Structure of Bis(1,4-diazacycloheptane)nickel(II) Chloride Dihydrate

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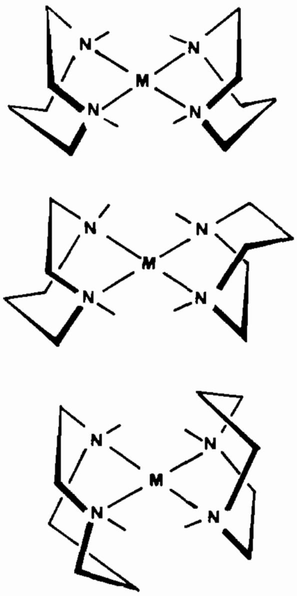
The crystal structure of bis(1,4-diazacycloheptane)nickel(II) chloride dihydrate, $[Ni(DACH)_2]Cl_2\cdot 2H_2O$ has been determined from single-crystal X-ray diffraction data measured on a CAD-4 diffractometer using graphite monochromatized Mo-K_α radiation. A full-matrix least-squares refinement with 1158 reflections gave a final R *value of 5.0%. The compound crystallizes in the orthorhombic space group* Pbca *with* a = *9.801(3),* b = *11.690(4),* c = *14.376(3)* Å *and Z = 4. The structure consists of discrete $[Ni(DACH)_2]^{2+}$ cations, Cl^- anions and water of crystallization. The DACH moieties in the cation are in* trans *form and individual six- and five-membered chelate rings are in chair and half-boat configurations respectively. The octahedral coordination is prohibited because of the steric hindrance of the axial sites by the hydrogen–carbon backbone of the ligand. The site symmetry of the Ni(II) atom is D_{2h}, which is consistent with the magnetic, spectral and conductance properties of the complex. Our results show that Ni(II) always forms four-coordinated planar complexes with mesocyclic diamines irrespective of their chelate ring conformations.*

Introduction

The unique steric requirements of medium ring systems (MESOCYCLES) having nitrogen or sulfur donor atoms were utilized for the preparation of non-octahedral cobalt(II), copper(II) and nickel(II) complexes [1, 2]. Square-pyramidal cobalt(II) [3] and square-planar nickel(II) and copper(II) complexes were reported for 1,5-diazacyclooctane (DACO). The ligand, 1,5-diazacyclooctane-N,N′-diacetic acid (DACODA) in which acetic acid arms are attached to the nitrogen atoms of DACO, yielded a square-pyramidal nickel(II) complex [4]. Similarly, 5:6:11:12-tetrahydro-2,8-dimethylphenhomazine (PHZ), which is another modification of DACO having phenyl wings attached at its 3, 4 and 7, 8 positions, gave a square-planar nickel(II) complex [5, 6]. Seven membered cyclic diamine, 1,4-diazacycloheptane (DACH) formed a square-pyramidal copper(II) complex [7]. All these complexes are of special interest because of their ability to form and maintain four- and five-coordinate geometry even in aqueous solution, a property seldom encountered.

In contrast to the symmetric disposition of DACO molecules around the metal atom in bis complexes, the DACH rings may be attached to the metal atom in one of the two different ways: (1) the two carbon chains are on the same side of the equatorial plane (*cis* Form I), (2) they may be on opposite sides of the plane (*trans* form). The *trans* form may have conformation II and III. In the square-pyramidal copper(II) complex, $[Cu(DACH)_2NO_3]NO_3\cdot[Cu(DACH)_2H_2O](NO_3)_2$ [7], the DACH moieties are in *cis* configuration with a nitrate ion or a water molecule attached at the fifth axial position. In the presence of coordinating solvents and anion, the



cis Form (I)
C_{2v}

trans Form (II)
C_2

trans Form (III)
C_2

Idealized conformations of two chelated 1,4-diazacycloheptane molecules in a bis-complex.

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trans form II with relatively open axial positions may dominate to give distorted octahedral species such as [Cu(DACH)$_2$Br$_2$] reported [8] on the basis of spectral data. In the absence of strong coordinating moieties, a *trans* form III having axial positions effectively blocked by the hydrogen–carbon backbone of DACH may exist. This conformation will only form square-planar complexes. In order to investigate these possibilities, and as part of our systematic program of studying stereochemistry of coordinated mesocyclic ligands using X-ray diffraction, the single crystal structure of bis(1,4-diazacycloheptane)nickel(II) chloride dihydrate, [Ni(DACH)$_2$]Cl$_2$·2H$_2$O, has been determined. Our results show that while *cis* form I is dominant in the case of copper(II) complexes [7], the structure of the nickel(II) complex is best described on the basis of the *trans* form II.

Experimental

Synthesis, Crystal Growth and Spectral Data

Bis(1,4-diazacycloheptane)nickel(II) chloride dihydrate was prepared [1] by adding an excess of 1,4-diazacycloheptane in anhydrous ether to an ethanolic solution of nickel(II) chloride hexahydrate already shaken with 10–15 ml of 2,2-dimethoxypropane for about an hour to remove water. Single orange-colored crystals of uniform morphology were obtained by slow evaporation of a dilute solution of the compound in nitromethane. The crystals were stable in the atmosphere and under X-radiation. The density of the crystals was determined by flotation. Infrared spectra of KBr pallates and ^{1}H NMR spectra in DMSO-d$_6$ recorded on a Perkin Elmer Model 180 spectrophotometer and a Varian T-60 agreed well with the reported [1] spectra. A strong band at 430 nm, indicative of planar nickel(II) ions, was observed on Perkin Elmer Model U.V. 202 spectrophotometer using KBr pallates of the complex.

Crystal and Intensity Data

The intensity and crystal data were obtained on a crystal having dimensions 0.1 × 0.2 × 0.15 mm, mounted on a glass fiber in an arbitrary orientation. The lattice constants were obtained by the least-squares refinement of the diffraction geometry of 25 independent centered reflections having $13.0 < \theta < 17.0°$. These reflections were located by use of the Enraf-Nonius program SEARCH.

NiC$_{10}$N$_4$H$_{24}$Cl$_2$·2H$_2$O: M = 365.8. Orthorhombic, a = 9.801(3), b = 11.690(4), c = 14.376(3) Å, U = 1647 Å^3, F(000) = 776, D_m = 1.48 g cm^{-3}, Z = 4, D_{calc} = 1.475 g cm^{-3}, space group = *Pbca*, Mo-K$_\alpha$ radiation, λ = 0.7107 Å, μ(Mo-K$_\alpha$) = 14.3 cm^{-1}.

Intensity data were collected on an Enraf-Nonius four-circle CAD-4 diffractometer using graphite monochromated Mo-K$_\alpha$ radiation and ZIGZAG mode in ω–2θ scan method with θ scan range of $(1.40 + 0.35^* \tan\theta)°$ centered about the calculated Mo-K$_\alpha$ peak positions. Background counts were measured for half of the total scan time by extending the scan range 25% on either side of the scan limits. A total of 2371 reflections with positive hkl and $2.0 < 2\theta < 54°$ were measured. Three standards were monitored after every 100 reflections. The crystal orientation was controlled by checking the orientation of reference reflections every 3 hours of X-ray exposure time. No systematic fluctuation in the intensities of reference reflections was observed during the course of data collection. The intensity data were corrected for background, Lorentz and polarization effects and observed structure factor amplitudes, F$_{obs}$, were calculated. No corrections for absorption were made. The systematic extinctions were excluded and intensities of duplicate and equivalent reflections were averaged to obtain 1805 unique measurements, 1158 of which having $I > 2\sigma/(I)$ were considered observed.

Solution and Refinement of the Structure

All calculations were done on the University of Petroleum and Minerals IBM Computer 3033 using the SHELX-76 Package of crystallographic programs [9].

The coordinates for the Ni and Cl atoms were obtained by the direct method as well as by a three-dimensional Patterson synthesis. A Fourier difference map phased on Ni atom at ½, ½, 0 and on isotropically refined coordinates of Cl atom revealed the location of both nitrogen atoms. All remaining non-hydrogen atoms were located after three cycles of isotropic least-squares refinement of located atoms followed by a difference-Fourier map. Several more cycles of anisotropic refinement, followed by a difference-Fourier map, led to the positions of the oxygen atom of water molecule and of most hydrogen atoms. The positions of the hydrogen atoms agreed well with calculated values. The coordinates for hydrogen atoms from a difference map were refined isotropically while holding non-hydrogen atoms at fixed positions. Three final cycles of anisotropic least-squares refinement on non-hydrogen atoms with hydrogens held fixed at their refined positions led to the final residual factors R = 0.05 and Rw = 0.069 for 88 variables and 1158 observations. The largest shift in any parameter during the final cycle of refinement was 0.009 times its estimated standard deviation. A final difference Fourier Synthesis was virtually featureless with some very small residual electron density within a half angstrom of nickel and chlorine atoms.

TABLE I. Positional Parameters ($\times 10^4$) for Non-hydrogen Atoms in $[Ni(DACH)_2]Cl_2 \cdot 2H_2O$.[a]

Atom	x/a	y/b	z/c
Ni	5000	5000	0
Cl	5758(2)	1780(2)	792(2)
O(1)	3784(6)	4649(6)	3997(4)
N(1)	3450(6)	4846(5)	803(4)
N(2)	5870(6)	5459(5)	1138(4)
C(1)	2953(7)	6036(6)	1014(5)
C(2)	3903(8)	6678(7)	1664(5)
C(3)	5423(8)	6633(7)	1386(5)
C(4)	3935(8)	4222(6)	1661(5)
C(5)	5440(8)	4553(7)	1850(5)

[a] Numbers in parentheses in this and all subsequent tables represent estimated standard deviations in the last digit.

Atomic scattering factors for non-hydrogen atoms were taken from Doyle and Turner [10] and for hydrogen atoms values from Stewart [11] were used. The effects of anomalous dispersion were included in $F_{calc.}$ by using values from Cromer [12]. Agreement factors are defined as $R = \Sigma[|F_o|-|F_c|]/\Sigma|F_o|$ and $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The final positional parameters for non-hydrogen atoms are given in Table I and those for the hydrogen atoms are listed in Table II. A listing of the observed and calculated structure factors and a table of anisotropic thermal parameters for non-hydrogen atoms are available as supplementary material.

TABLE II. Positional and Isotropic Thermal Parameters for Hydrogen Atoms ($\times 10^3$) in $[Ni(DACH)_2]Cl_2 \cdot 2H_2O$.

Atom	x/a	y/b	z/c	B(ISO)
HN1	261(12)	417(9)	59(7)	99(3)
HN2	701(7)	552(6)	118(5)	49(2)
H1O1	426(12)	35(10)	10(8)	65(4)
H2O1	403(9)	421(8)	443(6)	65(3)
H1C1	282(8)	678(6)	47(5)	67(2)
H2C1	213(7)	615(6)	127(5)	32(2)
H1C2	347(8)	748(7)	169(5)	56(2)
H2C2	364(8)	652(7)	226(5)	41(2)
H1C3	581(9)	717(8)	99(7)	76(3)
H2C3	606(10)	695(9)	196(7)	65(4)
H1C4	322(9)	417(8)	219(6)	67(4)
H2C4	383(9)	349(7)	148(6)	65(3)
H1C5	605(8)	382(6)	173(5)	65(2)
H2C5	557(9)	495(8)	248(7)	65(2)

Results and Discussion

Unit Cell and Packing Considerations

The unit cell consists of discrete $[Ni(DACH)_2]^{2+}$ cations, Cl^- anions and water of crystallization. A nickel atom at position ½, ½, 0, a coordinated DACH molecule, a chloride anion and a water molecule constitute the crystallographic asymmetric unit. Figure 1 gives a stereoscopic view of the packing of ions and water molecules in the unit cell. Contact distances between methylene carbon and

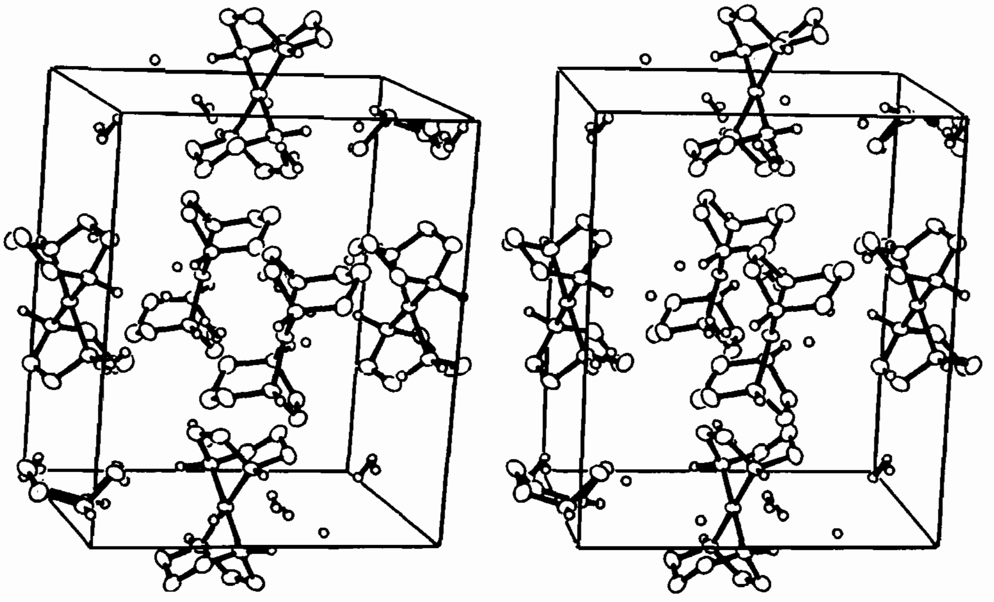

Fig. 1. Stereoscopic view of the unit cell showing packing of $[Ni(DACH)_2]^{2+}$ cations, Cl^- anions and H_2O molecules. The hydrogen atoms on carbon atoms are not plotted for clarity.

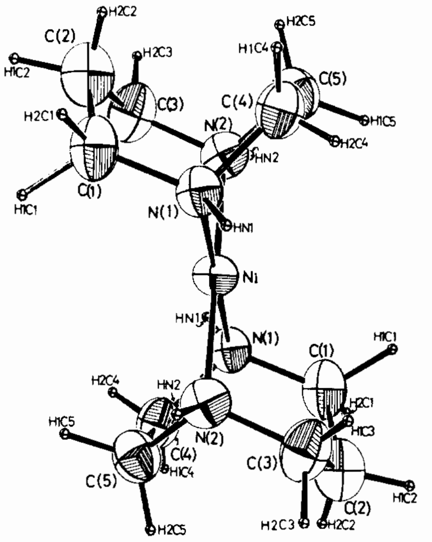

Fig. 2. ORTEP plot viewing $[Ni(DACH)_2]^{2+}$ cation approximately along N–N direction and showing the numbering of atoms and possible shielding of axial positions by Carbon–Hydrogen backbone.

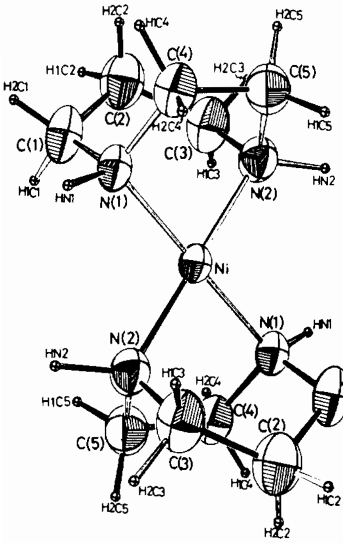

Fig. 3. ORTEP plot viewing $[Ni(DACH)_2]^{2+}$ cation approximately perpendicular to the coordination plane of the metal.

water oxygen atoms are greater than the range suggested for C–H···O hydrogen bonds (C···O = 2.6 Å) [13]. Thus there appear to be no significant packing forces or hydrogen bonds which are affecting the chelate ring geometry. The chloride ion is 4.002(5) Å from the nickel atom and 3.25(2) Å from the N(1) atom. It shows neither hydrogen bonding nor is it within non-bonded distances from any other atom in the cation. The oxygen atom of the water

TABLE III. Deviations from Least-Square Planes.

Atom	Distance, Å	Atom	Distance, Å
Plane 1:	N(1), N(2), C(4), C(5), Five-member Chelate Ring $-0.3344x + 0.7351y + 0.5898z + 3.723 = 0$		
N(1)	−0.009	C(1)	1.356
N(2)	0.009	C(2)	2.147
C(4)	0.024	C(3)	1.375
C(5)	−0.025	Ni	−1.065
Plane 2:	N(1), N(2), C(1), C(3); Six-member Chelate Ring $-0.1214x - 0.2678y + 0.9558z - 0.8331 = 0$		
N(1)	0.009	C(2)	0.565
N(2)	−0.010	C(4)	1.326
C(1)	−0.015	C(5)	1.303
C(3)	0.016	Ni	−1.327
Plane 3:	Ni, N(1), N(2) $0.2505x - 0.9510y + 0.1813z - 4.331 = 0$		
C(4)	1.037	C(1)	−1.389
C(5)	1.087	C(2)	−1.701
		C(3)	−1.350

TABLE IV. Bond Distances (Å) in $[Ni(DACH)_2]Cl_2 \cdot 2H_2O$.

(a) Bonding distances

Ni–N(1)	1.917(5)	C(3)–H1C3	0.931(8)
Ni–N(2)	1.921(6)	C(3)–H2C3	1.099(7)
N(1)–C(1)	1.504(9)	C(4)–H1C4	1.034(7)
N(1)–C(4)	1.510(9)	C(4)–H2C4	0.906(8)
N(2)–C(3)	1.49(1)	C(5)–H1C5	1.060(8)
N(2)–C(5)	1.533(9)	C(5)–H2C5	1.030(8)
C(1)–C(2)	1.52(1)	O(1)–H1O1	0.955(6)
C(2)–C(3)	1.54(1)	O(1)–H2O1	0.840(6)
C(4)–C(5)	1.55(1)		
N(1)–HN1	1.181(6)		
N(2)–HN2	1.122(6)		
C(1)–H1C1	1.177(7)		
C(1)–H2C1	0.902(7)		
C(2)–H1C2	1.025(8)		
C(2)–H2C2	0.913(8)		

(b) Non-bonding distances

Ni···Cl	4.002(5)	N(1)···N(2)	2.524
Cl···H1O1	2.23(1)	N(1)···N(2)	2.891
O(1)···Cl	3.11(1)	O(1)···N(2)	2.865
Cl···H2O1	2.29(1)	O(1)···HN2	1.766
Ni···H1C1	3.055	O(1)···N(1)	3.404
Ni···H1C3	3.004		
Ni···H2C4	2.991		
Ni···H1C5	3.025		

TABLE V. Bond Angles (°) in $[Ni(DACH)_2]Cl_2\cdot 2H_2O$.

(a) Bonding angles

N(1)–Ni–N(2)	82.2(2)	HN1–N(1)–Ni	117.0(4)
N(1)–NI–N(2)^a	97.8(2)	HN1–N(1)–C(1)	116.6(5)
C(1)–N(1)–Ni	106.9(4)	HN1–N(1)–C(4)	96.3(5)
C(4)–N(1)–Ni	106.7(4)	HN2–N(2)–Ni	120.2(4)
C(3)–N(2)–Ni	109.4(5)	HN2–N(2)–C(5)	106.4(5)
C(5)–N(2)–Ni	104.7(4)	HN2–N(2)–C(3)	103.0(5)
C(1)–N(1)–C(4)	112.6(5)		
C(3)–N(2)–C(5)	113.4(6)		
N(1)–C(1)–C(2)	112.5(6)		
N(2)–C(3)–C(2)	112.2(6)		
N(1)–C(4)–C(5)	108.8(6)		
N(2)–C(5)–C(4)	108.5(6)		
C(1)–C(2)–C(3)	114.6(6)		

(b) Non-bonding angles

O(1)–HN2–N(2)	164
N(1)–N(2)–N(1)^a	89.9
N(2)–N(1)–N(2)^a	90.2

[a] Coordinates related to those in Table I by the transformation $\bar{x}, \bar{y}, \bar{z}$.

TABLE VI. Comparison of Average Bond Lengths and Angles with Those of Related Structures.

Compound	Average M–N	N–N^a	N–N^b	N–M–N^a	N–M–N^b	Ref.
$[Cu(DACH)_2H_2O]^{2+}$	2.007(9)	2.54(1)	3.08(1)	78.6(4)	100.2(4)	7
$[Cu(DACH)_2NO_3]^{1+}$	2.011(9)	2.53(1)	3.10(1)	77.9(4)	100.9(4)	7
[Ni(DADACO)]	2.028(7)			87.7(3)		4
$[Ni(DACO)_2]^{2+}$	1.95(2)			89.5(9)	90.5(9)	16
$[Ni(PHZ)_2]^{2+}$	1.912(7)	2.622(8)	2.77(1)	86.6(2)	93.1(4)	5
$[Ni(DACH)_2]^{2+}$	1.919(6)	2.524(8)	2.891(7)	82.2	97.8(2)	This work

[a] Intra-ligand distances and angles. [b] Inter-ligand distances and angles.

molecule is approximately 4.0 Å from nickel on the opposite side of the chloride ion, and is hydrogen bonded to N(2) with a N(2)---O(1) distance of 2.87(2) Å and a N(2)–HN2---O(1) angle of 164.2°.

Conformation of the Chelate Rings

The perspective views of the $[Ni(DACH)_2]^{2+}$ cations are shown in Figs. 2 and 3. The ligand molecule adapts a skewed boat configuration so that the nitrogen atoms are suitably oriented for chelation. On coordination the ligand results in the formation of a six- and five-membered chelate ring. The six-membered ring is in a chair form with the central carbon, C(2), of the trimethylene portion furthest away (3.274 Å) from the nickel atom and the rest of the carbon atoms 2.76 to 2.79 Å away. The shortest Ni-hydrogen contact distance is 2.67 Å for HN1 and HN2 atoms in the equatorial plane. Though the central carbon atom, C(2), is directed away from the axial sites, the metal atom is partly shielded by the hydrogen atoms on C(1), C(3), C(4) and C(5) atoms preventing octahedral coordination. These hydrogen atoms are 2.99 to 3.05 Å from the nickel atom in the axial direction. The N(1), C(1), C(3) and N(2) atoms of the six-membered ring are coplanar with C(2) and Ni atoms at 0.565 Å and 1.327 Å respectively on the opposite side of the least-squares plane (Table III, Plane 2) defined by these atoms. Similarly, the N(1), C(4), C(5) and N(2) atoms of the five-membered chelate ring are coplanar with Ni at 1.065 Å and C(4) and C(5) in eclipsed positions (Table III, Plane 1). Thus, the five-membered ring is in a half-chair configuration.

Bond Distances, Angles and Comparison with Related Structures

Bond distances and angles are reported in Tables IV and V. A comparison of some important distances and angles with related structures is given in Table VI. Since the nickel atom occupies a site of inversion symmetry and the only atoms within bonding distance are four nitrogen atoms the coordination of the nickel is exactly planar. The two independent Ni–N distances (1.917(5) and 1.921(6) Å) in the present planar complex are significantly shorter than the corresponding distances (1.95 to 2.11 Å) observed in five-coordinate [14] and tetrahedral nickel(II) complexes [15]. The intra-ligand chelate bite angle is 82.2(2)° compared to an inter-ligand angle of 98.8(2)°. These angles in $[Ni(DACO)_2]^{2+}$ cation are, within experimental errors, equivalent [16]. Therefore, if only the donor atoms are considered, the point group symmetry for Ni atom in $[Ni(DACH)_2]^{2+}$ cation is approximately D_{2h} as compared to D_{4h} in the $[Ni(DACO)_2]^{2+}$. This is expected because the dimethylene portion in the DACH complex will force stronger bite, resulting in a lower value for the intra-ligand angle and higher value for the inter-ligand angle. Such strain in the chelate ring system is relieved in the case of DACO [16] or PHZ [5] complexes where dimethylene portion is substituted by trimethylene portions. A combination of five- and six-membered chelate ring has strain similar to the substituted ethylenediamines, whereas systems with two six-membered chelate rings are like unsubstituted ethylenediamines, *e.g.* $[Cu(en)_2](NO_3)_3$ has N–Cu–N angle of 86.2° and this angle in all other ethylenediamines is smaller [17]. Agreement between chemically equivalent bonds in $[Ni(DACH)_2]^{2+}$ is within experimental error. The C–H distances range from 0.902(7) to 1.07(7) Å. The average N–H distance is 1.152(6) Å. In contrast to the *cis* configuration of DACH moieties in the case of copper(II) complexes [7] these moieties are arranged in *trans* configuration in the present case. The central carbon atoms of the trimethylene portions of the DACH in both cases are folded away from the axial sites. The *cis* arrangement resulted in five-coordinate square-pyramidal copper(II) complex with water molecule or nitrate ion attached to the metal atom from relatively open five-membered chelate rings side. In the case of Ni(II), only four coordinate species were obtained irrespective of whether the axial positions were completely open [5] as in the case of $[Ni(PHZ)_2]^{2+}$, symmetrically shielded [16] as in $[Ni(DACO)_2]^{2+}$, or unsymmetrically blocked as in the present case.

The present crystal structure is consistent with the diamagnetism, 1:2-electrolytic behaviour and a strong band at 430 nm for the $[Ni(DACH)_2]Cl_2 \cdot 2H_2O$ complex. Since the polarized single crystal spectra of $[Ni(DACO)_2]^{2+}$ has been studied [16] and because of the similarity of the solid state spectra of $[Ni(DACH)_2]^{2+}$ with that of $[Ni(DACO)_2]^{2+}$, the present compound is another example of nickel(II) complexes having d orbital energy level order $d_{x^2-y^2} > d_{xy} > d_{xz} > d_{yz} > d_{z^2}$ without having any bonding or 'residual' interactions along the Z axis of the complex involving anions or solvent molecules.

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