of the Lehmann & Larsen (1974) procedure. The structure was solved by the Patterson and Fourier methods and the refinement was carried out by full-matrix least-squares cycles using the *SHELXS*86 and the *SHELX*76 computer programs, respectively (Sheldrick, 1985, 1976). The absolute configuration was established in the early stages of the refinement by assigning the (*S*) configuration to the prolinamide ligand. All isotropic H atoms (from a ΔF map) were included in the calculations but not refined. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A and 2.3.1 for Cu, O, N and C atoms, Table 2.2C for H). All calculations were carried out on a GOULD 6040 Powernode computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma) using the *PARST* (Nardelli, 1983) program for the geometrical description of the structure and *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1976) for the structure drawings.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71099 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1038]

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Sodium Ion Complexes with Ethylenediaminetetraacetic Acid

MERCÈ FONT-BARDIA, XAVIER SOLANS AND
MANUEL FONT-ALTABA

Department of Crystallography,
University of Barcelona, Martí Franqués s/n,
08028-Barcelona, Spain

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Abstract

The crystal structures of tetrasodium (1,2-ethanediyldinitrilo)tetraacetate pentahydrate and disodium dihydrogen (1,2-ethanediyldinitrilo)tetraacetate dihydrate have been determined. Na ions prefer to act as bridges between different edta ligands and only in the tetrasodium salt is the edta ligand hexadentate to one Na ion. Na ions display seven-coordination, when coordinated to one edta ligand (distorted pentagonal bipyramid), and six-coordination, when linked to several edta ligands (from distorted octahedral to trapezoidal bipyramidal geometry). An Na ion in the tetrasodium salt shows five-coordination, because the sixth site is blocked by the edta ligand. H atoms in the disodium salt are linked to amine groups. Only these two salts can be obtained on varying the pH of an aqueous solution containing Na^+ and ethylenediaminetetraacetic acid. The first is obtained around pH 2–5 and the second around pH 12.

Comment

The chelating capacity of the ethylenediaminetetraacetato (edta) ligand has attracted widespread interest and the literature contains a large number of studies on the crystal structures of metal complexes with this ligand, as well as spectroscopic and electrochemical studies (Hughes & Martell, 1953; Martell & Plumb, 1952; Scharzenbach & Freitag, 1951), aimed at determination of the behaviour of edta.

Crystal structure studies of edta complexes with Na have been carried out (Solans, Font-Altaba & García-Oricaín, 1984; Nassimbeni, Wright, van Niekerk & MacCullum, 1979; Templeton, Templeton, Zalkin & Ruben, 1982; Templeton, Templeton & Zalkin, 1985; Solans, Galí, Font-Altaba, Oliva & Herrera, 1988; Lee, 1967; Porai-Koshits, Novozhilova, Polyniva, Filippova & Martynenko, 1973; Pozhidaev, Polynova, Porai-Koshits & Dudakov, 1974), but always on complexes containing a second metal. It is the second metal that is coordinated to the edta ligand in all the crystal structures determined. In this paper we report the behaviour of the Na ion when it is alone with the edta ligand, in order to contribute to the understanding of the chemistry of $Na_nH_m\text{edta}^{4-n-m}$ complexes. The Na salts of ethylenediaminetetraacetic acid are interesting in the biochemical and medical field in spite of their toxic effects.

The syntheses of the title compounds were carried out in aqueous solutions of Na_2CO_3 and H_4edta at controlled pH; the acidity of the solutions was controlled by addition of HCl or piperazine. Within the pH range 0.5–14, only two compounds were obtained. Neither of the dry crystalline products obtained decomposes detectably on exposure to laboratory air. From pH-meter analysis we conclude that only the disodium and tetrasodium salts can be obtained from ethylenediaminetetraacetic acid in aqueous solution. This result disagrees with those of Palaty (1963) and does not support the existence of a commercial product with formula Hedta.Na_3. Powder diffraction analysis of the commercial product shows that it is an equimolar mixture of the disodium and the tetrasodium salt.

In the structure of the disodium salt, the edta ligand shows a molecular twofold axis, which is also a crystallographic symmetry axis. Therefore, the two Na ions of the formula have the same environment in the structure. The ethylenediaminetetraacetate moiety shows an antiplanar conformation (N—C—C—N torsion angle of 180°) which has been observed only in the dihydrogen ethylenediaminetetraacetate metal complexes of Ba (Meicheng, Zengren, Tongchang, Shiying & Youqi, 1979) and $[(H_2O)_6Mg]^{2+}$ (Julian, Day & Hoard, 1973).

The C—O acetate bond lengths are similar, while the C—N bond lengths are similar to those obtained for a protonated amine group (Borthwick, 1980). The *N*,*N*′-dihydrogen ethylenediaminetetraacetate conserves four (of the six) hydrogen bonds found in the structure of H_4edta (Cotrait, 1972).

The Na ion is linked to five acetate O atoms of different H_2edta ligands and water molecules of hydration. The coordination polyhedron is a trapezoidal bipyramid, with atoms O(11), O(12), O(21) and O(22) in the equatorial plane. The distortion from an octahedron is assigned to hydrogen bonds of the coordinated water molecule.

In the tetrasodium salt the four Na ions display different environments in the structure. The Na(1) ions shows seven-coordination, being linked to two amine N atoms and four O atoms of the same edta ligand. The seventh ligand atom is an acetate O atom belonging to a different edta ligand. This produces dimetallic units of formula $[(\text{edta})_2Na_2]$, which has been observed also in $[Mn(H_2O)_4][Cd(\text{edta})].2H_2O$ (Solans, Font-Altaba, Oliva & Herrera, 1985). This coordination produces a synclinal conformation in the ethylenediamine moiety, as observed in H_4edta and the transition-metal complexes of the edta ligand. The coordination polyhedron is a distorted pentagonal bipyramid with atoms O(31), N(1), N(2), O(21) and O(21′) in the equatorial plane (Fig. 3) and O(41) in an apical site. Theoretically, the transition from a pentagonal bipyramid to a monocapped trigonal prism is produced by loss of the equatorial planarity and the movement of the atoms occupying the apical sites; therefore, in order to quantify the distortion we computed the torsion angles N(2)—O(21′)—O(31)—O(21) and N(1)—O(21)—O(21′)—O(31), which will be equal to 0° for a pentagonal bipyramid and 90° for a monocapped trigonal prism. The mean value for the Na complex is 18.9°.

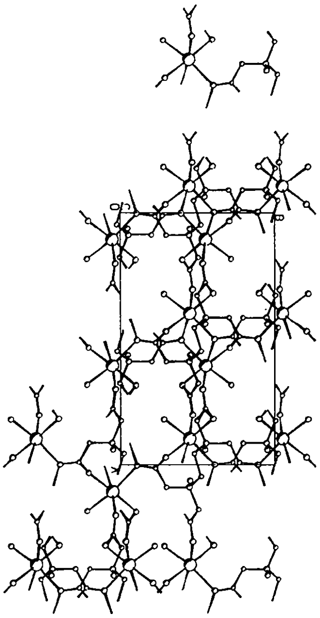

Fig. 1. Projection down the *c* axis of the unit-cell contents of $2Na^+.C_{10}H_{14}N_2O_8^{2-}.2H_2O$.

The remaining Na ions act as bridges between the different edta ligands. Na(2) is linked to three acetate O atoms of different edta ligands and two water molecules of hydration. The steric hindrance produced by the edta ligand blocks the sixth coordination site, so this ion displays a square-based pyramidal geometry, the Na(2) atom deviating 0.468 (9) Å from the basal plane.

Na(3) is linked to five acetate O atoms of three edta ligands, and a water molecule of hydration. Two O atoms belong to the same acetate group, which produces a trapezoidal bipyramidal polyhedron. Na(4) is linked to four acetate groups of different edta ligands and two water molecules of hydration, displaying a distorted octahedral coordination.

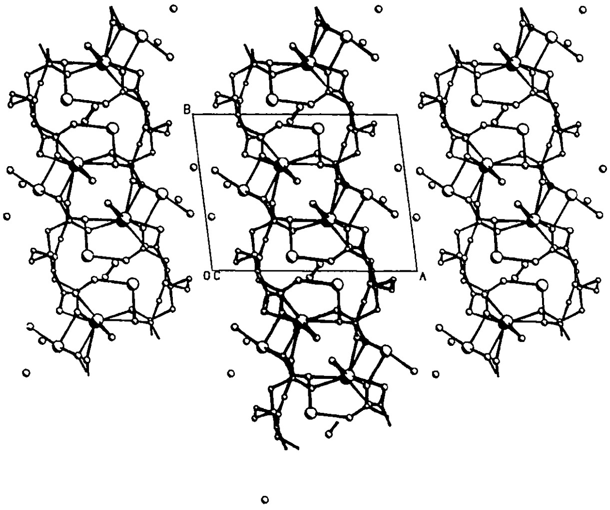

Fig. 2. Projection down the c axis of the unit-cell contents of $4Na^+.C_{10}H_{12}N_2O_8^{4-}.5H_2O$.

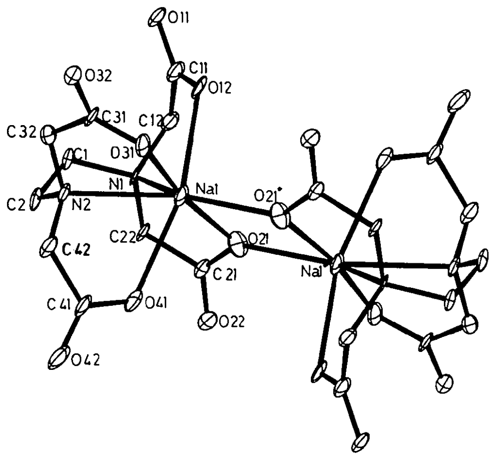

Fig. 3. View of the $Na_2(C_{10}H_{12}N_2O_8)_2$ unit of the tetrasodium salt.

Experimental

Disodium compound

Crystal data

$2Na^+.C_{10}H_{14}N_2O_8^{2-}.2H_2O$
$M_r = 372$
Orthorhombic
Pbca
$a = 15.945\ (4)$ Å
$b = 9.845\ (3)$ Å
$c = 8.912\ (3)$ Å
$V = 1399\ (1)$ Å^3
$Z = 4$
$D_x = 1.767$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8\text{-}12°$
$\mu = 0.196$ mm^{-1}
$T = 298$ K
Prismatic
0.2 × 0.1 × 0.1 mm
Colourless

Data collection

Phillips PW1100 diffractometer
ω scans
Absorption correction: none
734 measured reflections
734 independent reflections
438 observed reflections [$I \geq 2.5\sigma(I)$]

$\theta_{max} = 25°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 9$
3 standard reflections frequency: 120 min intensity variation: not significant

Refinement

Refinement on F
Final $R = 0.063$
$wR = 0.066$
438 reflections
128 parameters
$w = 1/[\sigma^2(F_o) + 0.01|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.03$ e Å^{-3}
$\Delta\rho_{min} = -0.03$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for the disodium compound*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Na	1.1050 (3)	−0.0516 (4)	0.5623 (5)	2.00 (18)
C(1)	0.9533 (6)	−0.5222 (11)	0.4930 (14)	1.70 (49)
N(1)	0.9121 (5)	−0.4475 (8)	0.3666 (11)	1.19 (34)
O(11)	0.9979 (4)	−0.1063 (7)	0.3557 (9)	1.66 (32)
O(12)	1.0323 (4)	−0.2934 (7)	0.2295 (9)	2.29 (38)
C(11)	0.9877 (6)	−0.2276 (11)	0.3179 (13)	1.63 (51)
C(12)	0.9116 (6)	−0.2969 (9)	0.3916 (11)	1.53 (48)
O(21)	0.6986 (4)	−0.4680 (9)	0.2318 (9)	2.60 (39)
O(22)	0.8163 (4)	−0.4015 (7)	0.1174 (9)	1.86 (33)
C(21)	0.7765 (6)	−0.4512 (10)	0.2226 (12)	1.47 (50)
C(22)	0.8250 (6)	−0.5040 (11)	0.3590 (14)	1.97 (49)
O(*W*)	1.1811 (4)	−0.2177 (7)	0.4341 (9)	2.61 (39)

Table 2. *Geometric parameters* (Å, °) *for the disodium compound*

O(11)—Na	2.569 (8)	O(22^{iv})—Na	2.515 (8)
O(11^{i})—Na	2.374 (8)	C(1)—C(1)	1.557 (20)
O(21^{ii})—Na	2.374 (8)	C(22)—N(1)	1.498 (12)
N(1)—C(1)	1.497 (14)	C(11)—O(11)	1.251 (12)
C(12)—N(1)	1.499 (12)	C(21)—O(21)	1.256 (12)
C(11)—O(12)	1.243 (12)	O(*W*)—Na	2.335 (8)
C(12)—C(11)	1.539 (14)	C(22)—C(21)	1.532 (14)
C(21)—O(22)	1.232 (12)	H(N1)—N(1)	0.96 (17)
O(12^{iii})—Na	2.428 (8)		

O(12$^{\rm iii}$)—Na—O(*W*)	96.2 (3)	O(11)—Na—O(21$^{\rm ii}$)	171.7 (3)
O(11)—Na—O(12$^{\rm iii}$)	89.5 (3)	O(11$^{\rm i}$)—Na—O(21$^{\rm ii}$)	98.2 (3)
O(*W*)—Na—O(11)	81.3 (3)	O(12$^{\rm iii}$)—Na—O(22$^{\rm iv}$)	177.0 (3)
O(11$^{\rm i}$)—Na—O(12$^{\rm iii}$)	83.8 (3)	O(*W*)—Na—O(22$^{\rm iv}$)	80.8 (3)
O(*W*)—Na—O(11$^{\rm i}$)	165.4 (3)	O(11)—Na—O(22$^{\rm iv}$)	89.9 (3)
O(11)—Na—O(11$^{\rm i}$)	84.2 (3)	O(11$^{\rm i}$)—Na—O(22$^{\rm iv}$)	99.0 (3)
O(12$^{\rm iii}$)—Na—O(21$^{\rm ii}$)	82.9 (3)	O(21$^{\rm ii}$)—Na—O(22$^{\rm iv}$)	97.5 (3)
O(*W*)—Na—O(21$^{\rm ii}$)	96.2 (3)		

Symmetry code: (i) $2 - x, -y, 1 - z$; (ii) $\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z$; (iii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iv) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Tetrasodium compound

Crystal data

$4Na^+.C_{10}H_{12}N_2O_8^{4-}.5H_2O$
$M_r = 470$
Triclinic
$P\bar{1}$
$a = 13.326$ (4) Å
$b = 9.353$ (3) Å
$c = 8.478$ (3) Å
$\alpha = 99.71$ (3)°
$\beta = 115.41$ (3)°
$\gamma = 92.34$ (3)°
$V = 933.1$ (9) Å^3
$Z = 2$

$D_x = 1.67$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$-$12°$
$\mu = 0.241$ mm^{-1}
$T = 298$ K
Prismatic
0.10 × 0.08 × 0.06 mm
Colourless

Data collection

Phillips PW1100 diffractometer
ω scans
Absorption correction: none
2663 measured reflections
2663 independent reflections
2134 observed reflections $[I \geq 2.5\sigma(I)]$

$\theta_{\rm max} = 25°$
$h = -14 \rightarrow 14$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 9$
3 standard reflections frequency: 120 min intensity variation: not significant

Refinement

Refinement on F
Final $R = 0.063$
$wR = 0.063$
2134 reflections
317 parameters
$w = \sigma^{-2}(F_o)$
$(\Delta/\sigma)_{\rm max} = 0.01$

$\Delta\rho_{\rm max} = 0.03$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.03$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for the tetrasodium compound*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Na(1)	0.6029 (2)	−0.0899 (2)	0.4233 (4)	2.49 (11)
Na(2)	0.8000 (2)	0.4884 (3)	0.9716 (4)	2.88 (13)
Na(3)	0.5911 (2)	0.3154 (3)	0.5196 (4)	3.14 (13)
Na(4)	0.6055 (2)	0.3299 (3)	1.0589 (4)	3.12 (13)
N(1)	0.7627 (3)	−0.0828 (5)	0.7306 (8)	2.27 (24)
C(1)	0.8652 (4)	−0.1224 (6)	0.7178 (10)	2.40 (29)
C(2)	0.8800 (4)	−0.0550 (6)	0.5748 (9)	2.24 (29)
N(2)	0.7846 (3)	−0.0992 (5)	0.3996 (8)	1.95 (23)
O(11)	0.7064 (3)	−0.4528 (4)	0.6903 (7)	2.72 (21)
O(12)	0.5922 (3)	−0.3224 (4)	0.5095 (7)	2.59 (21)
C(11)	0.6697 (4)	−0.3329 (6)	0.6561 (10)	2.64 (31)
C(12)	0.7221 (4)	−0.1953 (6)	0.8024 (10)	2.39 (29)
O(21)	0.5841 (3)	0.0626 (5)	0.6783 (9)	5.30 (29)
O(22)	0.6850 (3)	0.2678 (4)	0.8517 (7)	2.99 (23)
C(21)	0.6739 (4)	0.1374 (6)	0.7893 (9)	1.91 (29)
C(22)	0.7802 (4)	0.0624 (6)	0.8339 (11)	2.86 (31)
O(31)	0.5844 (3)	−0.2512 (5)	0.1461 (7)	3.45 (24)
O(32)	0.6675 (3)	−0.4257 (4)	0.0536 (7)	2.92 (23)
C(31)	0.6677 (4)	−0.3143 (6)	0.1548 (10)	2.59 (32)
C(32)	0.7828 (4)	−0.2459 (6)	0.3124 (9)	2.32 (29)
O(41)	0.6843 (4)	0.1498 (5)	0.4210 (8)	3.71 (28)
O(42)	0.7709 (3)	0.2587 (5)	0.2902 (8)	3.55 (24)
C(41)	0.7403 (5)	0.1464 (7)	0.3306 (11)	2.98 (33)
C(42)	0.7790 (5)	0.0028 (7)	0.2802 (11)	3.33 (35)
O(*W*1)	0.8756 (4)	0.4509 (5)	0.6106 (9)	4.79 (29)
O(*W*2)	0.9254 (3)	0.3598 (5)	1.1797 (7)	3.54 (25)
O(*W*3)	0.5313 (3)	0.4262 (5)	0.2581 (7)	3.44 (24)
O(*W*4)	0.9713 (3)	0.6601 (5)	1.0796 (8)	3.94 (26)
O(*W*5)	0.5289 (19)	0.0452 (24)	1.0178 (57)	17.44 (228)

Table 4. *Geometric parameters* (Å, °) *for the tetrasodium compound*

N(1)—Na(1)	2.549 (6)	N(2)—Na(1)	2.518 (4)
O(12)—Na(1)	2.425 (4)	O(21)—Na(1)	2.494 (7)
O(31)—Na(1)	2.477 (6)	O(41)—Na(1)	2.458 (4)
O(21$^{\rm i}$)—Na(1)	2.303 (6)	O(*W*2)—Na(2)	2.387 (5)
O(*W*4)—Na(2)	2.457 (5)	O(22)—Na(2)	2.310 (5)
O(32$^{\rm ii}$)—Na(2)	2.286 (5)	O(11$^{\rm iv}$)—Na(2)	2.344 (5)
O(22)—Na(3)	2.671 (6)	O(41)—Na(3)	2.292 (5)
O(*W*3)—Na(3)	2.440 (5)	O(21)—Na(3)	2.927 (5)
O(12$^{\rm i}$)—Na(3)	2.352 (5)	O(11$^{\rm iv}$)—Na(3)	2.432 (5)
O(22)—Na(4)	2.419 (5)	O(*W*5)—Na(4)	2.722 (5)
O(31$^{\rm i}$)—Na(4)	2.368 (5)	O(32$^{\rm ii}$)—Na(4)	2.414 (4)
O(42$^{\rm iii}$)—Na(4)	2.449 (5)	O(*W*3$^{\rm iii}$)—Na(4)	2.374 (6)
C(1)—N(1)	1.472 (6)	C(12)—N(1)	1.491 (7)
C(22)—N(1)	1.436 (8)	C(2)—C(1)	1.536 (8)
N(2)—C(2)	1.457 (8)	C(32)—N(2)	1.439 (7)
C(42)—N(2)	1.485 (8)	C(11)—O(11)	1.270 (6)
C(11)—O(12)	1.253 (8)	C(12)—C(11)	1.526 (9)
C(21)—O(21)	1.245 (7)	C(21)—O(22)	1.221 (7)
C(22)—C(21)	1.534 (6)	C(31)—O(31)	1.258 (6)
C(31)—O(32)	1.232 (8)	C(32)—C(31)	1.555 (8)
C(41)—O(41)	1.276 (8)	C(41)—O(42)	1.262 (7)
C(42)—C(41)	1.517 (8)		
N(2)—Na(1)—N(1)	70.4 (2)	O(12)—Na(1)—N(1)	70.3 (2)
O(12)—Na(1)—N(2)	98.7 (1)	O(21)—Na(1)—N(1)	64.6 (2)
O(21)—Na(1)—N(2)	123.8 (2)	O(21)—Na(1)—O(12)	96.4 (2)
O(31)—Na(1)—N(1)	123.7 (2)	O(31)—Na(1)—N(2)	66.5 (2)
O(31)—Na(1)—O(12)	82.1 (2)	O(31)—Na(1)—O(21)	169.7 (1)
O(41)—Na(1)—N(1)	89.7 (2)	O(41)—Na(1)—N(2)	67.1 (1)
O(41)—Na(1)—O(12)	158.8 (2)	O(41)—Na(1)—O(21)	80.4 (2)
O(21$^{\rm i}$)—Na(1)—O(21)	73.7 (2)	O(21$^{\rm i}$)—Na(1)—O(12)	96.8 (2)
O(21$^{\rm i}$)—Na(1)—N(1)	133.9 (2)	O(21$^{\rm i}$)—Na(1)—N(2)	154.8 (2)
O(21$^{\rm i}$)—Na(1)—O(31)	96.3 (2)	O(21$^{\rm i}$)—Na(1)—O(41)	102.2 (2)
O(41)—Na(1)—O(31)	104.6 (2)	O(22)—Na(2)—O(11$^{\rm iv}$)	87.0 (2)
O(32$^{\rm ii}$)—Na(2)—O(11$^{\rm iv}$)	91.2 (2)	O(32$^{\rm ii}$)—Na(2)—O(22)	86.6 (2)
O(*W*2)—Na(2)—O(11$^{\rm iv}$)	154.4 (2)	O(*W*2)—Na(2)—O(22)	84.9 (2)
O(*W*2)—Na(2)—O(32$^{\rm ii}$)	112.5 (2)	O(*W*4)—Na(2)—O(11$^{\rm iv}$)	97.3 (2)
O(*W*4)—Na(2)—O(22)	157.9 (2)	O(*W*4)—Na(2)—O(32$^{\rm ii}$)	114.8 (2)
O(*W*4)—Na(2)—O(*W*2)	81.9 (2)	O(22)—Na(3)—O(11$^{\rm iv}$)	77.6 (2)
O(41)—Na(3)—O(11$^{\rm iv}$)	113.3 (2)	O(41)—Na(3)—O(22)	93.6 (2)
O(*W*3)—Na(3)—O(11$^{\rm iv}$)	86.8 (2)	O(*W*3)—Na(3)—O(22)	164.3 (2)
O(*W*3)—Na(3)—O(41)	93.9 (2)	O(32$^{\rm ii}$)—Na(4)—O(22)	81.5 (2)
O(42$^{\rm iii}$)—Na(4)—O(22)	88.8 (2)	O(42$^{\rm iii}$)—Na(4)—O(32$^{\rm ii}$)	103.5 (2)
O(*W*3$^{\rm iii}$)—Na(4)—O(22)	171.7 (2)	O(*W*3$^{\rm iii}$)—Na(4)—O(32$^{\rm ii}$)	90.3 (2)
O(*W*3$^{\rm iii}$)—Na(4)—O(42$^{\rm iii}$)	94.5 (2)	Na(4)—O(*W*3$^{\rm iii}$)—Na(3$^{\rm iii}$)	113.1 (2)
Na(3)—O(11$^{\rm iv}$)—Na(2)	100.2 (2)	Na(4)—O(22)—Na(2)	89.9 (2)
Na(4)—O(22)—Na(3)	122.9 (2)	Na(4)—O(32$^{\rm ii}$)—Na(2)	90.6 (2)

Symmetry code: (i) $1 - x, -y, 1 - z$; (ii) $x, 1 + y, 1 + z$; (iii) $x, y, 1 + z$; (iv) $x, 1 + y, z$.

For both compounds the H-atom positions were obtained from difference Fourier syntheses and refined with an overall isotropic temperature factor. For the disodium compound the bond length was fixed for H atoms bonded to O atoms of water molecules and free for H atoms bonded to N atoms, and a riding model was used for H atoms bonded to C atoms.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71083 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1024]

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Structure of [1,2-Bis(diphenylphosphino)ethane]chloro(η^5-cyclopentadienyl)ruthenium(II)

Sandhya Suravajjala and
Leigh Christopher Porter*

Department of Chemistry, The University of Texas,
El Paso, Texas 79968, USA

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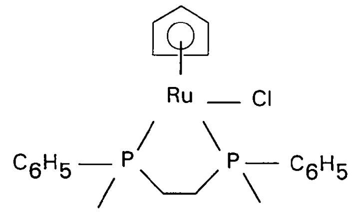
Abstract

The asymmetric unit is comprised of a molecule of (η^5-Cp)RuCl(dppe), where dppe is 1,2-bis(diphenylphosphino)ethane, and a co-crystallized molecule of trichloromethane-*d* solvent. Bonds to the P atoms of the chelating dppe ligand have an average length of 2.279 (2) Å and the Ru—Cl bond measures 2.452 (2) Å. The Ru atom is located at a distance of 1.851 Å from the centroid defined by the five C atoms of the Cp ring, which is planar and coordinates in an η^5 manner.

Comment

The chemistry of Ru complexes containing cyclopentadienyl ligands is extensive. A large number of bis(phosphine)(η^5-C_5H_5)Ru^{II} halide complexes have been prepared and the structures of (η^5-C_5H_5)RuClL_2 (L = PMe_3, PPh_3) have been described (Bruce, Wong, Skelton & White, 1981). The ancillary chloride and phosphine ligands in these complexes can be readily replaced to give a variety of neutral and cationic derivatives, including (η^5-Cp)Ru^{II} complexes containing chelating phosphines (Davies, McNally & Smallridge, 1990). The preparations of two complexes containing the chelating phosphines 1,2-bis(cyclohexylphosphino)methane (dcpm) and 2-methyl-1,2-bis(triphenylphosphino)ethane (prophos) have recently been described and their structures determined (Joslin, Mague & Roundhill, 1991; Morandini, Consiglio, Straub, Ciani & Sironi, 1983).

The title compound (I) was prepared according to the literature procedure (Ashby, Bruce, Tomkins & Wallis, 1979) and isolated fortuitously as well formed red crystals following crystallization from $CDCl_3$. The asymmetric unit consists of one complete molecule of (η^5-Cp)RuCl(dppe) and a co-crystallized molecule of $CDCl_3$ solvent. The Ru atom possesses an approximately octahedral coordination geometry and forms bonds to the two P atoms of the chelating dppe group, a chloride ligand and the cyclopentadienyl ligand. The bond to Cl(1) measures 2.452 (2) Å and bonds to the P atoms measure 2.275 (2) and 2.282 (2) Å for Ru(1)—P(1) and Ru(1)—P(2), respectively.



(I)

Within the cyclopentadienyl ligand we find the five C atoms to be essentially coplanar with a maximum out-of-plane displacement of 0.0123 Å (mean deviation of 0.0079 Å) and C—C bonds in the range 1.372 (8) to 1.421 (9) Å. The Ru atom is 1.851 Å