(Spackman & Maslen, 1985; Hall, 1986). Because of this shortcoming of the IAM, the oriented-atom model (OAM) was proposed by Schwarz, Valtazanos & Ruedenberg (1985). The OAM can be calculated from the multiple density functions (Takazawa, Ohba & Saito, 1989). Fig. 4(*b*) shows the deformation densities based on the OAM, where the number of electrons in one of the sp^3 atomic orbitals of N along the C—N bond axis is assumed to be unity. The peak height of the C—N bond increases from 0.32 to 0.68 e Å^{-3} and balances with that of the C—C bond. The bonding electron density on the C—C axis remains unchanged because the half-filled sp^3 orbitals of the C atom give a spherical electron density, which is identical with that of IAM.

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Structure of a Cobalt Complex Capable of Multiple Electron Transfer*

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Abstract

The compound [Co($C_{26}H_{42}N_8O_2$)]Cl_3.7.5H_2O [M_r = 799.1, $P6_522$, $a = b$ = 13.196 (1), c = 74.872 (6) Å, V = 11291 (2) Å^3, Z = 12, D_m = 1.41 g cm^{-3} (by flotation), D_x = 1.410 g cm^{-3}, Cu $K\alpha$, λ = 1.5418 Å, μ = 61.38 cm^{-1}, $F(000)$ = 5076] has an unusually long c axis for a coordination complex. Single-crystal X-ray diffractometer data were filtered to exclude reflections badly affected by adjacent reflections. The structure at room temperature is described as a commensurate displacive modulation of an idealized parent structure in space group $P6_422$ with axial lengths $a' = b' = a$, $c' = \frac{1}{2}c$, $Z = 6$. Some of the water molecules are disordered and ordering this disorder would further reduce the symmetry to $P3_212$. Sections of the structure perpendicular to **c** are described as strings of hydrogen-bond-connected cations propagated by 2_1 screw axes parallel to secondary crystal axes. The Cl anions are directly

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* Δ-(15,20,25,30*R*)-(1,12-Diammonio-2,11-dioxo-3,10,14,21,24,31-hexaazapentacyclo[10.10.10.$0^{4,9}$.$0^{15,20}$.$0^{25,30}$]dotriaconta-4,6,8-trienato)cobalt(III) trichloride heptasesquihydrate.

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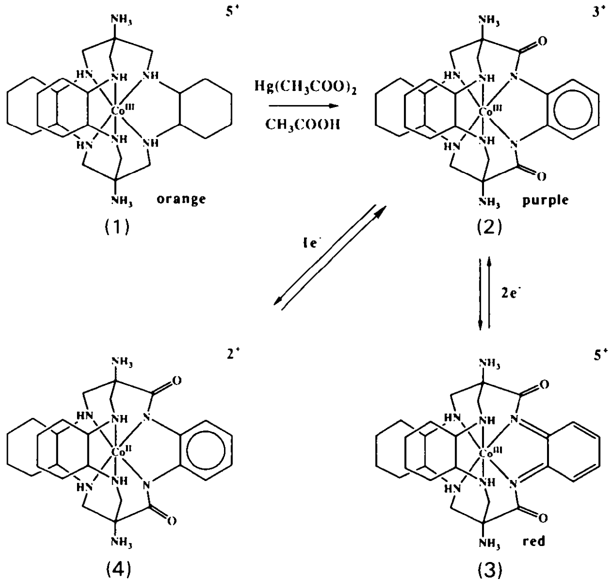
hydrogen bonded to protons attached to the N atoms in the cations. Parallel strings of water molecules are interspersed and have 222 symmetry in the parent structure but this is disrupted by the modulation. Per unit cell, half of each string maintains a twofold rotation symmetry parallel to the string but the other half loses all symmetry. An average structure in space group $P6_522$ is obtained as a consequence of disordering. A final value for $R_1 = \sum_{\mathbf{h}}||F_{\rm obs}(\mathbf{h})| - |F_{\rm calc}(\mathbf{h})||/\sum_{\mathbf{h}}|F_{\rm obs}(\mathbf{h})|$ of 0.070 was obtained from the least-squares refinement of 2060 independent merged data.

Introduction

The development of molecules which are capable of undergoing multiple electron transfers is important to understanding of the chemistry of energy capture and transformation. With this aim in mind the molecule (1) was synthesized (Geue, McCarthy & Sargeson, 1984) and oxidized (McCarthy, 1984) to give the variable oxidation levels shown in the scheme below.



Oxidation of the ligand was carried out with mercuric acetate in acetic acid and NMR spectroscopy of the isolated product (2) indicated aromatization of one cyclohexane ring as well as oxidation of a methylene group on each cap of the bicyclosexidentate ligand to form an amide. (2) undergoes a further $2\,e^-$ oxidation, presumably to (3) and a $1\,e^-$ reduction to a Co^{II} complex (4). The cage framework holds these rather fragile oxidized and reduced ligands together in a stable condition. This paper evaluates the crystal structure of the dark-purple crystals of the chloride salt of (2), confirms the NMR assignment and gives important structural detail.

Experimental

The title compound was recrystallized as hexagonal columns by evaporation from aqueous HCl solution.

Analysis

Observed: C 39.28, H 7.11, N 14.02, Co 7.05, Cl 13.42%. Calculated ($7.5H_2O$): C 39.07, H 7.18, N 14.02, Co 7.37, Cl 13.31%.

Data collection

Buerger precession photographs of *hk*0 and *hhl* data recorded on a Supper precession camera with Mo $K\alpha$ radiation gave preliminary cell dimensions with apparent $6/mmm$ Laue symmetry and an extinction condition $000l = 0$ unless $l = 6n$, consistent with space-group options $P6_522$ and $P6_122$. The extinction condition and the Laue symmetry $6/mmm$ were confirmed with the collected diffractometer data. A hexagonal prism of approximate dimensions $0.13 \times 0.15 \times 0.25$ mm was used for data collection. The length of the c axis implied care had to be taken to avoid overlap problems. Accurate lattice parameters were obtained from a least-squares fit of the setting angles for 25 reflections with 2θ values between 61 and 86° for Cu $K\alpha$ radiation. For the data collection a Philips PW1100/20 diffractometer was used in conventional $\theta/2\theta$ mode with θ scan width $(0.7 + 0.142\tan\theta)^\circ$, θ scan speed $1^\circ\,\mathrm{min}^{-1}$ and graphite-monochromatized Cu $K\alpha$ radiation. Background counting time was 12 s on either side of the scan. Square slits subtended angles $1 \times 1^\circ$ at the crystal. 12294 intensity data were collected between $\theta = 2.36$ and 55° including systematic absences. The three standard reflections measured every 90 min showed no significant change in intensity. Data were corrected for absorption using the Gaussian correction of *Xtal*3.0 (Hall & Stewart, 1990) with transmission factors in the range 0.372 to 0.527 and t in the range 0.0083 to 0.0152 cm.

Selection of data and space group

The crystal structure in space group $P6_522$, $a = b = 13.196\,(1)$, $c = 74.872\,(6)$ Å, $\gamma = 120^\circ$, $Z = 12$ can be described as a commensurate displacive modulation of an idealized parent structure in space group $P6_422$ with axial lengths $a' = b' = a$, $c' = \frac{1}{2}c$, $Z = 6$. Data for $l = 2n + 1$ have an average amplitude about half of that for $l = 2n$ data. In the parent structure the twofold rotation axis of the cation passing through the Co atom must coincide with a twofold rotation axis of the crystal. That this twofold rotation axis is parallel to $\mathbf{c}$ was confirmed in the structure solution. Four options for the modulation exist and correspond to the four singlet irreducible representations for the point $\frac{1}{2}\mathbf{c}'^* = \mathbf{c}^*$ in the Brillouin zone of the parent structure, see for example Bradley & Cracknell (1972). These correspond to space groups $P6_522$ and $P6_222$, each with alternative origins separated by $\frac{1}{2}\mathbf{c}' = \frac{1}{4}\mathbf{c}$. An x,y displacement of a molecule at $\frac{1}{2},\frac{1}{2},z$ creates space group $P6_522$. The twofold rotation axes parallel to **c** in the parent structure become 2_1 screw axes. The $P6_222$ option preserves the twofold axis parallel to **c** and corresponds to symmetry-breaking z displacements that should create observations for $00l$ reflections with $l = 6n + 3$. These reflections were unobserved and so the space group $P6_522$ was chosen.

The crystal was mounted with its c axis about 4° away from the goniometer axis with positive χ corresponding to negative l. Data were collected in parts. Below $\theta = 23°$ all data with $k \leq 0$ were collected for $l \leq 0$ while for $l > 0$ only data with $h \geq 0$ and $k \leq 0$ were collected. Above 23° only data with $l \leq 0$, $h \geq 0$ and $k \leq 0$ were collected. The diffraction symmetry was confirmed using data merging, evaluating $R_m = \sum_{\mathbf{h}}||F(\mathbf{h})| - \langle|F(\mathbf{h})|\rangle|/\sum_{\mathbf{h}}|F(\mathbf{h})|$ where $\langle|F(\mathbf{h})|\rangle$ is the average of symmetry equivalents of $F(\mathbf{h})$ and the summation is over those reflections where all collected equivalents were considered to be observed, *i.e.* $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$. There appears to be no justification for lowering the diffraction symmetry below that implied by the space group $P6_522$. For space-group options $P3_212$ and $P3_221$ the outer data shell is effectively not used. Values for R_m of 0.030 and 0.028 respectively were obtained for the *ca* 1100 instances of multiple observation for each of these subgroup options. Data with adjacent values of l are predominantly separated in χ and it was decided to filter data as to exclude data where adjacent reflections intruded into the data collection. Angle differences between the scattering vectors for the hkl reflection and the adjacent $hkl \pm 1$ were evaluated and separated into components in the vertical and horizontal plane of the diffractometer for the case when hkl was in the data-collection position. When differences in both these components were less than 0.5° intrusion of an adjacent reflection was implied. This process rendered suspect a cone of data about the $\mathbf{c}^*$ direction in reciprocal space, starting at about the edge of the first sphere of data collection and expanding as θ increases. So as to not lose resolution of the structure along **c**, it was decided to still include those data where both of the adjacent reflections were separately collected and were less than $\frac{1}{4}$ of the intensity of the reflection being collected. When the data are merged for space group $P6_522$ the outershell data are included in the statistic and using filtered data a value for R_m of 0.038 was obtained for 1998 sets of multiply observed reflections. Those acceptable reflections with $I(\mathbf{h}) > 3\sigma[I(\mathbf{h})]$ were used to create 2060 merged data which were monitored during refinement using four groupings. Sets (1) and (3) had l even while sets (2) and (4) had l odd. Sets (1) and (2) were free of adjacent reflection intrusion while sets (3) and (4) were obtained using reflections where data intrusion was considered to be small because of the weakness of adjacent reflections.

Structure solution and refinement

The Co atom was located by phase-determination methods using *SHELXS*86 (Sheldrick, 1985). The choice between $P6_522$ and the enantiomorphic $P6_122$ was determined by comparative refinement and confirmed at the completion of refinement. The value of R_1 for $P6_122$ was 0.109 compared with 0.070 for $P6_522$. In the modulated structure the molecular twofold axis is misaligned with the **c** axis by 4.5° and is translated sideways so that the Co atom takes up coordinates 0.4796 (2), 0.4824 (2), 0.46867 (2) in $P6_522$. An alternative origin for $P6_522$ that gives identical structure factors for $l = 2n$ data places the Co atom at 0.4796, 0.4824, 0.21867. However, structure factors for the $l = 2n + 1$ data are then totally different enabling this option to be excluded.

The remainder of the molecule and the three Cl ions were located by successive difference maps. The Cl(1) atom at 0.1497 (4), 0.3255 (4), 0.5020 (1) is modulated away from the twofold rotation axis position x, $2x$, 1.0 of the parent structure and the atoms Cl(2) at 0.6869 (5), 0.4972 (5), 0.3949 (1) and Cl(2)′ at 0.2697 (6), 0.4930 (7), 0.4013 (1) were symmetry related (operator $1 - x$, $1 - y$, z) in the parent structure but this is a pseudosymmetry operation for the modulated structure. The true symmetry element $1 + x - y$, $1 - y$, $1 - z$ acting on Cl(1) produces an equivalent atom at 0.8243, 0.6745, 0.4980 which is related to Cl(1) by the same pseudosymmetry operation. Constrained least-squares refinement using $F(\mathbf{h})$ data was carried out using the program *RAELS*89 (Rae, 1989). The operation $1 - x$, $1 - y$, z was used to maintain a relationship between the anisotropic thermal parameters of ligand atoms related by this pseudosymmetry element. Restraints were imposed to make differences between pseudosymmetry-related bond lengths (but not angles) approach zero. Refinement converged with R_1 about 0.20 and it was then necessary to unravel the rather complex hydrogen-bonded water network to obtain a satisfactory refinement.

Understanding how the modulation affected the hydrogen bonding was an essential part of the structure determination process, especially as disorder of certain of the water molecules occurs about the secondary twofold rotation axes. The most likely ordering of this disorder would reduce the symmetry from $P6_522$ to $P3_212$ with the same unit cell. However, data-merge statistics showed no significant improvement for any reduction in symmetry and there appears to be no geometric reason why such an ordering need occur.

The water O atoms were given individual anisotropic thermal parameters and in the final refinement cycle the symmetry constraints on anisotropic thermal parameters of pseudosymmetrically related atoms of the cation were relaxed so that all atoms were individually refined. This final expansion in the number of degrees of freedom had very little effect. The restraints on differences between pseudo-equivalent distances in the cation were not relaxed however and consequently quoted errors obtained from the inverse of the least-squares equations actually solved are more correctly errors in mean values of distances. The inherent nature of a commensurately modulated structure imposes the general observation that the averages of pseudosymmetry-related parameters are better determined than the differences between such parameters. The thermal-parameter differences between twofold-related atoms in the cation are probably not meaningful. The final value for $R_1 = \sum_{\mathbf{h}}||F_{\text{obs}}(\mathbf{h})| - |F_{\text{calc}}(\mathbf{h})||/\sum_{\mathbf{h}}|F_{\text{obs}}(\mathbf{h})|$ was 0.070, $wR = 0.095$ using 2060 independent reflections which included Friedel-related pairs. 444 variables were used representing 358 degrees of freedom once restraints on water H positions and bond-length differences were accounted for. H atoms on the cation atoms were unrefined and relocated at chemically sensible positions at the end of each refinement cycle. All H atoms were given the thermal parameters that were the same as the atom to which they were attached. Thermal parameters are deposited as U_{ij} values defined relative to orthonormal axes parallel to **a**, **b***, **c**.

Neutral-atom scattering factors and their wavelength-dependent corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The weights used for least squares included an arbitrary 4% error in $F(\mathbf{h})$ in excess of counting-statistics weights and gave a final goodness of fit of 2.0. Values of R_1 for the data sets described earlier were 0.068 for the 1056 $l = 2n$ data of set (1), 0.072 for the 905 $l = 2n + 1$ data of set (2), 0.066 for the 82 $l = 2n$ data of set (3) and 0.164 for the 17 $l = 2n + 1$ data of set (4). Data in set (4) have calculated values of $F(\mathbf{h})$ that are on average 10% less than the observed values, suggesting that contributions from the adjacent reflections were included in these peaks. The fact that the merge statistics were significantly better than the final value of R_1 is explained by the fact that the disorder about the secondary twofold rotation axes was not extended to all atoms but was limited to those atoms that were completely resolvable in terms of this disorder. The highest peaks on the final difference map were small and randomly distributed, though the two highest, *ca* 0.5 e Å^{-3}, were associated with the water molecule O(*w*1) and the Co atom, which are the two atoms that would lie on the twofold rotation axis of the cation that aligns with a twofold axis parallel to **c** in the idealized parent structure.

Description of the structure

Atoms were labelled in such a way as to show their pseudosymmetry relationships involving the pseudo twofold rotation axes parallel to **c**. Within the structure atom X is related to atom X', X = N(1) *etc.*, by the pseudosymmetry operation $1 - x$, $1 - y$, z. Fig. 1 shows the labelled atoms of the cation. Atomic coordinates for the non-H atoms are given in Table 1.* Bond distances for the cation are listed in Table 2 and bond angles are listed in Table 3. Distances between atoms involved in hydrogen bonding are listed in Table 4.

Description of the cation

The cation approximates D_3–32 symmetry and Fig. 2 shows the cation looking down the pseudo threefold rotation axis. The Co atom is in a slightly distorted octahedral coordination, being bonded to six N atoms of the sexidentate ligand. The cation retains an inherent twofold rotation axis that passes through the Co atom and the centre of the coordinated atoms N(1) and N(1)′ which are connected by the linkage, N(1)—C(10)—C(10)′—N(1)′, where the

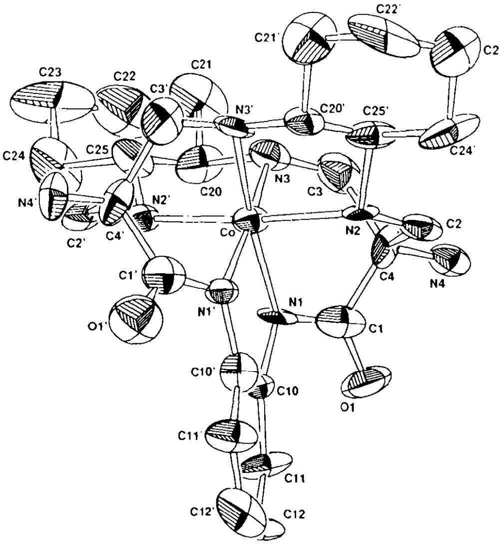


Fig. 1. The atom-labelling system for the cation.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55000 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates for the non-*H *atoms of the structure*

	x	*y*	*z*	U_{eq} (Å^2)
Co	0.4796 (2)	0.4824 (2)	0.46867 (2)	0.032 (1)
N(1)	0.4577 (9)	0.3816 (9)	0.4890 (1)	0.028 (2)
N(2)	0.6435 (7)	0.5157 (8)	0.4673 (1)	0.027 (2)
N(3)	0.4251 (9)	0.3451 (8)	0.4521 (1)	0.039 (2)
N(4)	0.5821 (9)	0.2079 (9)	0.4738 (2)	0.037 (3)
N(1)′	0.5097 (9)	0.6016 (8)	0.4864 (1)	0.031 (2)
N(2)′	0.3158 (7)	0.4499 (9)	0.4679 (1)	0.032 (2)
N(3)′	0.5261 (9)	0.6029 (9)	0.4492 (1)	0.042 (3)
N(4)′	0.3814 (11)	0.7633 (10)	0.4668 (2)	0.055 (3)
O(1)	0.4983 (9)	0.2488 (10)	0.5021 (1)	0.067 (3)
O(1)′	0.4839 (11)	0.7540 (10)	0.4948 (2)	0.073 (3)
C(1)	0.4991 (11)	0.3090 (13)	0.4893 (2)	0.043 (3)
C(2)	0.6649 (11)	0.4151 (12)	0.4694 (2)	0.040 (3)
C(3)	0.4719 (14)	0.2659 (13)	0.4551 (2)	0.054 (4)
C(4)	0.5531 (10)	0.3003 (10)	0.4720 (2)	0.035 (3)
C(1)′	0.4772 (13)	0.6800 (13)	0.4838 (2)	0.046 (4)
C(2)′	0.2969 (12)	0.5527 (12)	0.4681 (2)	0.047 (4)
C(3)′	0.4749 (14)	0.6802 (14)	0.4490 (2)	0.067 (4)
C(4)′	0.4087 (12)	0.6992 (12)	0.4670 (2)	0.051 (4)
C(10)	0.4685 (11)	0.4399 (11)	0.5057 (2)	0.029 (3)
C(11)	0.4452 (12)	0.3894 (14)	0.5227 (2)	0.050 (3)
C(12)	0.4738 (13)	0.4591 (16)	0.5374 (2)	0.061 (4)
C(12)′	0.5236 (14)	0.5791 (16)	0.5357 (2)	0.068 (4)
C(11)′	0.5402 (12)	0.6310 (14)	0.5193 (2)	0.047 (4)
C(10)′	0.5096 (11)	0.5601 (12)	0.5042 (2)	0.038 (3)
C(20)	0.2930 (10)	0.2781 (12)	0.4534 (2)	0.047 (4)
C(21)	0.2398 (13)	0.1886 (16)	0.4377 (2)	0.073 (4)
C(22)	0.1088 (15)	0.1311 (16)	0.4394 (3)	0.090 (5)
C(23)	0.0674 (16)	0.2213 (16)	0.4384 (2)	0.087 (5)
C(24)	0.1193 (11)	0.3033 (15)	0.4540 (2)	0.070 (4)
C(25)	0.2548 (10)	0.3660 (12)	0.4530 (2)	0.044 (3)
C(20)′	0.6583 (10)	0.6712 (11)	0.4488 (2)	0.032 (3)
C(21)′	0.7062 (14)	0.7435 (14)	0.4313 (2)	0.070 (4)
C(22)′	0.8372 (13)	0.8009 (13)	0.4314 (2)	0.068 (4)
C(23)′	0.8786 (13)	0.7118 (15)	0.4336 (2)	0.061 (4)
C(24)′	0.8322 (11)	0.6429 (14)	0.4507 (2)	0.056 (4)
C(25)′	0.6968 (10)	0.5842 (12)	0.4507 (2)	0.037 (3)
Cl(1)	0.1497 (4)	0.3255 (4)	0.5020 (1)	0.077 (1)
Cl(2)	0.6869 (5)	0.4972 (5)	0.3949 (1)	0.128 (2)
Cl(2)′	0.2697 (6)	0.4930 (7)	0.4013 (1)	0.197 (4)
O(*w*1)	0.462 (1)	0.445 (1)	0.4145 (1)	0.060 (3)
O(*w*2)	0.832 (2)	0.416 (1)	0.4167 ( )	0.13 (1)
O(*w*2)′	1.077 (2)	0.538 (1)	0.4167 ( )	0.25 (1)
O(*w*3)	0.365 (1)	0.001 (1)	0.4785 (2)	0.16 (1)
O(*w*3)′	0.642 (3)	−0.004 (2)	0.4855 (4)	0.20 (1)
O(*w*3)″	0.664 (3)	0.053 (2)	0.5397 (4)	0.20 (1)
O(*w*4)	0.189 (2)	−0.072 (2)	0.4548 (3)	0.36 (1)
O(*w*4)′	0.761 (3)	0.020 (3)	0.4551 (3)	0.26 (2)
O(*w*5)	0.122 (3)	0.089 (3)	0.5199 (4)	0.22 (1)
O(*w*5)′	0.905 (4)	0.079 (3)	0.4875 (6)	0.31 (2)
O(*w*5)″	0.878 (3)	0.065 (3)	0.5234 (6)	0.31 (2)
O(*w*5)‴	0.088 (5)	0.096 (5)	0.4983 (7)	0.22 (1)

Table 2. *Bond distances in the cation* (Å)

N(1)—Co	1.944 (8)	N(1)′—Co	1.943 (8)
N(2)—Co	1.983 (7)	N(2)′—Co	1.983 (7)
N(3)—Co	2.011 (8)	N(3)′—Co	2.011 (8)
C(1)—N(1)	1.319 (13)	C(1)′—N(1)′	1.318 (13)
C(1)—O(1)	1.242 (13)	C(1)′—O(1)′	1.247 (13)
C(2)—N(2)	1.498 (13)	C(2)′—N(2)′	1.498 (13)
C(3)—N(3)	1.473 (13)	C(3)′—N(3)′	1.479 (13)
C(4)—N(4)	1.455 (12)	C(4)′—N(4)′	1.456 (13)
C(4)—C(1)	1.507 (15)	C(4)′—C(1)′	1.509 (15)
C(4)—C(2)	1.508 (14)	C(4)′—C(2)′	1.510 (14)
C(4)—C(3)	1.572 (15)	C(4)′—C(3)′	1.574 (15)
C(10)—N(1)	1.440 (12)	C(10)′—N(1)′	1.440 (12)
C(11)—C(10)	1.394 (14)	C(10)′—C(11)′	1.395 (14)
C(12)—C(11)	1.365 (15)	C(11)′—C(12)′	1.366 (15)
C(10)′—C(10)	1.401 (19)	C(12)′—C(12)	1.384 (23)
C(20)—N(3)	1.514 (12)	C(20)′—N(3)′	1.511 (12)
C(21)—C(20)	1.558 (15)	C(21)′—C(20)′	1.560 (15)
C(22)—C(21)	1.506 (17)	C(22)′—C(21)′	1.501 (16)
C(23)—C(22)	1.540 (18)	C(23)′—C(22)′	1.534 (17)
C(24)—C(23)	1.509 (17)	C(24)′—C(23)′	1.506 (17)
C(25)—C(24)	1.552 (15)	C(25)′—C(24)′	1.551 (14)
C(25)—C(20)	1.477 (14)	C(25)′—C(20)′	1.476 (14)
C(25)—N(2)′	1.489 (12)	C(25)′—N(2)	1.492 (12)

Table 3. *Bond angles in the cation* (°)

N(1)—Co—N(2)	88.0 (4)	N(1)′—Co—N(2)′	87.4 (4)
N(1)—Co—N(3)	90.2 (4)	N(1)′—Co—N(3)′	89.8 (4)
N(2)—Co—N(3)	91.5 (4)	N(2)′—Co—N(3)′	91.1 (4)
N(1)—Co—N(2)′	95.8 (4)	N(2)—Co—N(1)′	95.6 (4)
N(2)—Co—N(3)′	85.4 (4)	N(3)—Co—N(2)′	85.8 (4)
N(1)—Co—N(1)′	85.4 (5)	N(3)—Co—N(3)′	95.5 (5)
N(1)—Co—N(3)′	171.4 (5)	N(3)—Co—N(1)′	171.5 (4)
N(2)—Co—N(2)′	175.4 (5)		
Co—N(1)—C(1)	122.5 (8)	Co—N(1)′—C(1)′	121.2 (9)
Co—N(1)—C(10)	112.0 (7)	Co—N(1)′—C(10)′	111.3 (8)
C(1)—N(1)—C(10)	114.0 (10)	C(1)′—N(1)′—C(10)′	120.0 (10)
Co—N(2)—C(2)	117.8 (7)	Co—N(2)′—C(2)′	117.5 (8)
Co—N(2)—C(25)′	108.0 (6)	Co—N(2)′—C(25)	107.9 (6)
C(2)—N(2)—C(25)′	112.5 (9)	C(2)′—N(2)′—C(25)	114.0 (9)
Co—N(3)—C(3)	117.1 (8)	Co—N(3)′—C(3)′	119.4 (8)
Co—N(3)—C(20)	105.9 (7)	Co—N(3)′—C(20)′	107.0 (7)
C(3)—N(3)—C(20)	110.2 (10)	C(3)′—N(3)′—C(20)′	112.2 (10)
N(1)—C(1)—O(1)	127.2 (13)	N(1)′—C(1)′—O(1)′	126.2 (13)
N(1)—C(1)—C(4)	115.1 (11)	N(1)′—C(1)′—C(4)′	117.7 (12)
O(1)—C(1)—C(4)	117.8 (12)	O(1)′—C(1)′—C(4)′	115.4 (12)
N(2)—C(2)—C(4)	112.4 (9)	N(2)′—C(2)′—C(4)′	113.6 (11)
N(3)—C(3)—C(4)	112.8 (10)	N(3)′—C(3)′—C(4)′	110.5 (10)
N(4)—C(4)—C(1)	108.4 (11)	N(4)′—C(4)′—C(1)′	108.7 (11)
N(4)—C(4)—C(2)	108.7 (9)	N(4)′—C(4)′—C(2)′	109.6 (10)
N(4)—C(4)—C(3)	105.1 (10)	N(4)′—C(4)′—C(3)′	105.9 (11)
C(1)—C(4)—C(2)	107.4 (11)	C(1)′—C(4)′—C(2)′	106.7 (12)
C(1)—C(4)—C(3)	115.6 (10)	C(1)′—C(4)′—C(3)′	115.2 (12)
C(2)—C(4)—C(3)	111.5 (11)	C(2)′—C(4)′—C(3)′	110.7 (12)
N(1)—C(10)—C(11)	126.8 (13)	N(1)′—C(10)′—C(11)′	123.4 (13)
N(1)—C(10)—C(10)′	114.4 (10)	N(1)′—C(10)′—C(10)	115.6 (11)
C(11)—C(10)—C(10)′	118.8 (11)	C(11)′—C(10)′—C(10)	120.9 (11)
C(10)—C(11)—C(12)	119.7 (14)	C(10)′—C(11)′—C(12)′	118.1 (14)
C(11)—C(12)—C(12)′	120.4 (15)	C(11)′—C(12)′—C(12)	121.7 (15)
N(3)—C(20)—C(21)	110.1 (10)	N(3)′—C(20)′—C(21)′	112.1 (10)
N(3)—C(20)—C(25)	106.6 (10)	N(3)′—C(20)′—C(25)′	106.1 (10)
C(21)—C(20)—C(25)	112.4 (12)	C(21)′—C(20)′—C(25)′	111.3 (10)
C(20)—C(21)—C(22)	106.7 (12)	C(20)′—C(21)′—C(22)′	108.5 (12)
C(21)—C(22)—C(23)	111.6 (16)	C(21)′—C(22)′—C(23)′	112.0 (12)
C(22)—C(23)—C(24)	107.8 (14)	C(22)′—C(23)′—C(24)′	111.3 (13)
C(23)—C(24)—C(25)	109.5 (12)	C(23)′—C(24)′—C(25)′	108.7 (10)
N(2)′—C(25)—C(20)	107.5 (10)	N(2)—C(25)′—C(20)′	107.9 (10)
N(2)′—C(25)—C(24)	114.3 (10)	N(2)—C(25)′—C(24)′	112.3 (9)
C(20)—C(25)—C(24)	109.5 (12)	C(20)′—C(25)′—C(24)′	111.7 (11)

C atoms are part of a phenyl ring, C(10)—C(11)—C(12)—C(12)′—C(11)′—C(10)′. This symmetry operation was used to label related halves of the cation. The coordinated atoms N(2) and N(3)′ are connected by the linkage, N(2)—C(25)′—C(20)′—N(3)′, where the C atoms are part of a cyclohexane ring C(20)′ to C(25)′. The twofold-related pair N(2)′ and N(3) are likewise connected by the linkage N(2)′—C(25)—C(20)—N(3) where the C atoms are part of the cyclohexane ring C(20) to C(25). The pseudo threefold rotation related atoms N(1), N(2), N(3) and the twofold rotation related N(1)′, N(2)′, N(3)′ are each capped by a (dimethylenecarbonyl)-methylammonium moiety, see Fig. 1.

The cation maintains the 3^+ charge ascribed to the central Co atom, counterbalanced by three Cl^- ions per formula unit. However the N(4) and N(4)′ atoms appear to have three attached H atoms to become formally $—NH_3^+$ moieties. The two additional protons come from the atoms N(1) and N(1)′ which would then have a formal negative charge. The sums of the three angles about N(1) and N(1)′ are 348.5 and 352.5° respectively which represents a distinctly more planar arrangement (ideal sum is 360°) than the sums for the corresponding three angles for the other four coordinated N atoms, *i.e.* 338.3, 339.4, 333.2, 338.6° for N(2), N(2)′, N(3), N(3)′ respectively, see Table 3. Each of these latter four atoms is assumed

Table 4. *Distances between atoms involved in hydrogen bonds* (Å)

N(3)—O(*w*1)	3.04 (1)	N(3)′—O(*w*1)	3.17 (2)
O(*w*1)—Cl(2)	3.07 (1)	O(*w*1)—Cl(2)′	3.07 (1)
O(*w*2)—Cl(2)	3.09 (1)	O(*w*2)′—Cl(2)′*a*	3.11 (2)
N(4)—O(1)′*b*	2.93 (2)	O(1)—N(4)′*b*	2.86 (2)
N(2)—Cl(1)*b*	3.22 (1)	N(2)′—Cl(1)	3.23 (1)
N(4)—Cl(2)*c*	3.06 (1)	N(4)′—Cl(2)′*d*	3.04 (1)
O(*w*3)—N(4)	2.82 (2)	O(*w*3)′′—N(4)′*b*	2.82 (3)
Cl(1)—O(*w*5)	3.24 (3)	O(*w*3)′—O(1)′*e*	2.90 (2)
Cl(1)—O(*w*5)′′′*f*	3.28 (5)	Cl(1) O(*w*5)′*g*	3.42 (4)
Cl(2)—O(*w*4)′*c*	3.12 (3)	Cl(2)′—O(*w*4)*c*	3.20 (3)
Cl(2)—O(*w*3)′′*h*	3.28 (2)	O(*w*3)′′—O(*w*5)′′	3.01 (6)
O(*w*)—O(*w*4)	2.69 (1)*	O(*w*3)′—O(*w*4)′	2.70 (1)*
O(*w*4)—O(*w*5)*f*	2.72 (4)	O(*w*4)′—O(*w*5)′	2.93 (5)
O(*w*5)—O(*w*5)′′′	2.77 (6)	O(*w*5)′—O(*w*5)′′	2.71 (7)
O(*w*5)—O(*w*5)′′*g*	3.09 (5)	O(*w*5)—O(*w*5)′*i*	3.45 (6)

Symmetry code: (*a*) $1 + x, y, z$; (*b*) $1 + x - y, 1 - y, 1 - z$; (*c*) $x, x - y, \frac{5}{6} - z$; (*d*) $x, 1 + x - y, \frac{5}{6} - z$; (*e*) $x, -1 + y, z$; (*f*) $x - y, -y, 1 - z$; (*g*) $-1 + x, y, z$; (*h*) $x - y, x, -\frac{1}{6} + z$; (*i*) $-1 + x - y, -y, 1 - z$; (*j*) $x - y, 1 - y, 1 - z$.

* The two distances that are less than or equal to 2.7 Å were restrained to approach 2.7 Å and this is reflected in their reduced error estimate which is an artifact from using an inverse of the matrix describing the least-squares equations that included restraints and constraints.

to have a coordinated H atom while N(1) and N(1)′ do not. Within the framework of this model all the H atoms attached to N atoms are involved in hydrogen bonding, see Table 4. No suitable contacts for hydrogen bonding exist for the N(1) and N(1)′ atoms.

The N(1)—C(1) and N(1)′—C(1)′ distances average 1.319 (13) Å and are too short for a single bond. They appear to have some double-bond character while the carbonyl C(1)—O(1) and C(1)′—O(1)′ distances average 1.245 (13) Å and appear to have some single-bond character, suggesting that the negative charge formally on the N(1) atoms has been delocalized over N—C—O so as to be placed on the O(1) atoms to some extent. Evidence for the extension of the conjugation of the phenyl ring as far as the O(1) atoms is not strong. The phenyl ring and the C(1) and C(1)′ coordinations are individually planar but are not coplanar. The three angles about C(1) sum to 360.0° and those about C(1)′ to 359.3°. However the torsion angles about C(10)—N(1) and C(10)′—N(1)′ are 135 (1), −43 (2), 139 (1) and −37 (2)° for the torsion angles C(10)′—C(10)—N(1)—C(1), C(11)—C(10)—N(1)—C(1), C(10)—C(10)′—N(1)′—C(1)′ and C(11)′—C(10)′—N(1)′—C(1)′ respectively. The N(1)—C(10) and N(1)′—C(10)′ distances average 1.440 (12) Å. The C(1)—C(4) and C(1)′—C(4)′ distances average 1.508 (15) Å and maintain essentially single-bond character. The loss of coplanarity is essentially a twist imposed by the coordination of the hexadentate ligand. The twofold symmetry of the cation is maintained and the Co—N(1)—C(10)—C(10)′—N(1)′—Co ring has torsion angles of 3 (1), −9 (1), 13 (2), −11 (1), 4 (1)° about the sequential bonds. The torsion angle of 13 (2)° is of opposite sign and of substantially less magnitude than the values of −56 (1)° for N(3)—C(20)—C(25)—N(2)′ and −55 (1)° for N(3)′—C(20)′—C(25)′—N(2). Parallelism with the pseudo C_3 axis of the cation holds for the C(20)—C(25) and C(20)′—C(25)′ bonds but not for the C(10)—C(10)′ bond. Relevant torsion angles C(20)—N(4)—N(4)′—C(25), C(20)′—N(4)′—N(4)—C(25)′ and C(10)—N(4)—N(4)′—C(10)′ are 1.7 (4), 1.7 (4) and 17.3 (4)° respectively (see Fig. 2).

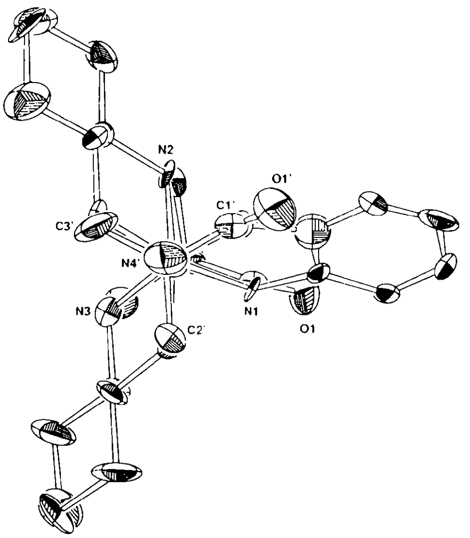

Fig. 2. A projection of the cation down the pseudo threefold rotation axis to show the pseudo 32 symmetrty of the cation, see text.

Positioning of the ions and waters within the crystal

Co and the water molecule O(*w*1) are displaced away from their special positions $\frac{1}{2}$, $\frac{1}{2}$, z on this symmetry axis in the parent structure. O(*w*1) hydrogen bonds to the pseudo twofold rotation related Cl^- ions Cl(2) and Cl(2)′ while the twofold rotation related N(3) and N(3)′ in the molecule hydrogen bond to O(*w*1). The pseudoequivalent water atoms O(*w*2) and O(*w*2)′ lie on a tertiary twofold rotation axis at special positions $2x, x, \frac{5}{12}$ of $P6_522$ related by the pseudosymmetry operation $2 - x, 1 - y, z$. These two atoms link the contents of the section $z = \frac{5}{12}$ to $\frac{1}{2}$ to the contents of the section $z = \frac{1}{3}$ to $\frac{5}{12}$ *via* the symmetry operation $x, x - y, \frac{5}{6} - z$. The atom O(*w*2) is hydrogen bonded to Cl(2) and its symmetry equivalent while the atom O(*w*2)′ is hydrogen bonded to two symmetry equivalents of Cl(2)′. O(*w*2) and O(*w*2)′ are 2.79 (3) Å apart but are in close contact rather than hydrogen bonded.

The remaining water molecules in the asymmetric unit are in the region of the secondary twofold rotation axis $x - y, -y, 1 - z$ parallel to **a** that relates the contents of the section $z = \frac{5}{12}$ to $\frac{1}{2}$ to the contents of the section $z = \frac{1}{2}$ to $\frac{7}{12}$. These water molecules are in between strings of molecules running parallel to **a** in the section $z = \frac{5}{12}$ to $\frac{7}{12}$. These strings are propagated by the 2_1 symmetry operation $b = 1 + x - y, 1 - y, 1 - z$ and contain intermolecular hydrogen bonds with N(4)—O(1)′*b* = 2.93 (2) and O(1)—N(4)′*b* = 2.86 (2) Å. The Cl(1) atom is intimately involved in these strings with N(2)—Cl(1)*b* = 3.22 (1) and N(2)′—Cl(1) = 3.23 (1) Å. Equivalents of atoms Cl(2) and Cl(2)′ are also hydrogen bonded to atoms in the molecule with N(4)—Cl(2)*c* = 3.06 (1) and N(4)′—Cl(2)′*d* = 3.04 (1) Å. The equivalent positions implied by *a*, *b etc.* are listed in Table 4.

Atoms O(*w*3), O(*w*4) fully occupy equivalent sites on either side of the rotation axis parallel to **a** but the pseudoequivalent O(*w*3)′, O(*w*3)″ and O(*w*4)′ only occupy one of the two symmetry-related sites. O(*w*3)′ and O(*w*3)″ are on opposite sides of the rotation axis parallel to **a**. The single water molecule O(*w*4)′ lies near this rotation axis and is contrasted to the two water molecules O(*w*4). This accounts for the 0.5 in the $7.5H_2O$ formulation. Atoms O(*w*5)′ and O(*w*5)″ also only occupy one of the two symmetry-related sites about this rotation axis. Hydrogen-bonding distance requirements determine that the sites as listed in Table 1 must be simultaneously occupied. The rotation about **a** creates an alternative occupancy arrangement. Atom O(*w*5) could occupy both symmetry-related sites but a separate disorder occurs in which the equivalents of an alternative site O(*w*5)‴ are occupied some of the time. The occupancies for the O(*w*5) and O(*w*5)‴ were constrained to total 1.0 and are in the ratio 0.648 (2):0.352. Should the O(*w*5)‴ sites have been unoccupied then the twofold axis parallel to **a** would have related sites that were both occupied for the region $x = 0$ to $\frac{1}{2}$, but sites where only one of the two equivalent sites were occupied for the region $x = \frac{1}{2}$ to 1. The modulation of the parent structure creates alternative hydrogen-bonding arrangements for the waters in these two regions. A long-range ordering would produce space group $P3_212$ as there appears to be no reason why the tertiary twofold rotation axis passing through the O(*w*2) and O(*w*2)′ positions should be destroyed. The ordering about the secondary twofold rotation axes every alternative half-cell repeat would suggest that no long-range ordering does occur and the diffraction symmetry supports this.

The O(*w*3)—N(4) hydrogen-bond distance of 2.82 (2) Å occurs on both sides of the rotation axis parallel to **a** but only the pseudoequivalent O(*w*3)″—N(4)′*b* distance of 2.82 (3) Å is comparable while O(*w*3)′—N(4)′*e* is 3.56 (3) Å which compares with other non-hydrogen-bonded contacts of 3.36 (2) Å for O(*w*3)—N(4)′*e* and 3.38 (3) Å for O(*w*3)′—N(4). The three hydrogens on N(4) are always hydrogen bonded [to equivalents of O(*w*3), Cl(2) and O(1)′]. However, two of the three hydrogens on N(4)′ are always hydrogen bonded [to equivalents of Cl(2)′ and O(1)] but the third is only hydrogen bonded half the time [to equivalents of O(*w*3)″] because of the disorder. Instead a hydrogen bond of 2.90 (2) Å for O(*w*3)′—O(1)′*e* is formed which compares with the longer distances of 3.34 (2) for O(*w*3)—O(1) and 3.21 (2) Å for O(*w*3)—O(1)*f*.

A possible location of H atoms on the water molecules can be evaluated by assuming that hydrogens are preferentially directed towards Cl ions and away from the N atoms. Such a set was evaluated included in the structure-factor calculations. Cl(1) is surrounded by atoms N(2)*j*, N(2)′, [O(*w*5) or O(*w*5)‴*f*], O(*w*5)′*g*, O(*w*5)″*g* at distances of 3.22 (1), 3.23 (1), 3.24 (3) or 3.28 (5), 3.42 (4), 3.87 (4) Å respectively. Cl(2) is surrounded by atoms O(*w*1), O(*w*2), N(4)*c*, O(*w*4)′*c*, O(*w*3)″*h* at distances 3.07 (1), 3.09 (1), 3.06 (1), 3.12 (3), 3.28 (2) Å respectively and Cl(2)′ is surrounded by atoms O(*w*1), O(*w*2)′*g*, N(4)′*d*, O(*w*4)*c*, at distances of 3.07 (1), 3.11 (2), 3.04 (1), 3.20 (3) Å, respectively, while Cl(2)′—O(*w*3)*c* is 4.33 (2) Å. There are thus four atoms hydrogen bonded to Cl(2)′ independent of the disorder in the rest of the structure but the disorder creates a varying number of hydrogen bonds (three to five) to other Cl ions.

O(*w*3) would not appear to be hydrogen bonded to its symmetry-related equivalent, O(*w*3)—O(*w*3)*f* = 3.22 (3) Å, one H presumably pointing at an equivalent of Cl(2)′ and the other to O(*w*4) since O(*w*3)—O(*w*4) is 2.69 (1) Å. Likewise O(*w*3)′ is not hydrogen bonded to O(*w*3)″ since O(*w*3)′—O(*w*3)″ = 4.12 (5) Å. While one hydrogen per water points at equivalents of Cl(2), the other probably points in the directions implied by the contacts O(*w*3)′—O(*w*4)′ = 2.70 (1) and O(*w*3)″—O(*w*5)″ = 3.01 (6) Å. A list of hydrogen-bonding contacts between waters in the disordered region is completed by distances O(*w*4)′—O(*w*5)′ = 2.93 (5) and O(*w*5)′—O(*w*5)″ = 2.71 (7) Å. On the other side of the pseudosymmetry axis at $\frac{1}{2}$, 0, *z* there is a disorder between the O(*w*5) and O(*w*5)‴ sites. O(*w*4)—O(*w*5)‴ is 3.47 (6) Å whereas O(*w*4)—O(*w*5)*f* is 2.72 (4) Å and O(*w*5)—O(*w*5)‴ is 2.77 (6) Å. Only three possibilities exist, *i.e.* two equivalents of O(*w*5) coexist, O(*w*5) and O(*w*5)‴ coexist or the symmetry equivalents of O(*w*5) and O(*w*5)‴ coexist. The remaining options are precluded by short contact distances. Completion of the string of waters running parallel to **a** is made by the contact distances O(*w*5)—O(*w*5)″*g* = 3.09 (5) and O(*w*5)—O(*w*5)′*i* = 3.45 (6) Å.

Fig. 3 shows the section of the structure between $z = \frac{5}{12}$ and $\frac{7}{12}$ viewed down **c**. Cations and anions that are related by a 2_1 screw axis parallel to **a** at $x = \frac{1}{2}$, $z = \frac{1}{2}$ are shown as is one of the two options for the water positions about the twofold rotation axis at $x = 0$, $z = \frac{1}{2}$. Fig. 4 shows this same section as viewed down **a**. Fig. 5 shows the section of the structure between $z = \frac{1}{3}$ and $\frac{1}{2}$ viewed down **a***, the direction of the tertiary twofold rotation axis at $z = \frac{5}{12}$. In this projection atoms related by a translation of **a** appear to be displaced sideways by $\frac{1}{2}$**b**. For clarity only atoms for one of these two positions have been shown. The atom O(w5)‴ has been omitted from all figures and again only one of the two ordering options for the other waters is shown. The misalignment by 4.5° of the twofold rotation axis of the cation with the crystal **c** axis is evident in Figs. 4 and 5.

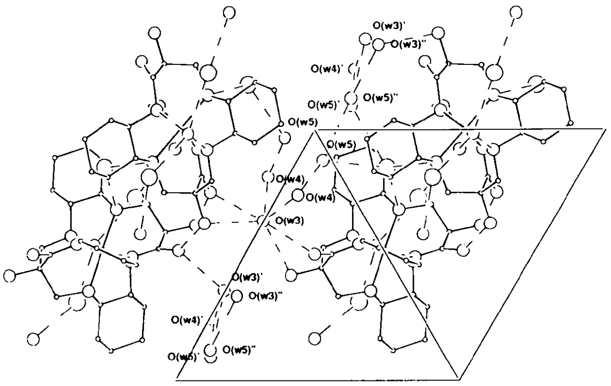

Fig. 3. The section of the structure between $z = \frac{5}{12}$ and $\frac{7}{12}$ viewed down **c**. The structure in this region appears as strings propagated by 2_1 screw axes parallel to **a**. The disordered water molecules are shown in just one of two coherent arrangments related by a twofold rotation axis parallel to **a**.

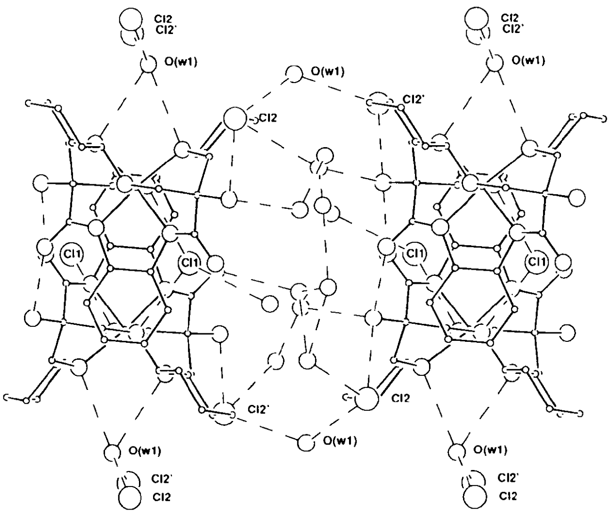

Fig. 4. The section of the structure between $z = \frac{5}{12}$ and $\frac{7}{12}$ viewed down **a**. The structure in this region appears as strings propagated by 2_1 screw axes parallel to **a**. The disordered water molecules are shown in just one of two coherent arrangments related by a twofold rotation axis parallel to **a**.

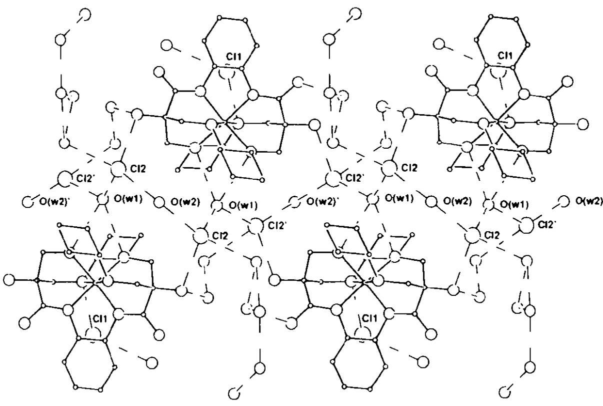

Fig. 5. The section of the structure between $z = \frac{1}{3}$ and $\frac{1}{2}$ viewed down **a***, the direction of the tertiary twofold rotation axis at $z = \frac{5}{12}$. In this projection atoms related by a translation of **a** appear to be displaced sideways by $\frac{1}{2}$**b**. For clarity only atoms for one of these two positions are shown.

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