cm^{-1}, F(000) = 552, space group *Pbcn* (D_{2h}^{11}, no. 60), T = 293 K.

Crystal data for (**7**). $C_{10}H_{22}MgO_{13}$, M = 374.6, monoclinic, a = 29.17(1), b = 6.758(2), c = 17.347(8) Å, β = 108.99(3)°, U = 3 234(2) Å^3, D_m = 1.51, D_c = 1.538 g cm^{-3}, Z = 8, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 1.9 cm^{-1}, F(000) = 1 584, space group $C2/c$ (C_{2h}^6, no. 15), T = 293 K.

Structure solution and refinement. 3 034 (**5**), 1 024 (**6**), and 1 448 (**7**) unique reflections with $I > 2.5\sigma(I)$ were considered observed out of 4 606, 1 238, and 1 448 respectively collected in unique sets [$2\theta_{max.}$ = 48, 55, and 45° for (**5**), (**6**), and (**7**)]. Crystal sizes: 0.40 × 0.20 × 0.10 mm, (**5**), 0.30 × 0.24 × 0.20 mm, (**6**), and 0.35 × 0.25 × 0.08 mm, (**7**). The structure of (**5**) could not be solved using the conventional direct methods approach of SHELX 76[8] but was solved using the SHELXS 86[9] structure solution package. The structure of (**6**) was solved by SHELX 76[8] direct methods while (**7**) was solved by Fourier methods after insertion of the basic co-ordinate set for the isomorphous zinc structure.[6] Refinement was by blocked-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms with the exception of four lattice water molecules in (**7**), which were found to be disordered and were refined isotropically with the appropriate occupancy factors. Hydrogen atoms were located by difference methods and were included in subsequent refinements at fixed positions with their isotropic U values set invariant at 0.05 Å^2 [(**5**) and (**7**)] or refined [(**6**)]. Final residuals ($R = \Sigma||F_o| - |F_c||/|F_o|$) and weighted residuals [$R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o{}^2|)^{\frac{1}{2}}$] were 0.044, 0.043 (**5**); 0.033, 0.034 (**6**); 0.071 (**7**) (unit weights). The values used in the weighting scheme, $w = A/(\sigma^2F_o + BF_o{}^2)$, were A = 1.6, B = 1.9 × 10^{-4} [(**5**)] and A = 2.5, B = 1.0 × 10^{-4} [(**6**)]. No corrections were made for absorption or extinction. Neutral-atom scattering factors were used[10] while f', f'' terms for anomalous dispersion were taken from ref. 10. The maximum residual peak in the difference map for (**7**) was 0.9 e Å^{-3}.

Final atomic positional parameters are listed in Table 1 while interatomic distances and angles about the co-ordination spheres for complexes (**5**) and (**7**) are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, remaining bond distances and angles.

Discussion

[$\{Na_4L_2(H_2O)_8\}_n$] (**5**).—The polymeric structure of (**5**) comprises a basic [$Na_4L_2(H_2O)_8$] repeating unit. Each L^{2-} anion and its sodium cation forms a complex unit with a stereochemistry based on a pentagonal bipyramid. However, one sodium [Na(2)] is seven-co-ordinate while the other [Na(4)] is six-co-ordinate. Both have four co-ordination positions occupied by the 'inner' donor oxygens of the L^{2-} ligand. For Na(2), Na–O distances are 2.447(3), 2.490(3) Å (to 'ether' oxygens) and 2.345(3), 2.376(3) Å (to 'carboxyl' oxygens). For Na(4), the equivalent distances are 2.429(3), 2.410(3) Å and 2.346(3), 2.339(3) Å respectively. The remaining three positions for Na(2) are occupied by water molecules [Na–O, 2.379(3)—2.693(4) Å] of which two [one axial, $O_w(3')$, and one in the pentagonal plane, $O_w(6)$] form bridges to the third sodium centre [Na(3)]. The seventh water occupies the other site of the pentagonal bipyramid. In contrast, Na(4) has only one bridging water [$O_w(1)$; Na–O 2.345(3) Å] with the fifth site of the

Table 1. Atomic co-ordinates (× 10^4) for [$\{Na_4L_2(H_2O)_8\}_n$] (**5**), $[NH_4]_2[L]$ (**6**), and $[MgL(H_2O)_3]\cdot4H_2O$ (**7**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*a*) Compound (**5**)							
Na(1)	8 162(2)	7 403(1)	4 622(1)	O_w(3)	8 371(3)	7 750(2)	6 293(2)
Na(2)	110(2)	9 211(1)	6 667(1)	O_w(4)	10 735(3)	6 414(2)	4 818(2)
Na(3)	3 200(2)	7 586(1)	4 896(1)	O_w(5)	5 670(4)	6 320(2)	4 877(2)
Na(4)	4 871(2)	5 825(1)	2 963(1)	O_w(6)	691(4)	8 898(2)	4 811(2)
O_w(1)	3 281(3)	7 276(2)	3 223(2)	O_w(7)	6 620(3)	4 656(2)	3 638(2)
O_w(2)	1 267(3)	10 805(2)	6 887(2)	O_w(8)	5 801(3)	8 618(2)	4 792(2)
		ligand A				ligand B	
C(1)	117(5)	8 638(2)	8 846(2)	C(1)	6 375(5)	4 580(2)	918(2)
C(2)	−1 462(5)	9 216(2)	8 854(2)	C(2)	4 769(5)	4 062(2)	1 025(2)
C(3)	−2 505(5)	9 403(3)	9 643(3)	C(3)	4 243(5)	3 266(2)	360(2)
C(4)	−2 005(5)	9 029(3)	10 431(3)	C(4)	5 282(5)	2 988(3)	−441(2)
C(5)	−485(5)	8 437(3)	10 409(2)	C(5)	6 845(5)	3 498(3)	−559(2)
C(6)	581(5)	8 246(2)	9 618(2)	C(6)	7 407(5)	4 299(2)	127(2)
O(71)	1 115(3)	8 532(2)	8 047(1)	O(71)	6 781(3)	5 362(2)	1 624(2)
C(81)	2 665(5)	7 908(2)	7 971(2)	C(81)	8 393(4)	5 919(2)	1 538(2)
C(91)	3 498(5)	7 838(2)	7 015(2)	C(91)	8 592(5)	6 751(2)	2 387(2)
O(101)	2 864(3)	8 338(2)	6 470(2)	O(101)	7 516(3)	6 800(2)	3 047(2)
O(111)	4 804(3)	7 249(2)	6 845(2)	O(111)	9 877(3)	7 329(2)	2 333(2)
O(72)	−1 811(3)	9 550(2)	8 044(1)	O(72)	3 800(3)	4 426(2)	1 815(2)
C(82)	−3 394(5)	10 135(2)	8 011(2)	C(82)	2 241(5)	3 888(2)	2 017(2)
C(92)	−3 671(5)	10 352(2)	7 028(3)	C(92)	1 448(5)	4 372(3)	2 935(3)
O(102)	−2 737(3)	9 945(2)	6 369(2)	O(102)	2 081(4)	5 164(2)	3 335(2)
O(112)	−4 934(3)	10 960(2)	6 984(2)	O(112)	142(3)	3 927(2)	3 214(2)
(*b*) Compound (**6**)							
C(1)	380(1)	4 822(1)	7 007(1)	C(9)	1 615(1)	1 827(2)	5 217(1)
C(2)	753(1)	6 129(2)	6 530(1)	O(10)	1 100(1)	850(1)	5 793(1)
C(3)	374(1)	7 432(2)	7 021(1)	O(11)	2 264(1)	1 617(1)	4 322(1)
O(7)	679(1)	3 468(1)	6 582(1)	N(1)	3 673(1)	3 904(1)	3 451(1)
C(8)	1 477(1)	3 406(1)	5 610(1)				
(*c*) Compound (**7**)							
Mg	1 030(1)	6 886(3)	5 148(1)	O_w(5)	1 041(2)	7 801(9)	7 593(3)
O_w(1)	1 056(2)	5 637(7)	6 240(3)	$O_w(6)^{a,b}$	0	3 718(39)	−2 500
O_w(2)	1 097(2)	8 488(7)	4 201(3)	$O_w(7)^{b,c}$	499(4)	2 572(16)	−2 328(6)
O_w(3)	328(2)	6 106(7)	4 485(3)	$O_w(8)^{b,c}$	468(4)	1 291(19)	−2 379(7)
O_w(4)	150(2)	2 113(8)	4 035(3)	$O_w(9)^{b,c}$	247(6)	6 628(27)	−2 400(9)
C(1)	2 263(3)	7 346(9)	5 993(4)	C(91)	1 551(3)	3 417(10)	4 684(4)
C(2)	2 084(2)	8 985(10)	6 295(4)	O(101)	1 159(2)	4 108(7)	4 706(3)
C(3)	2 401(3)	10 297(10)	6 837(4)	O(111)	1 609(2)	1 878(7)	4 308(3)
C(4)	2 899(3)	9 934(11)	7 040(4)	O(72)	1 582(2)	9 184(6)	6 032(3)
C(5)	3 065(3)	8 312(12)	6 729(4)	C(82)	1 376(2)	10 804(9)	6 338(4)
C(6)	2 751(3)	7 023(10)	6 191(4)	C(92)	840(2)	10 706(10)	5 946(4)
O(71)	1 892(2)	6 201(7)	5 493(3)	O(102)	655(2)	9 310(6)	5 472(3)
C(81)	2 024(3)	4 431(9)	5 159(4)	O(112)	602(2)	12 096(6)	6 129(3)

[a] Site occupancy factor = 0.25. [b] Isotropic thermal parameter. [c] Site occupancy factor = 0.50.

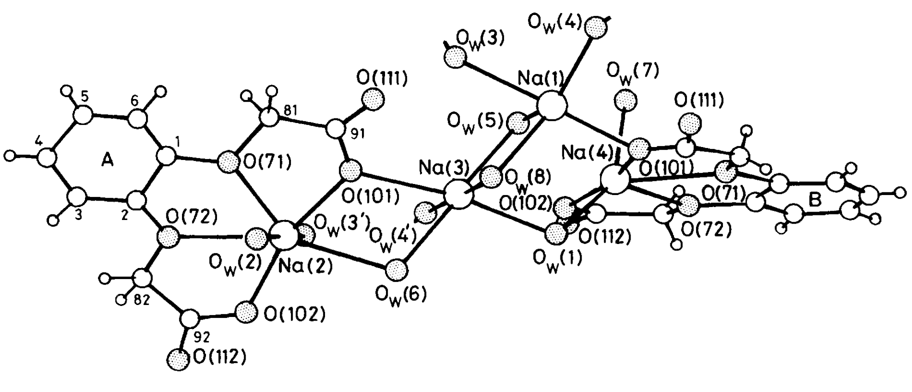


Figure 1. Molecular configuration and atom numbering scheme for [$\{Na_4L_2(H_2O)_8\}_n$] (**5**)

Table 2. Bond distances (Å) and angles (°) about the co-ordination spheres for complexes (**5**) and (**7**)

(*a*) $[\{Na_4L_2(H_2O)_8\}_n]$ (**5**)

Na(1)–O_w(3)	2.379(3)	Na(3)–O_w(1)	2.385(3)	Na(2)–O(71A)	2.490(3)	Na(4)–O(71B)	2.410(3)
Na(1)–O_w(4)	2.383(3)	Na(3)–O_w(5)	2.544(3)	Na(2)–O(72A)	2.447(3)	Na(4)–O(72B)	2.429(3)
Na(1)–O_w(5)	2.454(3)	Na(3)–O_w(6)	2.630(3)	Na(2)–O(101A)	2.345(3)	Na(4)–O(101B)	2.339(3)
Na(1)–O_w(8)	2.421(3)	Na(3)–O_w(8)	2.407(3)	Na(2)–O(102A)	2.376(3)	Na(4)–O(102B)	2.346(3)
Na(1)–O(101B)	2.304(2)	Na(3)–O_w(4′)	2.419(3)	Na(2)–O_w(2)	2.379(3)	Na(4)–O_w(1)	2.345(3)
		Na(3)–O(101A)	2.344(3)	Na(2)–O_w(6)	2.693(4)	Na(4)–O_w(7)	2.441(3)
				Na(2)–O_w(3′)	2.384(2)		

O_w(3)–Na(1)–O_w(4)	82.2(1)	O_w(1)–Na(3)–O_w(5)	87.7(1)	Na(1)–O_w(3)–Na(2*)	103.5(1)	O_w(6)–Na(3)–O_w(4′)	150.3(1)
O_w(3)–Na(1)–O_w(5)	82.4(1)	O_w(1)–Na(3)–O_w(6)	88.9(1)	Na(1)–O_w(4)–Na(3*)	98.6(1)	O_w(6)–Na(3)–O(101A)	76.0(1)
O_w(3)–Na(1)–O_w(8)	85.3(1)	O_w(1)–Na(3)–O_w(8)	82.8(1)	Na(1)–O_w(5)–Na(3)	92.7(1)	O_w(8)–Na(3)–O_w(4′)	172.5(1)
O_w(3)–Na(1)–O(101B)	167.2(1)	O_w(1)–Na(3)–O_w(4′)	91.0(1)	Na(1)–O_w(8)–Na(3)	97.0(1)	O_w(8)–Na(3)–O(101A)	90.5(1)
O_w(4)–Na(1)–O_w(5)	98.2(1)	O_w(1)–Na(3)–O_w(101A)	163.0(1)	Na(1)–O(101B)–Na(4)	106.3(1)	O_w(4′)–Na(3)–O(101A)	96.1(1)
O_w(4)–Na(1)–O_w(8)	166.2(1)	O_w(5)–Na(3)–O_w(6)	176.6(1)	Na(1)–O(101B)–C(91B)	127.5(2)	Na(3)–O_w(1)–Na(4)	99.8(1)
O_w(4)–Na(1)–O(101B)	97.7(1)	O_w(5)–Na(3)–O_w(8)	84.0(1)	O(71A)–Na(2)–O(72A)	62.7(1)	Na(3)–O_w(6)–Na(2)	93.4(1)
O_w(5)–Na(1)–O_w(8)	85.7(1)	O_w(5)–Na(3)–O_w(4′)	91.5(1)	O(71A)–Na(2)–O(101A)	65.9(1)	Na(3)–O(101A)–Na(2)	111.5(1)
O_w(5)–Na(1)–O(101B)	85.0(1)	O_w(5)–Na(3)–O_w(101A)	107.1(1)	O(71A)–Na(2)–O(102A)	129.2(1)	Na(3)–O(101A)–C(91A)	111.2(1)
O_w(8)–Na(1)–O(101B)	95.8(1)	O_w(6)–Na(3)–O_w(8)	94.6(1)				

O(71A)–Na(2)–O_w(2)	109.0(1)	O(71B)–Na(4)–O(72B)	64.4(1)	O(101A)–Na(2)–O_w(3′)	89.4(1)	O(101B)–Na(4)–O_w(7)	91.2(1)
O(71A)–Na(2)–O_w(6)	138.1(1)	O(71B)–Na(4)–O(101B)	67.4(1)	O(102A)–Na(2)–O_w(2)	82.5(1)	O(102B)–Na(4)–O_w(1)	85.2(1)
O(71A)–Na(2)–O_w(3′)	81.3(1)	O(71B)–Na(4)–O(102B)	130.6(1)	O(102A)–Na(2)–O_w(6)	88.5(1)	O(102B)–Na(4)–O_w(7)	90.0(1)
O(72A)–Na(2)–O(101A)	128.4(1)	O(71B)–Na(4)–O_w(1)	121.3(1)	O(102A)–Na(2)–O_w(3′)	85.3(1)	O_w(1)–Na(4)–O_w(7)	147.6(1)
O(72A)–Na(2)–O(102A)	67.3(1)	O(71B)–Na(4)–O_w(7)	85.6(1)	O_w(2)–Na(2)–O_w(6)	91.5(1)	Na(4)–O(101B)–C(91B)	123.2(2)
O(72A)–Na(2)–O_w(2)	94.0(1)	O(72B)–Na(4)–O(101B)	131.8(1)	O_w(2)–Na(2)–O_w(3′)	167.4(1)	Na(4)–O(102B)–C(92B)	124.3(2)
O(72A)–Na(2)–O_w(6)	154.2(1)	O(72B)–Na(4)–O(102B)	66.2(1)	O_w(6)–Na(2)–O_w(3′)	85.1(1)	Na(4)–O(71B)–C(81B)	119.7(2)
O(72A)–Na(2)–O_w(3′)	84.1(1)	O(72B)–Na(4)–O_w(1)	123.0(1)	Na(4)–O(71B)–C(1B)	122.7(2)	Na(4)–O(72B)–C(82B)	119.2(2)
O(101A)–Na(2)–O(102A)	162.8(1)	O(72B)–Na(4)–O_w(7)	83.4(1)	Na(4)–O(72B)–C(2B)	122.3(2)	Na(2)–O(101A)–C(91A)	125.2(2)
O(101A)–Na(2)–O_w(2)	101.4(1)	O(101B)–Na(4)–O(102B)	162.0(1)	Na(2)–O(102A)–C(92A)	120.5(2)	Na(2)–O(71A)–C(1A)	122.8(2)
O(101A)–Na(2)–O_w(6)	74.8(1)	O(101B)–Na(4)–O_w(1)	84.1(1)	Na(2)–O(71A)–C(81A)	119.1(2)	Na(2)–O(72A)–C(82A)	118.1(2)
				Na(2)–O(72A)–C(2A)	120.4(2)		

(*b*) $[MgL(H_2O)_3]\cdot 4H_2O$ (**7**)

Mg–O(71)	2.435(5)	Mg–O(101)	2.108(5)	Mg–O_w(1)	2.064(5)	Mg–O_w(3)	2.052(5)
Mg–O(72)	2.398(4)	Mg–O(102)	2.144(5)	Mg–O_w(2)	2.031(6)		

O(71)–Mg–O(72)	62.6(2)	O(101)–Mg–O_w(3)	80.3(2)	O(72)–Mg–O(102)	68.3(2)	Mg–O(101)–C(91)	128.2(4)
O(71)–Mg–O(101)	68.1(2)	O(102)–Mg–O_w(1)	86.6(2)	O(72)–Mg–O_w(1)	82.0(2)	Mg–O(102)–C(92)	126.8(4)
O(71)–Mg–O(102)	131.0(2)	O(102)–Mg–O_w(2)	89.8(2)	O(72)–Mg–O_w(2)	87.1(2)	Mg–O(71)–C(81)	116.8(4)
O(71)–Mg–O_w(1)	88.3(2)	O(102)–Mg–O_w(3)	81.0(2)	O(72)–Mg–O_w(3)	149.3(2)	Mg–O(71)–C(1)	125.7(4)
O(71)–Mg–O_w(2)	86.3(2)	O_w(1)–Mg–O_w(2)	169.1(2)	O(101)–Mg–O(102)	160.5(2)	Mg–O(72)–C(82)	117.3(4)
O(71)–Mg–O_w(3)	147.9(2)	O_w(1)–Mg–O_w(3)	98.1(2)	O(101)–Mg–O_w(1)	90.7(2)	Mg–O(72)–C(2)	124.3(4)
O(72)–Mg–O(101)	130.3(2)	O_w(2)–Mg–O_w(3)	91.4(2)	O(101)–Mg–O_w(2)	96.0(2)		

(*) 1 + *x*, *y*, *z*. (′) −1 + *x*, *y*, *z*.

pentagonal plane [occupied with Na(2) by O_w(6)] vacant. The bridge links Na(4) to the fourth sodium [Na(3)].

These two complex units are linked by bis-polyaqua sodium bridges (Figure 1). The two linking sodiums [Na(1) and Na(3)] are themselves joined by two symmetrical water bridges: Na(1)–O_w(5) 2.454(3), Na(3)–O_w(5) 2.544(3), Na(3)–O_w(8) 2.407(3), Na(1)–O_w(8) 2.421(3) Å; Na–O_w–Na 92.7(1), 97.0(1)°. The six-co-ordinate stereochemistry about Na(3) is distorted octahedral with the remaining four sites consisting of the two water links to Na(1), one link to the carboxyl oxygen of the L^{2-} anion [O(101A), 2.344(3) Å], and one to a water, O_w(4), which forms a bridge to Na(3), resulting in a linear polymer chain extending through the structure down the *a* direction in the unit cell (Figure 2). About Na(1), the stereochemistry is approximately square pyramidal with the additional links to L^{2-} [Na(1)–O(101B), 2.304(2) Å] and to the four bridging waters [O_w(3), O_w(4), O_w(5), O_w(8)]. Some lability of the waters is in evidence in the loss of crystallinity of this compound in the solid state, although there was no indication of this in the behaviour of the crystal in the *X*-ray beam during the data collection period. Nor is there evidence of water lability in the results of the structure analysis. Therefore, this structure represents a very stable compound analogous to the lithium complex $[Li_4L_2(H_2O)_6]$,[5] although the latter is discretely dimeric and

Table 3. Comparative intraligand O···O separations (Å) for the complexes of H_2L

Cation	O(ether)···O(ether)	O(ether)···O(carboxyl)	Ref.
Na^+	A 2.570(4)	2.625, 2.674(4)	This work
	B 2.579(4)	2.608, 2.636(4)	
NH_4^+	2.571(2)	2.606, 2.606(2)	
Mg^{2+}	2.512(9)	2.559, 2.559(9)	
Ni^{2+}	2.610(15)	2.628, 2.646(15)	6
Ca^{2+}	2.563(5)	2.600, 2.614(5)	6
Mn^{2+}	2.528(15)	2.553, 2.580(15)	6
Zn^{2+}	2.519(8)	2.573, 2.608(8)	6
Li^+	2.450(3)	2.552, 2.557(3)	5
K^+	2.570(6)	2.620, 2.610(6)	3
La^{3+}	A 2.600(10)	2.569, 2.637(10)	
	B 2.608(10)	2.594, 2.632(10)	4
Series mean	2.557(8)	2.604(8)	

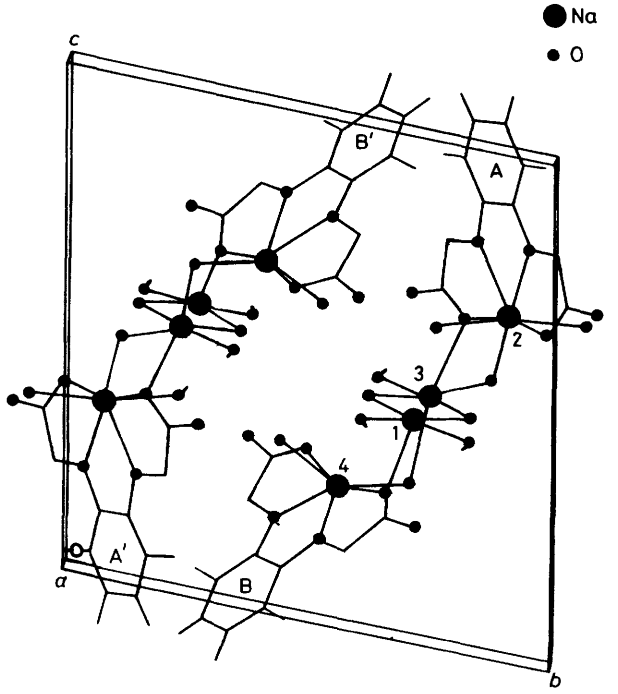


Figure 2. Packing of (5) in the unit cell viewed perpendicular to *bc*

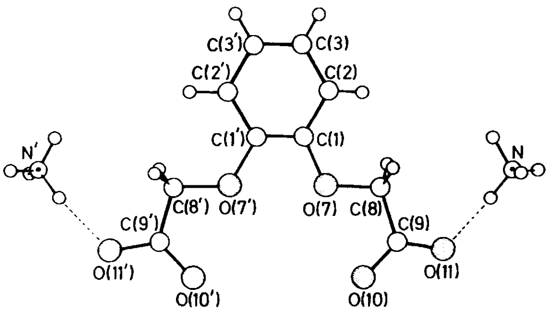


Figure 3. Molecular structure of $[NH_4]_2[L]$ (**6**)

centrosymmetric. In the lithium compound, there is a more regular bis-$[Li(H_2O)_2]^+$ bridging system between the two $[LiL(H_2O)]^-$ centres. For these univalent complexes of L^{2-} as well as the complexes of the divalent metals,[6] it may be generalized that the ligand is important in influencing the metal stereochemistry rather than *vice versa*. This is also the case with the analogous neutral ligand system, the (*o*-phenylenedioxy)-diacetamides, and their related compounds.[11,12] Invariably, in these compounds, the ligand is essentially planar, providing the four 'inner' oxygens for co-ordination to the metal. These, together with a fifth site at the open 'end' of the ligand, provide a basic co-ordination based on a pentagonal planar array of donor groups. This contrasts with the irregular arrays found for the Group 1A complexes of the phenoxyalkanoates, *e.g.* sodium phenoxyacetate hemihydrate[13] and potassium (2,4-dichlorophenoxy)acetate.[14]

$[NH_4]_2[L]$ (**6**).—The structure of (**6**) (Figure 3) comprises discrete and separate (*o*-phenylenedioxy)diacetate anions and ammonium cations. The anions have crystallographically imposed two-fold rotational symmetry relating one oxyacetate side-chain to the other, with the ligand essentially planar. This confirms the contention[5] that the preferred conformation for the L^{2-} species (and the free acid H_2L) is planar. The important structural parameters of L^{2-} in (**6**) are compared with those for the ligands in (**5**) and (**7**) and the mean for the divalent species (Table 3). Of particular note is the relative consistency of the intramolecular O ··· O distances within the ionophore cavity. The O(ether) ··· O(ether) and O(ether) ··· O(carboxylate) distances for (**6**) are 2.571(2) and 2.606(2) Å respectively, comparing with 2.557 and 2.604 Å as the mean for the series. This regularity is observed for the ligand irrespective of the mode of co-ordination, whether it be pentagonal pyramidal [(**2**), (**5**)], bipyramidal [(**3**), (**5**)], or if the ligand is unidentate as in $[Ni(HL)_2(H_2O)_4]\cdot H_2O$ (**4**).[5] The apparently anomalous short value for the O(ether) ··· O(ether) separation in the Li complex (**1**) (2.450 Å) is a consequence of the small cation radius. The short equidimensional Li–O bonds (2.054 Å mean) result in an inward contraction of the oxyacetate side-chains, reflected in the C–C–O(7) bond angles [112.1(2), 112.8(2)°].

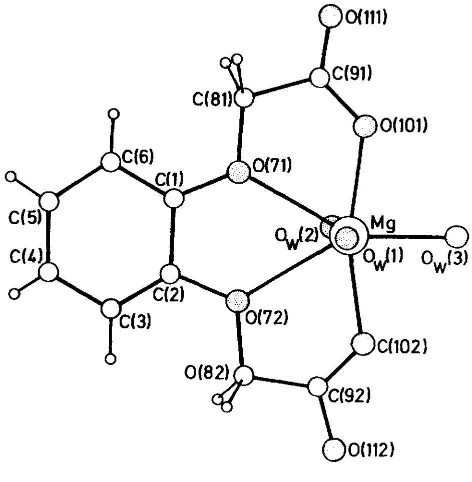


Figure 4. The complex unit in $[MgL(H_2O)_3]\cdot 4H_2O$ (**7**)

For (**6**), the ammonium ions do not lie within the ionophore cavity as might be expected intuitively. Instead they lie outside the cavity with hydrogen bonds linking them to the carboxylate oxygens of the anion (Figure 3). In this respect (**6**) is similar to the mixed cation complex of the analogous ligand 1-[(*o*-carboxymethoxy)phenoxy]-2-(*o*-hydroxyphenoxy)ethane (HL'), $[Zn(NH_4)_2L'_4]$, in which the NH_4^+ cations stabilize complex layers in the structure.[15]

In the structure of (**6**), the hydrogen bonds give stability to the solid-state structure, in evidence in the general morphological properties of the crystal and in the case of its formation from ammoniacal solutions of the ligand.

$[MgL(H_2O)_3]\cdot 4H_2O$ (**7**).—The structure of (**7**) is isostructural and isomorphous with the Zn^{II} and Co^{II} complexes (**3**).[5] The magnesium ion lies at the centre of a pentagonal bipyramid comprising the four 'inner' oxygens of the L^{2-} ligand and three water molecules (Figure 4). One of the waters lies in the pentagonal plane while the other two are at the apices. Although no data are available for the Co^{II} isomorph, isostructurality is inferred from single-crystal *X*-ray data, i.r. spectra, and elemental analysis.[5] Comparative bond distances and angles for the Zn^{II} and Mg^{II} isomorphs are as follows: M–O(ether) 2.475(7), 2.417(5); M–O(carboxyl) 2.150(8), 2.126(5); M–O_w (axial) 2.038(9), 2.047(5) (mean); M–O_w (equatorial) 2.112(7), 2.052(5) Å respectively. The comparative angles are: O(71)–M–O(72), 61.2(2), 62.6(2); O_w(1)–M–O_w(2), 166.0(3), 169.1(2)° respectively.

The only difference between the two structures is in the number of lattice waters which is 4 for (**7**) compared to 3.5 for the Zn polymorph. In both structures these waters are involved in extensive hydrogen bonding. It has been observed[5] that for the zinc structure these waters were relatively labile so that the 4-hydrate probably corresponds to the most stable form. The i.r. spectrum shows only minor differences attributable to slight variation in lattice water.

The stability constants for the series of type 3 divalent metal–L^{2-} complexes[2] [log *K*: Zn (2.0); Co (1.1); Mg (< 1.5)] are not significantly different from those for the isomorphous type 2 complexes of Mn (2.8) and Ca (3.1). However, the latter polytype, which is based on a pentagonal bipyramid but with a polymer structure linked through the fifth site of the pentagonal plane, is considered to derive stability through polymer formation. However, there is only a subtle structural difference compared with the type 3 Zn, Co, and Mg polymorphs.

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