Acta Cryst. (1999). B**55**, 380–388

Four-component intergrowth structures of the metal-ion cage complexes *fac*-(1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane)M^{II} diperchlorate hydrate, $[M(C_{22}H_{48}N_6)](ClO_4)_2.xH_2O$, M = Ni, Zn

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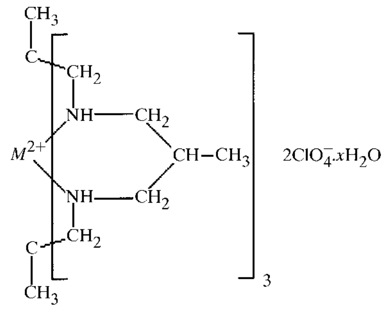
(*Received 3 February 1998; accepted 7 October 1998*)

Abstract

The crystal structures of (1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane-$\kappa^6N,N',N'',N''',N'''',N'''''$)nickel(II) diperchlorate–x(water) (x = 0.530), $[Ni(C_{22}H_{48}N_6)](ClO_4)_2.0.530H_2O$, and (1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo-[7.7.7]tricosane-$\kappa^6N,N',N'',N''',N'''',N'''''$)zinc(II) diperchlorate–$x$(water) ($x$ = 0.608), $[Zn(C_{22}H_{48}N_6)](ClO_4)_2.0.608H_2O$, are isomorphic and each is described as an intergrowth of four substructures, consistent with different modulations of an idealized parent structure of space group $C2/c$. Two substructures correspond to alternative orientations of a $C\bar{1}$ structure for which $x = 0$ in the general formula $[M(C_{22}H_{48}N_6)](ClO_4)_2.xH_2O$, and two substructures correspond to alternative origins of a $P2_1/n$ structure for which $x = 1$. Twinning also occurs. An analysis of the pseudosymmetry, a description of the refinement and a description of the refined structures are presented. The MN_6 coordination geometry is essentially octahedral, in contrast to the trigonal-prismatic geometry observed for the Cd^{II} and Hg^{II} complexes of the same ligand.

1. Introduction

Bicyclic hexaamine cage structures with expanded coordination cavities can induce fundamental changes in the chromophore electron chemistry of MN_6 complexes. They are also capable of stabilizing larger metal ions in the cavity and therefore lower oxidation states in general. In this context, the ligand *fac*-Me$_5$-D_{3h}tricosaneN$_6$ [*fac*-1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane] was recently synthesized using a template strategy (Geue *et al.*, 1994). Extrusion of the metal from the Co^{II} complex cation was achieved quantitatively under relatively mild conditions. This afforded the free ligand which was then used to complex other transition and post-transition metals. Nickel(II), zinc(II), cadmium(II) and mercury(II) complexes of the hexaamine cage ligand were readily isolated. In solution, variable-temperature ^{13}C NMR spectroscopy implies an effectively octahedral geometry for the six coordinating N atoms in the Ni^{II} and Zn^{II} cations but an effectively trigonal-prismatic geometry for the larger Cd^{II} and Hg^{II} cations. The trigonal-prismatic geometries have been established by the single-crystal structure analyses of Cd^{II}- and Hg^{II}(*fac*-Me$_5$-D_{3h}tricosaneN$_6$).$(PF_6)_2$.3H_2O (Bygott *et al.*, 1999). The structures of the perchlorate salts of the Ni^{II} and Zn^{II} complex ions, (I) and (II), are the subject of this paper.



(I) M = Ni
(II) M = Zn

2. Experimental

2.1. *Preparation of the Ni^{II} and Zn^{II} complexes*

An ethanol solution of $NiCl_2.6H_2O$ was added with stirring to an ethanol suspension of an equivalent quantity of the ligand and stirred for 30 min. $NaClO_4.H_2O$ was then added and stirring was continued for a further 30 min. The resulting pink precipitate was washed, dried and then recrystallized from water.

Similarly, an ethanol solution of $Zn(ClO_4)_2.6H_2O$ was added to an ethanol suspension of an equivalent quantity of the ligand and stirred for 1 h. The colourless precipitate was washed, dried and then recrystallized from water.

ISSN 0108-7681

Table 1. *Experimental details for* $[M(C_{22}H_{48}N_6)](ClO_4)_2.xH_2O$

Crystal data		
Chemical formula†	$[Zn(C_{22}H_{48}N_6)](ClO_4)_2.xH_2O$	$[Ni(C_{22}H_{48}N_6)](ClO_4)_2.xH_2O$
Chemical formula weight	670.6	665.2
Cell setting‡	Triclinic	Triclinic
Space group‡	$C\bar{1}$	$P\bar{1}$
a (Å)	10.191 (5)	10.177 (1)
b (Å)	17.678 (8)	17.648 (2)
c (Å)	17.754 (9)	17.605 (2)
β (°)	99.42 (2)	99.70 (1)
V (Å^3)	3155 (3)	3117 (1)
Z	4	4
D_x (Mg m^{-3})	1.41	1.42
Radiation type	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.5418	1.5418
No. of reflections for cell parameters	25	25
θ range (°)	31.9–38.6	31.9–39.5
μ (mm^{-1})	3.15	2.96
Temperature (K)	295 (2)	295 (2)
Crystal form	Block	Block
Crystal size (mm)	0.26 × 0.20 × 0.16	0.24 × 0.18 × 0.14
Crystal colour	Colourless	Pink
Data collection		
Diffractometer	Philips PW1100/20 four-circle	Rigaku AFC-6*R* four-circle
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	Analytical (de Meulenaer & Tompa, 1965)	Analytical (de Meulenaer & Tompa, 1965)
T_{min}	0.567	0.629
T_{max}	0.725	0.733
No. of measured reflections	2798	9441
No. of independent reflections	2798	9441
No. of observed reflections	2255	4104
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
θ_{max} (°)	64	60.5
Range of h, k, l	$-11 \rightarrow h \rightarrow 11$	$-11 \rightarrow h \rightarrow 11$
	$0 \rightarrow k \rightarrow 20$	$-20 \rightarrow k \rightarrow 0$
	$0 \rightarrow l \rightarrow 20$	$-20 \rightarrow l \rightarrow 20$
No. of standard reflections	3	3
Frequency of standard reflections	Every 90 min	Every 150 reflections
Intensity decay (%)	7.1	4.6
Refinement		
Refinement on	F	F
R	0.054	0.074
wR	0.083	0.121
S	1.78	2.55
No. of reflections used in refinement	2255	4104
No. of parameters used	254	269
H-atom treatment	H-atom parameters not refined	H-atom parameters not refined
Weighting scheme	$w = 1/[\sigma^2(F_o) + (0.04F_o)^2]$	$w = 1/[\sigma^2(F_o) + (0.04F_o)^2]$
$(\Delta/\sigma)_{max}$	0.29	0.32
$\Delta\rho_{max}$ (e Å^{-3})	0.26	0.29
$\Delta\rho_{min}$ (e Å^{-3})	−0.25	−0.27
Extinction method	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1)
Computer programs		
Data collection	Philips PW1100/20 software (1976)	*MSC/AFC Diffractometer Control Software*
Cell refinement	Philips PW1100/20 software (1976)	Philips PW1100/20 software (1976)
Data reduction	*Xtal*3.0 (Hall & Stewart, 1990)	*Xtal*3.0 (Hall & Stewart, 1990)
Structure solution	*SHELXS*86 (Sheldrick, 1985)	*SHELXS*86 (Sheldrick, 1985)
Structure refinement	*RAELS*96 (Rae, 1996)	*RAELS*96 (Rae, 1996)

† Water molecules are associated with two of the four substructures: $x = 0.608$ (8) for M = Zn and $x = 0.530$ (7) for M = Ni (see text). ‡ Both structures are an intergrowth of two $C\bar{1}$ and two $P2_1/n$ substructures with an apparently monoclinic cell (see text). Equal populations for the $P2_1/n$ substructures causes reflections to be unobserved when $h + k$ is odd (see text and Appendix).

2.2. *Analyses for* $[M(C_{22}H_{48}N_6)](ClO_4)_2.xH_2O$

M = Ni: observed C 39.66, H 8.15, N 12.28, Ni 8.53; calculated (x = 1) C 39.30, H 7.50, N 12.50, Ni 8.73; (x = 0) C 40.39, H 7.39, N 12.84, Ni 8.97%. M = Zn: observed C 39.43, H 7.68, N 12.46, Zn 9.94; calculated (x = 1) C 38.92, H 7.42, N 12.38, Zn 9.63; (x = 0) C 39.97, H 7.32, N 12.71, Zn 9.89%.

2.3. *Data collection*

Details of the data collections, structure solution and refinements are given in Table 1. Refinement statistics for reflections that violated $C2/c$ absence conditions [$I > 3\sigma(I)$] were isolated in the refinement statistics and details of refinement statistics for different classes of reflections are given in Table 2.

It is of particular interest that for M = Zn a C-centred data set was collected (violations of the C-centre condition were not observed) whereas for M = Ni a primitive-cell data set was collected. Intensities for all reflections which are absent for both $C\bar{1}$ and $P2_1/n$ ($0k0$, k odd and $h0l$, h odd, l even) were observed to be less than $2\sigma(I)$ and were not included in the refinements. Weak observed $h0l$, l odd reflections are consistent with $P2_1/n$ for $h + k$ odd but $C\bar{1}$ for $h + k$ even.

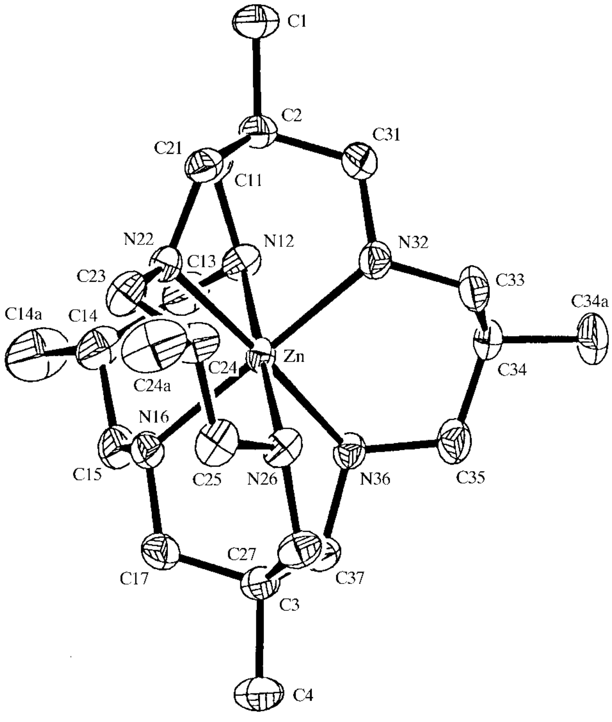


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the $[Zn(C_{22}H_{48}N_6)]^{2+}$ cation illustrating the reference-atom labelling scheme. Displacement ellipsoids are drawn to represent 30% probability surfaces. H atoms are omitted for clarity. The Ni-complex cation is numbered analogously.

3. Results

A general view of the reference cation showing the atom labelling is given in Fig. 1. A view down the pseudo-threefold axis of the Zn complex cation is given in Fig. 2.

The structures are each described as an intergrowth of four component structures (see §4). Fractional coordinates for non-H atoms of the isomorphic structures are given in Tables 3 and 4. Only atoms in the asymmetric unit of two of the four substructures are listed, the other two being obtained using the operator $-x$, y, $\frac{1}{2} - z$. Anion atoms labelled A and B refer to a component with space group $C\bar{1}$ while those labelled C and D and the water refer to a component with space group $P2_1/n$. Bond lengths are given in Tables 5 and 6. Equal-object constraints were applied. For the Ni complex, local coordinates relative to different axial systems were constrained to be identical for both space-group components. Further constraints were imposed for the Zn complex because $h + k$ odd reflections were unobserved. These constraints made the cations have identical crystal coordinates for both reference component structures and imposed an exact $-x, y, \frac{1}{2} - z$ relationship between anions labelled A and C.

The quoted standard uncertainties more correctly describe the errors in the means of pseudo-twofold-rotation-related quantities since restraints were imposed to minimize differences between pseudo-32-related bond lengths and constraints were imposed to exactly relate certain displacement parameters. If unconstrained refinement had been attempted, the departures from these means would have been uncontrollable as the structure, modulo the unit cell, is an overlap of four structures. H-atom coordinates were incorporated in geometrically sensible positions and given the displacement parameters of the atoms to which they are attached. H-atom parameters, anisotropic displacement parameters U^{ij} and selected interatomic angles and torsional angles have been deposited†.

4. Structure solution and refinement

It is recommended that the Appendix be read at this point in order to fully appreciate the nature of the refinement problem. All refinements used the program *RAELS* (Rae, 1996). Atoms were defined using refinable local coordinates, relative to refinable local orthonormal axial systems, to define orthonormal crystal coordinates relative to unit axes parallel to **a**, **c*** × **a**, **c*** (Rae, 1975). The equal-object constraints used in our refinement are imposed by using different axial systems but the same local coordinates. A local axial system is initially determined by the program from the overlay of an actual and an idealized structure fragment. The

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA0004). Services for accessing these data are described at the back of the journal.

Table 2. *Final-cycle refinement statistics for* $[M(C_{22}H_{48}N_6)](ClO_4)_2.xH_2O$

$R = \Sigma_{\mathbf{h}}|F_o(\mathbf{h}) - F_c(\mathbf{h})|/\Sigma_{\mathbf{h}}|F_o(\mathbf{h})|$, g.o.f. $= [\Sigma_{\mathbf{h}} w_{\mathbf{h}}|F_o(\mathbf{h}) - F_c(\mathbf{h})|^2/(n-m)]^{1/2}$.

	Data class	R	G.o.f.
M = Zn	All 2255 reflections with $h + k$ even, $I > 3\sigma(I)$	0.054	1.78
	Subset of 5 $h0l$ reflections with l odd, $I > 3\sigma(I)$	0.621	11.31
	543† reflections with $I < 3\sigma(I)$	0.649	1.44
M = Ni	All 3919 reflections with $h + k$ even, $I > 3\sigma(I)$	0.072	2.48
	Subset of 20 $h0l$ reflections with h even, l odd	0.377	6.32
	All 185 reflections with $h + k$ odd, $I > 3\sigma(I)$	0.340	4.41
	5337† reflections with $I < 3\sigma(I)$	0.915	1.14

† Data omitted during refinement.

idealized fragment is described in local orthonormal coordinates whereas the actual fragment is in orthonormal crystal coordinates. Local coordinates can also be evaluated from known crystal coordinates if the axis transformation or sequence of transformations is known. The program *RAELS* allows up to three sequential coordinate transformations to define atom positions (Haller *et al.*, 1995).

The Zn complex was investigated first and was initially developed as an ordered structure in space group $C2/c$, $Z = 4$, using Patterson and Fourier methods. The cation had apparent 32 symmetry and lay about a crystallographic twofold rotation axis with atoms Zn, C14 and C14a on this axis. This local symmetry is impossible since C14 has an attached H atom and must have a tetrahedral coordination. The ClO_4^- ions appeared to be disordered with only the Cl position well determined. However, a major component could be identified and the ClO_4^- ion was included as an exact tetrahedron of refinable bond length, location and orientation with rigid-body *TLX* displacement parameters (Rae, 1975). Least-squares refinement converged with $R(F) = 0.23$.

Attempts were then made to refine the structure as a disordered structure in $C2/c$ using restraints to maintain an effective 32 symmetry equivalence between bond lengths and some bond angles but not torsional angles. The initial lowering from 32 to 3 symmetry was made by removing the apparent planarity of the C14, C24, C34 coordinations, *i.e.* moving C14 and C14a equal but opposite distances perpendicular to the coordination plane with the effective 3 symmetry relating the shifts for C24 and C24a, C34 and C34a.

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* $[Zn(C_{22}H_{48}N_6)](ClO_4)_2.0.608H_2O$

Anion C is obtained from anion A by the operation $1 - x, y, \frac{1}{2} - z$.

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn	0.5005 (2)	0.1568 (1)	0.2552 (1)	0.043 (1)
C1	0.8091 (6)	0.1506 (3)	0.0856 (4)	0.084 (2)
C2	0.7066 (5)	0.1529 (2)	0.1412 (3)	0.059 (1)
C3	0.2953 (5)	0.1619 (2)	0.3732 (3)	0.059 (1)
C4	0.1979 (6)	0.1638 (3)	0.4317 (4)	0.084 (2)
C11	0.6538 (5)	0.2337 (3)	0.1399 (3)	0.065 (2)
N12	0.5206 (5)	0.2388 (2)	0.1648 (2)	0.057 (1)
C13	0.4833 (7)	0.3201 (3)	0.1721 (4)	0.075 (2)
C14	0.5238 (7)	0.3528 (2)	0.2510 (4)	0.082 (2)
C14a	0.5108 (19)	0.4389 (3)	0.2465 (7)	0.150 (3)
C15	0.4413 (7)	0.3234 (3)	0.3080 (4)	0.075 (2)
N16	0.4810 (6)	0.2462 (2)	0.3386 (2)	0.057 (1)
C17	0.3988 (5)	0.2232 (3)	0.3975 (3)	0.065 (2)
C21	0.7811 (5)	0.1308 (3)	0.2196 (3)	0.058 (1)
N22	0.7183 (3)	0.1582 (3)	0.2851 (3)	0.048 (1)
C23	0.7872 (6)	0.1234 (4)	0.3579 (3)	0.069 (2)
C24	0.7283 (4)	0.0494 (3)	0.3784 (3)	0.072 (2)
C24a	0.8269 (6)	0.0109 (6)	0.4408 (5)	0.115 (2)
C25	0.5971 (5)	0.0582 (4)	0.4064 (3)	0.069 (1)
N26	0.4812 (4)	0.0737 (3)	0.3446 (3)	0.056 (1)
C27	0.3560 (5)	0.0828 (3)	0.3778 (3)	0.063 (2)
C31	0.5978 (5)	0.0962 (3)	0.1112 (3)	0.063 (2)
N32	0.5185 (5)	0.0692 (2)	0.1698 (3)	0.056 (1)
C33	0.3964 (5)	0.0289 (3)	0.1314 (4)	0.069 (1)
C34	0.2751 (5)	0.0786 (3)	0.1123 (3)	0.072 (2)
C34a	0.1725 (6)	0.0372 (6)	0.0542 (5)	0.115 (2)
C35	0.2105 (6)	0.1000 (4)	0.1800 (3)	0.069 (2)
N36	0.2823 (3)	0.1608 (3)	0.2293 (3)	0.048 (1)
C37	0.2123 (5)	0.1779 (3)	0.2953 (3)	0.058 (1)
ClA	0.9053 (4)	0.3531 (1)	0.3671 (2)	0.139 (5)
O1A	0.8938 (11)	0.2835 (3)	0.3319 (6)	0.232 (8)
O2A	0.8153 (10)	0.3581 (7)	0.4168 (6)	0.413 (19)
O3A	1.0322 (7)	0.3615 (5)	0.4068 (6)	0.255 (8)
O4A	0.8801 (11)	0.4091 (4)	0.3129 (5)	0.257 (6)
ClB	0.0648 (7)	0.3414 (4)	0.1140 (7)	0.247 (21)
O1B	0.1150 (17)	0.2949 (10)	0.1739 (11)	0.155 (14)
O2B	0.0532 (24)	0.3014 (11)	0.0467 (10)	0.561 (32)
O3B	−0.0584 (11)	0.3676 (10)	0.1239 (15)	0.795 (70)
O4B	0.1493 (12)	0.4017 (7)	0.1114 (13)	0.154 (19)
ClD	0.8646 (6)	0.3186 (3)	0.4248 (3)	0.140 (9)
O1D	0.8836 (14)	0.2933 (7)	0.3541 (5)	0.194 (15)
O2D	0.8968 (12)	0.3941 (4)	0.4320 (7)	0.107 (6)
O3D	0.7335 (9)	0.3089 (8)	0.4324 (8)	0.254 (15)
O4D	0.9444 (15)	0.2781 (6)	0.4806 (7)	0.325 (22)
Ow	0.6423 (19)	−0.0780 (7)	0.2429 (12)	0.176 (6)

Little improvement resulted because the perchlorate ions were inadequately modelled. An essential step was realizing that the largest peak in the difference map near the perchlorate ions was not an alternative O-atom site but an alternative Cl-atom site, *viz*. ClD in Table 3. If a choice is made for the orientation of the cation about the crystallographic twofold rotation axis, then only one of the rotation-related sites of ClD can accommodate a perchlorate ion. This gives a principle for local ordering

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$) *for* $[Ni(C_{22}H_{48}N_6)](ClO_4)_2.0.530H_2O$

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
$C\bar{1}$ component				
Ni	0.5038 (5)	0.1588 (1)	0.2506 (3)	0.047 (1)
C1	0.8115 (7)	0.1517 (3)	0.0825 (4)	0.091 (2)
C2	0.7099 (6)	0.1541 (2)	0.1378 (4)	0.063 (1)
C3	0.2996 (6)	0.1635 (2)	0.3697 (4)	0.063 (1)
C4	0.2026 (7)	0.1656 (3)	0.4276 (4)	0.091 (2)
C11	0.6535 (6)	0.2340 (3)	0.1366 (4)	0.067 (1)
N12	0.5219 (6)	0.2387 (2)	0.1618 (4)	0.059 (1)
C13	0.4795 (7)	0.3186 (3)	0.1690 (4)	0.079 (2)
C14	0.5272 (7)	0.3529 (2)	0.2469 (4)	0.082 (2)
C14a	0.5068 (23)	0.4390 (3)	0.2407 (7)	0.141 (2)
C15	0.4547 (8)	0.3236 (3)	0.3085 (4)	0.079 (2)
N16	0.4878 (6)	0.2443 (2)	0.3345 (3)	0.059 (1)
C17	0.4058 (6)	0.2233 (3)	0.3944 (4)	0.067 (1)
C21	0.7834 (6)	0.1337 (3)	0.2177 (4)	0.064 (1)
N22	0.7165 (5)	0.1594 (3)	0.2816 (3)	0.052 (1)
C23	0.7829 (6)	0.1274 (3)	0.3565 (4)	0.073 (2)
C24	0.7304 (6)	0.0513 (3)	0.3754 (4)	0.080 (2)
C24a	0.8288 (7)	0.0155 (6)	0.4412 (6)	0.130 (1)
C25	0.5963 (6)	0.0579 (4)	0.3998 (4)	0.079 (1)
N26	0.4824 (6)	0.0767 (3)	0.3374 (4)	0.061 (1)
C27	0.3586 (6)	0.0842 (3)	0.3725 (4)	0.074 (2)
C31	0.6010 (6)	0.0966 (3)	0.1100 (4)	0.074 (2)
N32	0.5213 (6)	0.0712 (2)	0.1686 (4)	0.061 (1)
C33	0.3995 (6)	0.0299 (3)	0.1318 (4)	0.079 (1)
C34	0.2796 (6)	0.0797 (3)	0.1087 (4)	0.080 (2)
C34a	0.1756 (7)	0.0355 (5)	0.0526 (6)	0.130 (1)
C35	0.2153 (6)	0.1057 (4)	0.1750 (4)	0.073 (2)
N36	0.2907 (5)	0.1647 (3)	0.2254 (4)	0.052 (1)
C37	0.2187 (6)	0.1813 (3)	0.2910 (4)	0.064 (1)
Cl*A*	0.9027 (9)	0.3535 (3)	0.3664 (3)	0.144 (4)
O1*A*	0.8912 (23)	0.2826 (7)	0.3321 (13)	0.273 (7)
O2*A*	0.8182 (21)	0.3581 (14)	0.4202 (11)	0.417 (16)
O3*A*	1.0331 (12)	0.3647 (12)	0.4026 (12)	0.240 (7)
O4*A*	0.8685 (22)	0.4088 (10)	0.3105 (10)	0.238 (6)
Cl*B*	0.0678 (6)	0.3433 (3)	0.1148 (6)	0.251 (15)
O1*B*	0.1135 (13)	0.3019 (8)	0.1809 (8)	0.176 (10)
O2*B*	0.0679 (20)	0.2978 (8)	0.0506 (8)	0.531 (23)
O3*B*	−0.0608 (8)	0.3683 (8)	0.1166 (12)	0.720 (46)
O4*B*	0.1505 (10)	0.4051 (5)	0.1111 (10)	0.190 (14)
$P2_1/n$ component				
Ni″	0.4986 (3)	0.1585 (1)	0.2589 (2)	0.047 (1)
C1″	0.8069 (7)	0.1511 (5)	0.0913 (4)	0.091 (2)
C2″	0.7052 (5)	0.1536 (3)	0.1464 (3)	0.063 (1)
C3″	0.2940 (5)	0.1636 (3)	0.3777 (3)	0.063 (1)
C4″	0.1968 (7)	0.1658 (5)	0.4355 (4)	0.091 (2)
C11″	0.6480 (6)	0.2334 (3)	0.1445 (4)	0.067 (1)
N12″	0.5162 (6)	0.2379 (3)	0.1695 (3)	0.059 (1)
C13″	0.4730 (7)	0.3178 (3)	0.1761 (4)	0.079 (2)
C14″	0.5202 (8)	0.3527 (2)	0.2537 (5)	0.082 (2)
C14a″	0.4990 (25)	0.4387 (3)	0.2468 (8)	0.141 (2)
C15″	0.4477 (8)	0.3237 (3)	0.3155 (5)	0.079 (2)
N16″	0.4815 (6)	0.2446 (2)	0.3421 (3)	0.059 (1)
C17″	0.3996 (6)	0.2238 (4)	0.4021 (3)	0.067 (1)
C21″	0.7787 (5)	0.1339 (3)	0.2264 (3)	0.064 (1)
N22″	0.7113 (4)	0.1599 (3)	0.2901 (3)	0.052 (1)
C23″	0.7778 (6)	0.1286 (4)	0.3653 (3)	0.073 (2)
C24″	0.7259 (6)	0.0525 (4)	0.3847 (4)	0.080 (2)
C24a″	0.8245 (8)	0.0174 (7)	0.4509 (6)	0.130 (1)
C25″	0.5917 (6)	0.0589 (4)	0.4090 (4)	0.079 (1)
N26″	0.4777 (6)	0.0770 (3)	0.3463 (3)	0.061 (1)

Table 4 (*cont.*)

	x	y	z	U_{eq}
C27″	0.3538 (6)	0.0845 (4)	0.3812 (4)	0.074 (2)
C31″	0.5969 (6)	0.0957 (4)	0.1190 (4)	0.074 (2)
N32″	0.5172 (6)	0.0705 (3)	0.1776 (3)	0.061 (1)
C33″	0.3959 (6)	0.0287 (3)	0.1410 (4)	0.079 (1)
C34″	0.2755 (6)	0.0780 (4)	0.1175 (4)	0.080 (2)
C34a″	0.1721 (8)	0.0331 (7)	0.0616 (6)	0.130 (1)
C35″	0.2108 (6)	0.1042 (4)	0.1835 (4)	0.073 (2)
N36″	0.2855 (4)	0.1638 (3)	0.2335 (3)	0.052 (1)
C37″	0.2131 (5)	0.1807 (4)	0.2989 (3)	0.064 (1)
Cl*C*	0.0909 (8)	0.3542 (3)	0.1323 (3)	0.144 (5)
O1*C*	0.1043 (21)	0.2845 (6)	0.1690 (11)	0.268 (4)
O2*C*	0.1819 (18)	0.3596 (12)	0.0821 (10)	0.407 (18)
O3*C*	−0.0373 (11)	0.3613 (11)	0.0912 (11)	0.250 (7)
O4*C*	0.1146 (20)	0.4115 (9)	0.1867 (9)	0.243 (7)
Cl*D*	0.8649 (6)	0.3201 (3)	0.4266 (2)	0.129 (6)
O1*D*	0.8875 (11)	0.2915 (6)	0.3566 (4)	0.137 (5)
O2*D*	0.9043 (11)	0.3953 (3)	0.4332 (6)	0.135 (5)
O3*D*	0.7302 (7)	0.3149 (7)	0.4305 (7)	0.208 (9)
O4*D*	0.9375 (12)	0.2786 (5)	0.4862 (5)	0.236 (15)
O*w*	0.6538 (15)	−0.0784 (7)	0.2480 (8)	0.145 (4)

and results in hydrogen bonds O1*D* to N22 (effectively coincident with O1*A* to N22) and O3*D* to N16.

Refinement then proceeded using a twin-disorder model in space group $C\bar{1}$, which allowed a lowering of diffraction symmetry and the violation of the c-glide absence condition. This used six occupancy parameters, one for each of the two $1 - x, y, \frac{1}{2} - z$-related orientations of the cation and two anions, *A* and *D*. Constraints to maintain chemical content reduce the occupancy degrees of freedom to three.

Displacement parameters were a separate consideration. Cation atoms related by the pseudo-twofold rotation were constrained to have this symmetry relationship exactly. Atoms Zn, C14 and C14a which lie on the pseudo axis had U^{12} and U^{23} set to zero. The twofold rotation symmetry was also used to relate the *TLX* displacement parameters used to describe the anions. Initially both orientations of the anion on one side of the cation were associated with a single set of parameters, later altered so that each component had its own set of 15 *TLX* parameters.

The final model development used three sites for the anion and included a water molecule with $1 - x, y, \frac{1}{2} - z$ used to disorder the structure in a partially twinned $C\bar{1}$ crystal. The third anion site, *B* in Table 3, was deduced by the apparent disorder of the *A* anion about the bond O1*A*—Cl*A* where O1*A* is hydrogen-bonded to an N—H group. The water is associated with the *D* anion and pushes the *D* anion into a position where two O atoms are involved in N—H···O hydrogen bonds. Each of the other anion-site options involve only one such bond. All perchlorates were constrained to have the same exactly tetrahedral geometry and a common refinable bond length.

Subsequent refinement used ten occupancy parameters, one each for both the x, y, z- and $1 - x, y, \frac{1}{2} - z$-

Table 5. *Selected geometric parameters (Å) for* $[Zn(C_{22}H_{48}N_6)](ClO_4)_2.0.608H_2O$

Zn—N12	2.196 (2)	Zn—N16	2.196 (2)
Zn—N22	2.196 (2)	Zn—N26	2.196 (2)
Zn—N32	2.196 (2)	Zn—N36	2.196 (2)
C1—C2	1.549 (6)	C3—C4	1.549 (6)
C2—C11	1.524 (3)	C11—N12	1.497 (4)
N12—C13	1.498 (4)	C13—C14	1.509 (4)
C14—C14a	1.529 (5)	C14—C15	1.509 (4)
C15—N16	1.500 (4)	C3—C17	1.524 (3)
N16—C17	1.499 (4)	C2—C21	1.524 (3)
C21—N22	1.497 (4)	N22—C23	1.497 (4)
C23—C24	1.509 (4)	C24—C24a	1.529 (5)
C24—C25	1.509 (4)	C25—N26	1.500 (4)
C3—C27	1.524 (3)	N26—C27	1.499 (4)
C2—C31	1.524 (3)	C31—N32	1.497 (4)
N32—C33	1.497 (4)	C33—C34	1.509 (4)
C34—C34a	1.529 (5)	C34—C35	1.509 (4)
C35—N36	1.500 (4)	C3—C37	1.524 (3)
N36—C37	1.499 (4)	Cl*A*—O1*A*	1.376 (3)
N22···O1*A*	2.882 (9)	N36···O1*B*	2.990 (14)
N36···O1*C*	2.909 (8)	N22···O1*D*	3.060 (12)
N16···O3*D*	3.037 (11)	N32···O*w*	3.083 (15)
O4*C*^{i}···O*w*	3.134 (23)	O1*D*^{ii}···O*w*	2.839 (22)

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

related sites of the cation, three anions and one water. This involved seven degrees of freedom. The refined occupancies were found to be consistent with the intergrowth concept described in the Appendix, implying four occupancy parameters p_m with $\Sigma_m p_m = 1$. This model was then adopted. For the $C\bar{1}$ case, anion C' (the $1-x, y, \frac{1}{2}-z$-related equivalent of C) and A were assumed identical and $1-x, y, \frac{1}{2}-z$-related to anions A' and C so that C was omitted and occupancies p_1+p_3, p_1+p_4, p_1, p_3 and p_3 were used for the cation, anions A, B and D, and the water, respectively, with p_2+p_4, p_2+p_3, p_2, p_4 and p_4 for the $1-x, y, \frac{1}{2}-z$-related sites. The use of space group $C\bar{1}$ rather than $P\bar{1}$ imposes $p_4 = p_3$ $[= \frac{1}{2} - (p_1+p_2)/2]$ leaving just two degrees of freedom for occupancy.

The near-1:1 twinning creates observations that are essentially $Y(hkl) = |F_A(hkl)|^2 + |F_B(hkl)|^2$, where the subscripts A and B denote symmetrized components (see the Appendix). Only the weak $h0l$, h even, l odd reflections see the minor component $F_B(hkl)$ in isolation. $F_B(hkl)$ is associated with the departure from $C2/c$ symmetry. The overall scale for the $F_B(hkl)$ component correlates with $p_1 - p_2$ and the displacement of the Zn atom from the rotation axis at $\frac{1}{2}, y, \frac{1}{4}$. The lack of $h+k$ odd data precludes separating the cation into two overlapping cations with individual occupancies p_2 and p_4. As a consequence the fit to $h0l$, h even, l odd is poor. However, the indices of the five observed reflections also correspond to observed reflections of the Ni structure which permitted the additional parameterization.

Refinement of the Ni structure was initiated from the refined Zn structure using space group $P2_1/n$ by making $p_1 = p_2$. Making $p_3 > p_4$ chooses between alternative origins. Because refinement statistics for the $h+k$ odd reflections were poor, reflections were segmented according to whether $\sin\theta/\lambda$ was greater or less than 0.2. It was immediately obvious that reflections at high angle were calculated too small, which is consistent with the need for the displacement of the cation from the pseudo-rotation axis at $\frac{1}{2}, y, \frac{1}{4}$ to be larger for the $P2_1/n$ intergrowths than for the $C\bar{1}$ intergrowths. (The low-angle data are primarily associated with occupancy modulation.) The limitations of $h+k$ odd data implied that the only refinable differences between intergrowth components involve the location and orientation of identical objects. As a consequence reflections were calculated too small in general.

The refinement program *RAELS* had to be modified to allow this final refinement of a partially twinned structure in space group $P\bar{1}$. The drop in $R(F)$ associated with allowing p_1 to not equal p_2 and including a twin parameter was only 0.0013 for $h+k$ even data excluding the $h0l$, l odd reflections. However the $h0l$, h even, l odd reflections now fitted much better than for the Zn structure. The Ni atom is much closer to the pseudo-twofold rotation axis for the $C\bar{1}$ components than for the $P2_1/n$ components, implying that the use of a cation position that is the average of the values for the two space groups creates a displacive-mode parameter that is too large for the $C\bar{1}$ component. Since the $P2_1/n$ component has a water of crystallization on one side of the cation but not the other, it is reasonable to assume that in the Zn analogue the cation is also closer to $\frac{1}{2}, y, \frac{1}{4}$

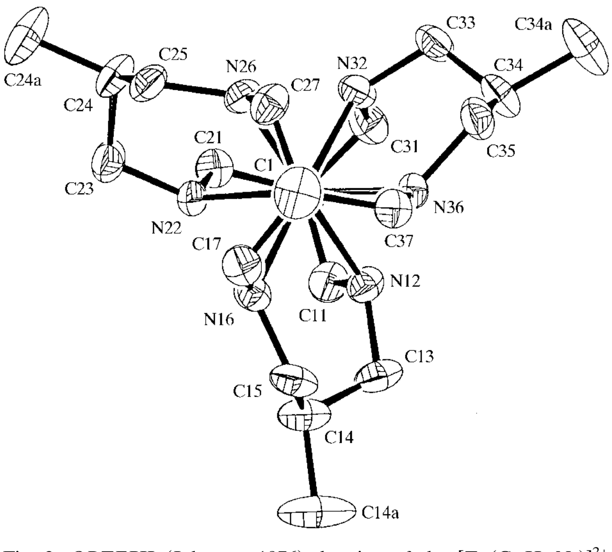


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of the $[Zn(C_{22}H_{48}N_6)]^{2+}$ cation viewed down the pseudo-threefold axis, which is coincident with C1, C2, Zn, C3 and C4. Displacement ellipsoids are drawn to represent 30% probability surfaces. H atoms are omitted for clarity. A similarly oriented view of the Ni-complex cation exhibits the same geometric features.

Table 6. *Selected geometric parameters (Å) for $[Ni(C_{22}H_{48}N_6)](ClO_4)_2.0.530H_2O$*

Ni—N12	2.136 (2)	Ni—N16	2.137 (2)
Ni—N22	2.142 (2)	Ni—N26	2.143 (2)
Ni—N32	2.143 (2)	Ni—N36	2.141 (2)
C1—C2	1.535 (5)	C3—C4	1.535 (5)
C2—C11	1.522 (3)	C11—N12	1.483 (4)
N12—C13	1.488 (4)	C13—C14	1.503 (3)
C14—C14a	1.534 (4)	C14—C15	1.503 (3)
C15—N16	1.493 (4)	C3—C17	1.521 (3)
N16—C17	1.498 (4)	C2—C21	1.520 (3)
C21—N22	1.482 (4)	N22—C23	1.488 (4)
C23—C24	1.503 (3)	C24—C24a	1.534 (4)
C24—C25	1.503 (3)	C25—N26	1.494 (4)
C3—C27	1.520 (3)	N26—C27	1.499 (4)
C2—C31	1.521 (3)	C31—N32	1.484 (4)
N32—C33	1.488 (4)	C33—C34	1.503 (3)
C34—C34a	1.534 (4)	C34—C35	1.503 (3)
C35—N36	1.494 (4)	C3—C37	1.520 (3)
N36—C37	1.497 (4)	Cl*A*—O1*A*	1.386 (3)
N22···O1*A*	2.853 (15)	N36···O1*B*	3.042 (13)
N36″···O1*C*	2.919 (14)	N22″···O1*D*	3.044 (11)
N16″···O3*D*	3.007 (10)	N32″···O*w*	3.129 (13)
O4C^{i}···O*w*	3.142 (26)	O1D^{ii}···O*w*	2.929 (17)

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

for the $C\bar{1}$ component which has no water of crystallization.

The *TLX* displacement parameters for anions *A* and *C* were constrained to be pseudosymmetry related. H atoms were included in geometrically sensible positions and given the same anisotropic displacement parameters as the atoms to which they are attached.

The overriding chemical interest was to obtain reliable geometry for the cation. Personal intervention in the refinement process was necessary. The $C2/c$ component of the scattering density dominates the refinement process, *i.e.* the occupancy-weighted mean of atom positions are well determined as are the mean-square displacements from these means. However, it is usually difficult to make component atoms of a disorder switch places during refinement, even with the aid of constraints and restraints. If errors are evaluated with the restraints included as observations then geometric features that differ from their ideal value by more than the calculated error are associated with a systematic error, either in the restraint or in the relative positions of component atoms of a disorder. In this context differences in pseudoequivalent features prove to be more reliable restraints than absolute values for individual features, and distance restraints hold better than angle restraints.

Obvious cases of systematic error may be remedied by file editing prior to further refinement. In less obvious cases, overlapping atoms involved in disorder can be edited to coincide on their mean position before restraint-assisted refinement again tries to resolve the problem. As refinement progresses weights on restraints can be reduced. If a model imposed by the restraints is consistent with the scattering density these weakened restraints will maintain geometric features. The inherent threefold symmetry of the cation was used to impose restraints on differences between pseudoequivalent bond lengths. In the initial stages the pseudo-32 symmetry was also used to impose additional distance difference restraints. Angle difference restraints were imposed using differences between second-nearest-neighbour atoms. Torsional angles were monitored to detect likely errors. Sensible refinement is implied by the fact that the inherent threefold symmetry of the cation was obtained for the unconstrained torsional angles.

The observed reflections that violate $C2/c$ absences are modelled by very few parameters. The vast improvement with a slightly expanded model for the Ni complex was significant. We can be confident about the intergrowth model and the nature of the 'average cation'. However, it is not feasible to remove the restraints and constraints even though the limitations of the weak reflections can probably be associated with these restrictions on the model. The high libration associated with the ClO_4^- anions of the $C\bar{1}$ components is not surprising since there is no water associated with this component.

5. Comments

Two substructures correspond to alternative orientations of a $C\bar{1}$ structure with no water, and two substructures correspond to alternative origins of a $P2_1/n$ structure for which x = 1. Partial twinning also occurs. For the crystals studied the volume ratios of the substructures were 0.299 (6): 0.093 (6): 0.304 (4): 0.304 (4) with twin ratio 0.466 (10): 0.534 (M = Zn) and 0.299 (4): 0.171 (4): 0.306 (4): 0.224 (4) with twin ratio 0.635 (13): 0.365 (M = Ni).

The Zn^{II} and Ni^{II} crystal structures are isomorphous and both cations display MN_6 geometries that are close to octahedral. The average trigonal twist angles φ (average magnitude of torsional angle N12···C2···C3···N16 and its pseudoequivalents) are 60.7 (2) (Zn) and 62.4 (2)° (Ni) and the average polar angles θ (average of C2···M—N12 and its pseudoequivalents) are 52.8 (1) (Zn) and 53.0 (1)° (Ni). Values for an octahedron are φ = 60 and θ = 54.74°. Each cation has effective C_3 symmetry and all the N centres have the same *R* (or *S* for the enantiomer) configuration. This geometry is in contrast to that found in the Cd^{II} and Hg^{II} complexes of the same ligand in which an essentially trigonal-prismatic coordination geometry (φ = 0°) is adopted for the MN_6 core (Bygott *et al.*, 1999). These latter structures have an effective C_{3h} symmetry where three N centres have an *R* configuration and three have an *S* configuration. This geometry has not been observed previously for saturated amine complexes, and this ligand configuration has a larger natural cavity than that of the pseudo-octahedral configuration of the Zn^{II} and

Ni^{II} structures. The C_{3h} (R_3, S_3) form thus appears to be preferred for larger metal ions such as Cd^{II} and Hg^{II} when no structural preferences arise from ligand-field-stabilization or π-bonding effects.

The average Ni—N bond length of 2.140 (3) Å is longer than the value of 2.110 Å (range ± 0.010 Å) in the smaller, more flexible $[Ni\{(NH_3)_2\text{-sar}\}]^{4+}$ homologue [$\{(NH_3)_2$-sar$\}$ = 1,8-diammonio-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane], which has a fairly typical Ni—N(secondary amine) distance. However, in this smaller homologue, the ligand conformation is strained by the Ni^{II} ion and has a trigonal twist φ of 47° (range ± 1°) compared with 24° (range ± 7°) for the metal-free ligand (Comba *et al.*, 1985). This distortion also changes the centre-to-N distance of the ligand cavity in order to accommodate the bond-length demands of the Ni. Less ligand deformation is associated with the larger Ni cage complex of *fac*-Me_5-D_{3h}tricosaneN_6 because of a stronger resistance to contraction of the centre-to-N distance in the more crowded, less flexible ligand conformation. This in fact results in an Ni—N bond length that is larger than is optimal by about 0.03 Å.

In contrast, the average Zn—N bond lengths for our reported structure [2.196 (2) Å] and for $[Zn\{(NH_3)_2\text{-sar}\}]^{4+}$ (2.190 Å, range ± 0.012 Å) are essentially the same and close to the expected value (*ca* 2.20 Å) for $Zn^{II}N_6$(secondary amine) distances. Also, the twist angles of 29 ± 1° for $[Zn\{(NH_3)_2\text{-sar}\}]^{4+}$ are close to those of the metal-free ligand.

In conclusion, we see that for the less flexible cage structures reported in this paper, the major effect of a mismatch between the preferred cavity size and the preferred *M*—N bond length is a change in the size of the MN_6 chromophore. This important aspect of the larger cage systems can be used to develop new chemistry for MN_6 complexes (Geue *et al.*, 1994, 1999).

APPENDIX A

A1. *Selection of space group*

The crystal structure can be regarded as a commensurately modulated structure with four formula units per cell and a monoclinic $C2/c$ space group describing the idealized parent structure. The cation has inherent 3 symmetry but approximates 32 symmetry and must lie on a twofold axis in the idealized parent structure. The fact that this twofold axis cannot exist on a local scale implies ordering of the structure will lower the symmetry. This gives four possible subgroups of $C2/c$ that exclude a twofold rotation axis while allowing four equivalent positions per unit cell. These are $C\bar{1}$, Cc, $P2_1/n$ and $P2_1/c$. It was shown that packing arguments preclude a c glide. Weak observed $h0l$, l odd reflections are consistent with $P2_1/n$ for $h + k$ odd but $C\bar{1}$ for $h + k$ even.

It is possible to refine the structure assuming an intergrowth model in which different regions of the crystal correspond to different orderings of the necessarily disordered $C2/c$ average structure. In each region we pick four out of eight equivalent positions of $C2/c$. For each space group we may pick either x, y, z or $-x, y, \frac{1}{2} - z$ to describe the reference asymmetric unit.

A2. *Distribution of information*

We let m = 1, 2 correspond to the components with space group $C\bar{1}$ and m = 3, 4 correspond to the components with space group $P2_1/n$. We assume perfectly ordered component structures each with its own occupancy factor p_m and say

$$F(hkl) = \sum_m p_m F_m(hkl)$$

where

$$F_{m+1}(hkl) = (-1)^l F_m(\bar{h}k\bar{l}), m = 1, 3.$$

Since $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ is a symmetry element of $P2_1/n$ we can also say that

$$F_4(hkl) = (-1)^{h+k} F_3(hkl).$$

$F(hkl)$ can then be re-expressed as

$$\begin{aligned} F(hkl) = {} & (p_1 + p_2)[F_1(hkl) + (-1)^l F_1(\bar{h}k\bar{l})]/2 \\ & + (p_1 - p_2)[F_1(hkl) - (-1)^l F_1(\bar{h}k\bar{l})]/2 \\ & + (p_3 + p_4)[1 + (-1)^{h+k}]F_3(hkl)/2 \\ & + (p_3 - p_4)[1 - (-1)^{h+k}]F_3(hkl)/2. \end{aligned}$$

The information distribution can now be assessed. The scattering density can be described as the sum of components each with the symmetry of a different irreducible representation (Rae *et al.*, 1990). Each component can be designated a space-group label corresponding to the subgroup of symmetry elements which transform the component into itself. (In our example the remaining symmetry operations of $C2/c$ turn the component into minus itself.) The structure-factor information can then be described using the Fourier transforms of the symmetrized scattering-density components.

The $C2/c$ component corresponds to $h + k$ even and has

$$\begin{aligned} F_A(hkl) & = [F(hkl) + (-1)^l F(\bar{h}k\bar{l})]/2 \\ & = (p_1 + p_2)[F_1(hkl) + (-1)^l F_1(\bar{h}k\bar{l})]/2 \\ & \quad + (p_3 + p_4)F_3(hkl). \end{aligned}$$

The $C\bar{1}$ component corresponds to $h + k$ even and has

$$\begin{aligned} F_B(hkl) & = [F(hkl) - (-1)^l F(\bar{h}k\bar{l})]/2 \\ & = (p_1 - p_2)[F_1(hkl) - (-1)^l F_1(\bar{h}k\bar{l})]/2. \end{aligned}$$

The $P2_1/n$ component corresponds to $h + k$ odd and has

$$F_C(hkl) = F(hkl) = (p_3 - p_4)F_3(hkl).$$

The space group for the disordered structure arising from unequal but positive amounts of the four component structures is $P\bar{1}$, this being the common subgroup of $C\bar{1}$ and $P2_1/n$. However, when $p_1 = p_2$, $F_B(hkl) = 0$, and the scattering density corresponds to $P2_1/n$. Likewise, when $p_3 = p_4$, $F_C(hkl) = 0$, and the scattering density corresponds to $C\bar{1}$. When h is even and $k = 0$, $F_A(hkl) = 0$ if l is odd and $F_B(hkl) = 0$ if l is even.

The crystal may also twin so as to give an observed intensity

$$Y(hkl) = (1-q)|F(hkl)|^2 + q|F(\bar{h}k\bar{l})|^2.$$

For $h + k$ odd data $Y(hkl) = |F_C(hkl)|^2$ as before with $Y(hkl) = Y(\bar{h}k\bar{l})$.

However, for $h + k$ even reflections

$$Y(hkl) = |F_A(hkl)|^2 + |F_B(hkl)|^2 + (1-2q)[F_A(hkl)F_B(hkl)^* + F_A(hkl)^*F_B(hkl)].$$

so that

$$Y(hkl) - Y(\bar{h}k\bar{l}) = 2(1-2q)[F_A(hkl)F_B(hkl)^* + F_A(hkl)^*F_B(hkl)],$$

reducing the difference between the intensities of pseudoequivalent reflections.

Twinning and disorder reduced the effect of $F_B(hkl)$ and $F_C(hkl)$ on calculated intensities and the limited number of weakly observed reflections that see these contributions in isolation must be described by a very restricted parametrization to avoid refinement problems.

*A*3. *Implementation of the structure-factor calculation*

The program *RAELS* was modified to include a factor as an additional unrefinable multiplier of the contribution of an atom to the structure factor. Using a job-specific subroutine, the default value of 1.0 was modified according to atom number, symmetry operator and whether $h + k$ was even or odd. In this way the equivalent positions of $P2_1/n$ could be used to simulate both $P2_1/n$ and $C\bar{1}$ components of an average structure of $P\bar{1}$ symmetry. Components related by the disorder operation $1 - x, y, \frac{1}{2} - z$ were each included in the asymmetric unit with relevant positional and displacement parameters constrained to hold this relationship exactly.

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