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The Role Played by Water in Spin State Variations among Nickel(II) Halide Complexes Containing (7*R*, 14*S*)-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane

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A complex dihydrate formed with nickel(II) bromide and the title macrocyclic ligand (*meso*-$Me_6[14]aneN_4$) crystallizes in triclinic space group P$\bar{1}$ and in orthorhombic space group Pcab. The crystal and molecular structures of the two crystal modifications have been determined by single crystal X-ray diffraction. In each compound, the nickel(II) is surrounded by a square-planar array of nitrogen atoms, giving low-spin complexes. In both compounds, water of crystallization and bromide ions are located above the hydrogen atoms of N–H groups and form hydrogen-bonded chelate rings of the type $\overline{\mathrm{Ni{-}N{-}H\cdots Br^{-}\cdots H{-}O\cdots H{-}N}}$. The N–H groups adjacent to the single methyl carbon and the geminal dimethyl carbon interact with bromide ion and water, respectively, in the P$\bar{1}$ form, whereas *vice versa* in the Pcab form. Water molecules in the present crystals and those in the previously reported crystal structure of [Ni(*meso*-$Me_6[14]aneN_4$)]$Cl_2\cdot 2H_2O$ are involved in the same type of specific hydrogen-bonds. Because of the specific hydrogen-bonding effects, the presence of water prevents coordination of not only water itself but also halide ions, yielding thereby low-spin four coordinate complexes.

Nickel(II) halide (Cl^- and Br^-) and the title macrocyclic ligand form orange low-spin complexes, [Ni(*meso*-$Me_6[14]aneN_4$)]$X_2\cdot 2H_2O$, and violet high-spin complexes, [NiX_2(*meso*-$Me_6[14]aneN_4$)].[1,2] The macrocyclic ligand *meso*-$Me_6[14]aneN_4$ is constrained by steric requirements to coordinate in a single plane. From their electronic spectra and magnetic properties[1] and the X-ray analyses on [Ni(*meso*-$Me_6[14]aneN_4$)]$Cl_2\cdot 2H_2O$ and [$NiCl_2$(*meso*-$Me_6[14]aneN_4$)],[3] it has been shown that the orange dihydrates are square-planar four coordinate complexes having a singlet ground state, whereas the violet anhydrides are *trans*-dihalogeno six coordinate complexes having a triplet ground state. The solid, orange diamagnetic dihydrates are converted upon heating to violet paramagnetic anhydrides.[4] Conversely, the solid, violet, paramagnetic anhydrous complexes readily revert to [Ni(*meso*-$Me_6[14]aneN_4$)]$X_2\cdot 2H_2O$ when moisture is available.[1] Of particular interest is the fact that the low-spin four coordinate complexes are dihydrates, whereas the six coordinate high-spin complexes are anhydrides. Although water has considerably high coordinating ability as compared with halide ion, the water molecules in the dihydrates are not involved in coordination.

Spin states of the complexes are affected also in the solution states by the presence or the absence of water. The anhydrous, violet high-spin complex dissolves in water to give an orange solution, which indicates that the complex turns to the low-spin four coordinate complex.[1] When the anhydrous high-spin complex is dissolved in freshly purified stabilizer-free chloroform, almost all the complexes remain high-spin six coordinate, but the solution contains a small amount of the four coordinate singlet form, giving an equilibrium mixture of the low- and high-spin species. The amount of the singlet species depends on the water content in the chloroform solution and increases with an increase in the amount of water in solution.[5]

Busch has pointed out the importance of the role played by water in the spin state variations and proposed a model for the interaction between water and the complex ions.[1,2]

The present study is a part of series of investigations on the spin state variations, *viz.*, coordination number isomerism among the nickel(II) complexes of the title and related macrocyclic ligands.[3-7] The main feature of interest in the present study is the elucidation of the role of water in spin-state variations. For this purpose, the crystal structures of two crystal modifications of [Ni(*meso*-$Me_6[14]aneN_4$)]$Br_2\cdot 2H_2O$ were determined by X-ray analyses. The dispositions of the water molecules in the vicinities of the nickel(II) ions in the present crystals and those in the previously reported crystal structures of [Ni(*meso*-$Me_6[14]aneN_4$)]$Cl_2\cdot 2H_2O$[3] and [NiF_2(*meso*-$Me_6[14]aneN_4$)]$\cdot 5H_2O$[7] were examined.

Experimental

Materials. The bromide dihydrate of the complex ion, [Ni(*meso*-$Me_6[14]aneN_4$)]$Br_2\cdot 2H_2O$, was prepared from the corresponding perchlorate salt [Ni(*meso*-$Me_6[14]aneN_4$)]-$(ClO_4)_2$[8] by ion exchange (Dowex 1X8). Slow evaporation of the eluate from the column yielded mixture of orange needle (P$\bar{1}$) and large reddish orange plate (Pcab) crystals of [Ni(*meso*-$Me_6[14]aneN_4$)]$Br_2\cdot 2H_2O$. The orange and reddish orange forms can be separated mechanically under a microscope or more easily in carbon tetrachloride, using the difference in the crystal densities. The density of neat carbon tetrachloride (D=1.59 g cm^{-3}), in which the compounds are not soluble, is between densities of the crystals of the reddish orange (D=1.57 g cm^{-3}) and the orange (D=1.62 g cm^{-3}) form. The crystals of the compounds consists of 61% of the orange and 39% of the reddish orange form. Found for the orange (P$\bar{1}$) form; C, 35.56; H, 7.41; N, 10.24; Br, 30.09%. Found for the reddish orange (Pcab) form; C, 35.40; H, 7.44; N, 10.11; Br, 30.09%. Calcd for $NiC_{16}H_{40}N_4Br_2O_2$: C, 35.65; H, 7.48; N, 10.40; Br, 29.64%.

X-Ray Analyses. Preliminary X-ray work showed that the crystals of the orange complex belong to the triclinic space group P$\bar{1}$, whereas those of the reddish orange complex belong to the orthorhombic space group Pcab. Intensities of reflections were measured on a Rigaku automated four circle diffractometer AFC-5 with graphite monochromatized Mo *Kα*

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radiation ($\lambda = 0.71073$ Å), the θ-2θ scan technique being employed.

For the orange $P\bar{1}$ form, a specimen with dimensions of $0.40 \times 0.44 \times 0.36$ mm was used for the intensity measurements. A total of 5126 reflections was measured up to $2\theta = 70°$. Of these, 3681 reflections with $|F_o| > 3\sigma(|F_o|)$ were used in the calculations. Crystal data are: Triclinic, $P\bar{1}$, $Z=1$, $a=8.650(1)$, $b=9.417(1)$, $c=7.813(1)$ Å, $\alpha=94.47(1)$, $\beta=100.07(1)$, $\gamma=115.39(1)°$, $U=557.1(1)$ Å^3, $D_x=1.62$, $D_m=1.61$ g cm^{-3}, μ(Mo $K\alpha$)$=46.84$ cm^{-1}.

For the reddish orange Pcab form, a specimen shaped approximately into a sphere with a diameter of 0.42 mm was used for the intensity measurements. A total of 4935 intensities was measured up to $2\theta = 70°$. Of these, 1938 reflections with $|F_o| > 3\sigma(|F_o|)$ were used in the calculations. Crystal data are: Orthorhombic, Pcab, $Z=4$, $a=14.146(2)$, $b=15.739(2)$, $c=10.338(2)$ Å, $U=2301.7(5)$ Å^3, $D_x=1.57$, $D_m=1.56$ g cm^{-3}, μ(Mo $K\alpha$)$=45.40$ cm^{-1}.

The intensity data used in the structure refinements were corrected for Lorentz and polarization factors and for absorptions. In the absorption corrections, the specimen of the Pcab form was assumed to be a sphere, whereas, for the $P\bar{1}$ form, the numerical Gaussian integration method[9] was used. Both the structures were solved by the heavy atom method and refined by a block-diagonal least-squares method. The weighting scheme, $w=[\sigma_{\text{count}}^2+(0.015|F_o|)^2]^{-1}$, was employed. All hydrogen atoms were located by the difference Fourier syntheses, and included in the final refinements with the isotropic temperature factors. The scattering factors for non-hydrogen atoms were taken from International Tables for X-Ray Crystallography.[10] For hydrogen atom, the values given by Stewart *et al.* were used.[11] The final R indices were $R=0.046$ and $R_w=0.051$ for the $P\bar{1}$ form, and $R=0.056$ and $R_w=0.046$ for the Pcab form, respectively. Atomic parameters for each crystal are given in Table 1.[12]

The calculations were carried out on the HITAC M-180 computer at the Computer Center of the Institute for Molecular Science with Universal Crystallographic Computation Program System UNICS III.[13]

Results and Discussion

Description of the Molecular and Crystal Structures of $[Ni(\text{meso-}Me_6[14]aneN_4)]Br_2 \cdot 2H_2O$. In both the $P\bar{1}$ and Pcab forms, the nickel(II) ions are required to lie on a center of symmetry. Table 2 lists bond lengths and angles within the complex ion in the two crystal modifications. As shown in Table 2, the structures of the complex ion, $[\text{Ni}(\textit{meso-}\text{Me}_6[14]\text{aneN}_4)]^{2+}$, in the $P\bar{1}$

TABLE 1. FRACTIONAL ATOMIC COORDINATES ($\times 10^5$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS (Å^2) FOR NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B_{eq}/Å^2
A) Atomic parameters for the $P\bar{1}$ form				
Ni	50000(0)	50000(0)	50000(0)	1.8
Br	91122(4)	72142(4)	33329(4)	3.9
N(1)	54174(25)	71608(23)	59263(24)	2.3
N(2)	72047(24)	52436(23)	64421(23)	2.2
C(1)	30084(37)	63990(33)	34307(34)	3.2
C(2)	38078(38)	73363(34)	52526(37)	3.5
C(3)	62160(32)	78122(28)	78650(28)	2.5
C(4)	80462(31)	78877(30)	82557(30)	2.8
C(5)	81468(31)	63116(30)	82000(28)	2.6
C(6)	64483(43)	95240(33)	82922(39)	3.8
C(7)	50420(38)	67504(35)	89542(33)	3.4
C(8)	100766(36)	66409(37)	86415(37)	3.7
O	74235(33)	97034(32)	37985(34)	5.3
B) Atomic parameters for the Pcab form				
Ni	0(0)	0(0)	0(0)	2.3
Br	15510(4)	13181(3)	21769(6)	5.3
N(1)	−476(25)	−2571(21)	18432(34)	2.9
N(2)	10906(24)	−7357(20)	−3193(32)	2.7
C(1)	−10938(33)	9331(33)	17122(49)	4.0
C(2)	−9183(35)	1189(34)	24296(46)	4.3
C(3)	1689(30)	−11396(28)	23247(43)	3.2
C(4)	11532(33)	−13718(27)	18747(49)	3.5
C(5)	12810(33)	−15291(27)	4493(49)	3.5
C(6)	1662(42)	−11524(35)	38113(50)	5.3
C(7)	−5712(35)	−17573(33)	18117(55)	4.7
C(8)	22735(42)	−18691(35)	1991(52)	5.6
O	−22326(27)	−3748(24)	51086(37)	5.8

The equivalent isotropic thermal parameter is calculated using the expression $B_{eq}=4/3\,(\sum_i\sum_j a_i a_j \beta_{ij})$, where the a_i's are the unit-cell edges in direct space.

TABLE 2. BOND DISTANCES (l/Å) AND ANGLES (ϕ/°) WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

	The $P\bar{1}$ form	The Pcab form
(A) Bond lengths		
Ni–N(1)	1.961(2)	1.949(4)
Ni–N(2)	1.947(2)	1.957(3)
N(2)–C(1′)	1.491(4)	1.473(6)
N(1)–C(2)	1.482(4)	1.495(6)
N(1)–C(3)	1.508(3)	1.507(6)
N(2)–C(5)	1.501(3)	1.504(6)
C(1)–C(2)	1.490(4)	1.501(7)
C(3)–C(4)	1.528(4)	1.513(6)
C(4)–C(5)	1.521(4)	1.505(7)
C(3)–C(6)	1.538(4)	1.537(7)
C(3)–C(7)	1.523(4)	1.524(7)
C(5)–C(8)	1.530(4)	1.525(8)
(B) Bond angles		
N(1)–Ni–N(2)	93.5(1)	94.0(1)
Ni–N(1)–C(2)	108.6(1)	110.0(3)
Ni–N(2)–C(1′)	106.5(1)	107.0(3)
Ni–N(1)–C(3)	119.1(2)	120.5(3)
Ni–N(2)–C(5)	125.5(2)	122.9(3)
C(2)–N(1)–C(3)	113.8(2)	113.5(3)
C(1′)–N(2)–C(5)	109.9(2)	109.9(3)
N(2′)–C(1)–C(2)	106.3(2)	107.6(4)
N(1)–C(2)–C(1)	107.4(3)	105.9(4)
N(1)–C(3)–C(4)	107.3(2)	107.9(3)
N(2)–C(5)–C(4)	111.9(2)	111.0(4)
N(1)–C(3)–C(6)	110.3(2)	110.0(4)
N(1)–C(3)–C(7)	109.9(2)	109.5(4)
N(2)–C(5)–C(8)	110.6(2)	111.5(4)
C(3)–C(4)–C(5)	117.3(2)	116.8(4)
C(4)–C(3)–C(6)	107.6(2)	107.9(4)
C(4)–C(3)–C(7)	111.9(2)	111.8(4)
C(4)–C(5)–C(8)	109.3(2)	109.5(4)
C(6)–C(3)–C(7)	109.9(3)	109.8(4)

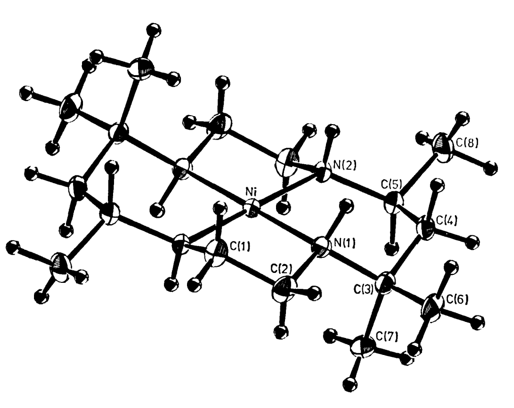
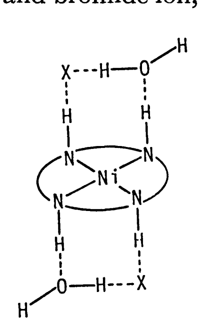


Fig. 1. A perspective drawing of [Ni(*meso*-Me_6[14]-aneN_4)]$^{2+}$ in the crystal structure of the $P\bar{1}$ form.

and Pcab forms are not significantly different. Figure 1 shows a perspective drawing of [Ni(*meso*-Me_6[14]-aneN_4)]$^{2+}$ in the $P\bar{1}$ form, which is essentially the same as those in the Pcab form and in [Ni(*meso*-Me_6[14]-aneN_4)]$Cl_2 \cdot 2H_2O$.[3] The nickel(II) is surrounded by four secondary nitrogen atoms of the macrocyclic ligand in a single plane, yielding a square-planar, diamagnetic nickel(II) complex. The average Ni–N bond distances are 1.954(7) Å for the $P\bar{1}$ form and 1.953(4) Å for the Pcab form, which are in the normal range for a low-spin nickel(II) complex with four planar nitrogen donors.[3,14,15] The macrocyclic skeleton adopts the most stable conformation: the six-membered chelate rings take the chair form with the C(5)–CH_3 bonds in equatorial positions; the five-membered rings are in the gauche conformation.

Three significant deviations from tetrahedral angles are noted. These are the large angles of Ni–N(1)–C(3), Ni–N(2)–C(5), and C(3)–C(4)–C(5) (see Table 2). These distortions are in common with six-membered chelate rings of metal complexes which have the title ligand in planar coordination.[3,7,16]

Figures 2(a) and 2(b) show dispositions of bromide ions and water of crystallization around the complex ions, as viewed along the normal to the coordination plane, in the $P\bar{1}$ and Pcab forms, respectively. The structures around the nickel(II) ions in the two different crystal modifications are very similar to each other as depicted in Fig. 2 in the following sense: (i) the bromide ions are located above the hydrogen atoms of N–H groups and the oxygen atoms of water lie also above the hydrogen atoms of the other crystallographically independent N–H groups; (ii) bromide ions and water molecules are involved in the hydrogen-bonds of the type shown in **1**, forming hydrogen-bonded chelate rings. The hydrogen-bond distances are normal (see Figs. 4(c) and 4(d)). Although the N–H···Y (Y=Br^- or H_2O) interactions in the two structures are very similar to each other in their features and lengths, the nitrogen atoms involved in such interactions are chemically different, N(1) and N(2) being hydrogen-bonded to the oxygen atom and bromide ion, respectively, in the $P\bar{1}$ form, whereas *vice versa* in the Pcab form. A very similar situations has been found for the N–H···O interactions around the two crystallographically independent nickel(II) complexes in the crystals of [NiF_2(*meso*-Me_6[14]aneN_4)]$\cdot 5H_2O$ (see Figs. 4(e) and 4(f)).[7] The positions of bromide ions in [Ni(*meso*-Me_6[14]aneN_4)]$Br_2 \cdot 2H_2O$ are nearer to the axial coordination sites than that of the chloride ion in



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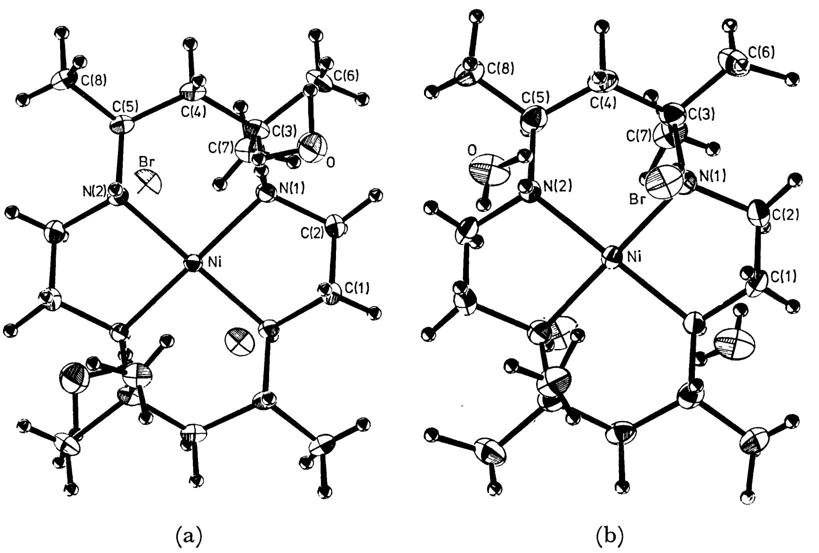


(a) (b)

Fig. 2. Dispositions of bromide ions and water molecules around the nickel(II) ion in the crystal structures of the $P\bar{1}$ (a) and Pcab forms (b), as viewed along the normal to each of the coordination planes.

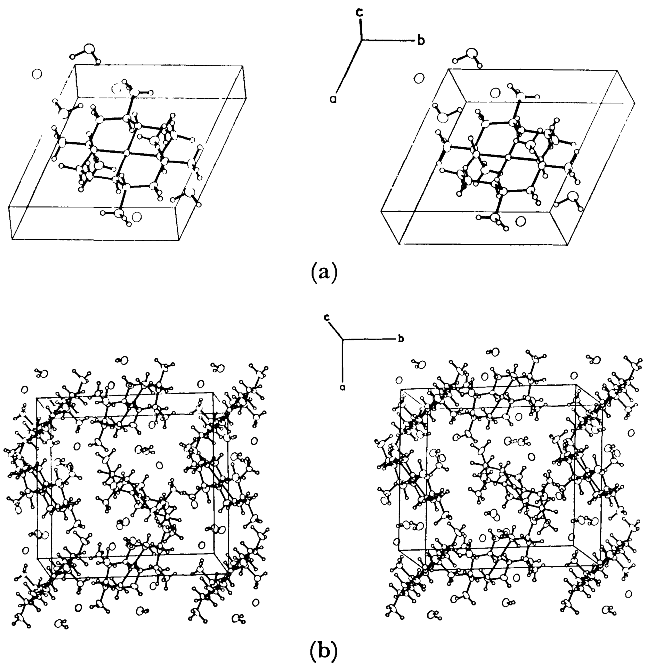
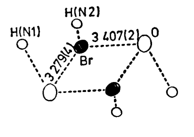


Fig. 3. Crystal structures of the P$\bar{1}$ (a) and Pcab forms (b).

$[Ni(\textit{meso}\text{-}Me_6[14]aneN_4)]Cl_2 \cdot 2H_2O$ (see Fig. 4). This may be related to the fact that $[NiBr_2(\textit{meso}\text{-}Me_6[14]aneN_4)]$ reverts more easily to the bromide dihydrate than $[NiCl_2(\textit{meso}\text{-}Me_6[14]aneN_4)]$ to the chloride dihydrate, when moisture is available.[1,5]

Stereoscopic views of the crystal structures for the P$\bar{1}$ and Pcab forms are presented in Figs. 3(a) and 3(b), respectively. Bromide ions and water molecules are further hydrogen-bonded with adjacent water molecules and bromide ions, respectively. Through these interactions the adjacent complex ions are held together, but the features of the interactions differ in the P$\bar{1}$ and Pcab forms. In the P$\bar{1}$ form, the interaction appears to be of the type shown in **2**, whereas that in the Pcab form, an infinite zigzag chain parallel to the c-axis as shown in **3**. The hydrogen-bond parameters are given in **2**, **3**, and Figs. 4(c) and 4(d). All other intermolecular contacts appear to be normal both in the two structures.



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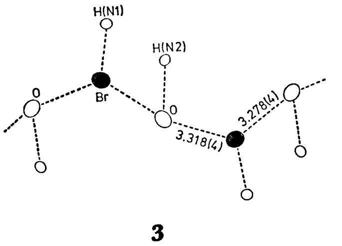

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Specific Hydrogen-bonding Effects. The occurence of the spin-state variation is invariably associated with the presence or the absence of water. One exception is the fluoride system in the solid state, *trans*-$[NiF_2(\textit{meso}\text{-}Me_6[14]aneN_4)] \cdot 5H_2O$, where fluoride ions occupy the axial coordination sites yielding a high-spin six coordinate complex in the hydrate.[7] Although water has high coordinating ability as compared with halogen ions for a nickel(II) ion in general, no evidence has been reported for coordination of water to a nickel(II) ion in the present systems.

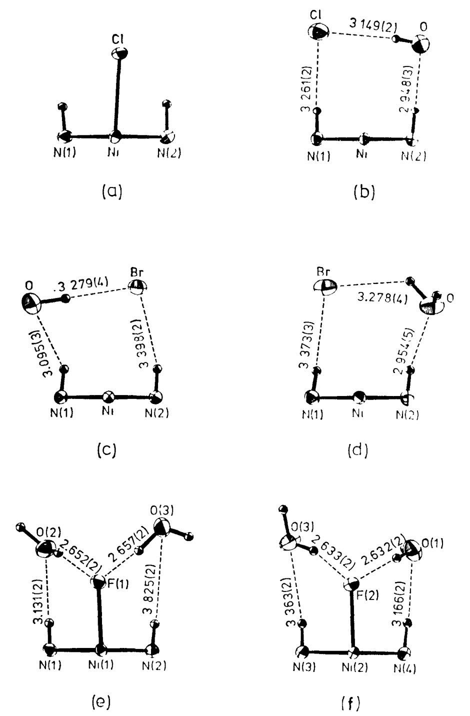

Fig. 4. Dispositions of halide ions and water of crystallization in the vicinities of the nickel(II) ions in $[NiCl_2(\textit{meso}\text{-}Me_6[14]aneN_4)] \cdot 2CHCl_3$ (a),[3] $[Ni(\textit{meso}\text{-}Me_6[14]aneN_4)]Cl_2 \cdot 2H_2O$ (b),[3] $[Ni(\textit{meso}\text{-}Me_6[14]aneN_4)]Br_2 \cdot 2H_2O$ in the P$\bar{1}$ (c) and Pcab (d) form, and $[NiF_2(\textit{meso}\text{-}Me_6[14]aneN_4)] \cdot 5H_2O$ ((e) and (f)).[7] In each compound, the nickel(II) ion sits on a crystallographic inversion center. In the fluoride system, there are two crystallographically independent complexes.[7] Hydrogen-bond distances corresponding to the lengths between donor and accepter atoms are given in Å.

Figure 4 shows the dispositions of water and halide ion in the vicinity of the nickel(II) ion found in the present study together with those in the crystal structures of $[Ni(\textit{meso}\text{-}Me_6[14]aneN_4)]Cl_2 \cdot 2H_2O$,[3] $[NiCl_2(\textit{meso}\text{-}Me_6[14]aneN_4)] \cdot 2CHCl_3$,[3] and $[NiF_2(\textit{meso}\text{-}Me_6[14]aneN_4)] \cdot 5H_2O$,[7] as viewed along each coordination plane. Note that all the nickel(II) ions in these complexes lie on centers of symmetry. Therefore, for simplicity, only the crystallographically independent two nitrogen atoms and a nickel(II) ion are depicted for each complex. In the fluoride system, there are two crystallographically independent complexes, which are shown in Figs. 4(e) and 4(f). Of particular interest in Fig. 4 is the fact that the dispositions of water and a halide ion and the features of the hydrogen-bond framework in the vicinity of the nickel(II) ion are very similar to each other in each hydrate. In all the hydrates except for the pentahydrate of the fluoro complex, water molecules and halide ions are located above the hydrogen atoms of N–H groups. As can be seen in Figs. 4(b), 4(c), and 4(d), hydrogen-bonded chelate rings of the type **1** are invariably formed.

Busch proposed that the halogen ions in the dihydrates occupy the axial coordination sites but are displaced from the nickel(II) ion so that the ligand field of the halide ions cannot exert on the nickel(II) ions.[1)] It was found in the present and previous studies that neither water molecules nor the halide ions are located near the axial coordination sites in the dihydrates. The specific hydrogen-bond effects such as the hydrogen-bonded chelate rings are undoubtedly responsible for failure of coordination of the water molecule. The occurence of such specific interactions would be much more favorable over the hypothetical occupation by the water molecules at the coordination sites. Because of the specific hydrogen-bonding effects, the presence of water not only prevents coordination of water itself but also prevents halide ions from coordinating, giving low-spin four coordinate complexes. Under water free circumstances such as in dry chloroform solutions or in solid states of the anhydride, halide ions can coordinate to nickel(II) to produce high-spin six coordinate complexes. These specific hydrogen-bonding effects also produce large enthalpy values for dehydrations of the hydrates of the present complexes.[4,7)]

In the case of the fluoride system, axial coordination sites are occupied by fluoride ions even in the hydrate. Water molecules are located above the hydrogen atoms of all the N–H groups. Hydrogen-bonded chelate rings different from the type **1** can be seen in Figs. 4(e) and 4(f), which contain O–H···F–Ni bond. The reason for the change in geometry is most likely due to the ionic size of the fluoride ion. The fluoride ion is too small to form hydrogen-bonded chelate ring of the type **1**. In addition, a fluoride ion has high coordinating ability as compared with other halide ions for a nickel(II) ion.[1)]

As described earlier, the spin state variations in solutions are also associated with the presence or the absence of water. In aqueous solutions or solutions of organic solvents containing water, hydrations take place around N–H groups. Structural feature of the hydration would be similar to the disposition of water molecules in solid state shown in Fig. 4. Water molecules involved in the hydration would play a role similar to water of crystallization in the solid dihydrates to give low-spin complexes.

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