*Contribution from the Centro di Strutturistica Chimica del C.N.R.
and Istituto di Chimica Generale, Università di Padova, Padua, Italy*

Structural Investigation on Dihalide Diaquo N,N,N',N'-Tetramethyl *o*-Phenylenediamine Nickel(II) Complexes

G. Bombieri, E. Forsellini, G. Bandoli, L. Sindellari, R. Graziani, and C. Panattoni

Received December 5, 1967

The studies on the isomorphous pair $NiCl_2.2H_2O$-(N–N′) and $NiBr_2.2H_2O$(N–N′) (where N–N′ is N,N,N′,N′-tetramethyl-o-phenylenediamine, o-C_6H_4-$(N(CH_3)_2)_2$) have been carried out by three-dimensional single-crystal X-ray diffraction, infrared, visible and ultraviolet techniques. The nickel atom shows a distorted octahedral coordination configuration with the nitrogen atoms of the ligand and the halogen atoms lying in layers parallel to (001) and with the two water molecules in apical positions. The Ni–N bond lengths were found to be 2.12 Å and 2.15 Å and the Ni–O 2.12 Å and 2.04 Å in the chloride and bromide respectively. All other distances are reasonable. The existence of molecular chains hydrogen-bonded parallel to c-axis is inferred from the results of spectral studies.

Introduction

In the last few years an increasing number of studies has been devoted to metal complexes with bidentate tertiary amines.

For various nickel(II) complexes with N- and C-substituted ethylenediamines planar, octahedral and tetrahedral configurations have been proposed, on the basis of spectrophotometric and magnetic measurements[1,2] or of X-ray diffraction data.[3]

However no systematic investigation has been made on the ability of N,N,N′,N′-tetramethyl-*o*-phenylenediamine (N–N′) to form complexes of the type MLX_2 with salts of transition metals, except for the complex $PdCl_2$(N–N′) prepared by Stewart,[4] in which (N–N′) is believed to act as a chelating agent.

We have prepared the complexes $NiX_2.nH_2O$-(N–N′) where X=Cl, Br, I, NO_3, NO_2, SCN.

The present note reports the structural analysis of the $NiCl_2.2H_2O$(N–N′) and $NiBr_2.2H_2O$(N–N′) complexes.

Experimental Section

Preparation of the compounds. $NiCl_2.2H_2O$(N–N′) was prepared by the reaction of $NiCl_2.6H_2O$ with tetramethyl *o*-phenylenediamine and was recrystallized from ethanol.[5] $NiBr_2.2H_2O$(N–N′) was prepared by the reaction of a solution of 10 mmoles of the (N–N′) ligand with 10 mmoles of $NiBr_2.3H_2O$ in 30 ml of ethanol at room temperature. After a few hours a crystalline green precipitate was obtained. The compound was purified by recrystallization from acetone solution and dried on P_2O_5.

Analysis for the latter new compound: % Calcd. for $C_{10}H_{20}O_2N_2Br_2Ni$: C, 28.70; H, 4.70; N, 6.70. % Found: C, 28,78; H, 4.74; N, 6.56.

Spectral Measurements

Visible and ultraviolet spectra. A Beckman DK2A spectrophotometer was used to record the spectra of solid and solutions (in methanol).

Infrared spectra. The spectra were obtained with a Perkin-Elmer 621 Infracord double-beam spectrophotometer using a Rock salt prism. The Nujol mull technique was employed.

Description of Crystals. The crystals of the nickel chloride complex obtained by recrystallization from ethanol solution are pale green with prismatic c habit. The crystals of the bromide complex, recrystallized from acetone solution are green with prismatic c habit. The densities for both compound were determined by flotation in carbon tetrachloride-bromoform mixture.

Crystal data. Dibromo diaquo N,N,N′,N′-tetramethyl-*o*-phenylenediamine nickel(II), $NiBr_2.2H_2O$-$C_6H_4N_2(CH_3)_4$, *M.W.* = 418.8, orthorhombic, $a = 14.71 \pm 0.02$ Å, $b = 11.21 \pm 0.02$ Å, $c = 8.93 \pm 0.02$ Å. (The errors given are three times the standard errors of the averages of a number of measurements). $V = 1473$ Å^3, $D_c = 1.89$ g.cm^{-3} for four formula units per cell, $D_m = 1.88$ g.cm^{-3}. Total number of electrons per unit cell $F(000) = 832$. Systematic absences hkl $h+k = 2n+1$, h0l $l = 2n+1$. Space group Cmcm or $Cmc2_1$.

Dichloro diaquo N,N,N′,N′-tetramethyl *o*-phenylenediamine nickel (II), $NiCl_2.2H_2OC_6H_4N_2(CH_3)_4$, *M.W.* = 329.9, orthorhombic, $a = 14.28 \pm 0.02$ Å, $b = 10.93 \pm 0.02$ Å, $c = 8.90 \pm 0.02$ Å. (The errors given are three times the standard errors of the averages of a number of measurements). $V = 1384$ Å^3, $D_c = 1.58$ g.cm^{-3} for four formula units per cell, $D_m = 1.56$ g.cm^{-3}. Total number of electrons per unit cell $F(000) = 688$. Systematic absences hkl $h+k = 2n+1$, h0l $l = 2n+1$. Space group Cmcm or $Cmc2_1$.

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(1) D. W. Meek, *Inorg. Chem.*, 4, 250 (1965).
(2) L. Sacconi and I. Bertini, *Inorg. Nucl. Chem. Letters*, 2, 29 (1966).
(3) M. G. B. Drew and D. Rogers, *Chem. Com.*, 20, 476 (1965).
(4) F. H. C. Stewart, *Chem. and Ind.*, 264 (1958).
(5) L. Sindellari, *Ann. Chim.*, 56, 386 (1966).

The cell dimensions were determined by precession camera photographs using nickel-filtered CuK_α radiation (1.5418 Å). The space-group absences were found from Weissenberg and precession photographs.

From an examination of the diffraction spectra of the two complexes it appears that they are isomorphous.

Structure Determinations

$NiCl_2.2H_2O(N{-}N')$. The X-ray intensity data were obtained with the multiple-film technique from equi-inclination Weissenberg photographs about *c* (hk0 through kh5) using nickel-filtered CuK_α radiation (1.5418 Å).

Intensities from different levels were initially placed on a common scale by the use of an 0kl precession photograph. Integrated intensities were obtained with the use of a Joyce Loebl Flying Spot Microdensitometer. The unique reflections measured were 364.

The usual correction factors were applied but no allowance was made for absorption or extinction. The linear absorption coefficient for CuK_α radiation is 54.3 cm^{-1} and the crystal size was 0.23×0.08×0.10 mm.

In fact it is generally accepted that neglect of absorption corrections does not affect atomic positional parameters but only thermal parameters, as has been shown by R.C. Srivastava and E. C. Lingafelter.[6]

The structure determination was begun using only the hk0 and 0kl data.

By the study of the projections of Patterson synthesis it was possible to define the position of the nickel atom but not the space group.

The $Cmc2_1$ space group was assumed as an initial hypothesis for the structural analysis. However a possible increasing symmetry consequent to the refinement, could indicate the space group Cmcm. The electron density projection along the direction [001] and [100] wer calculated using the phases obtained from a structure factor calculation based on the contribution of the nickel atom only. This permitted the determination of the positions of the chlorine atoms. Several sets of structure factor calculations and electron density projections followed until all the light atoms were resolved.

The phenylenediamine group is found in the same plane, at z = 1/4, in which the nickel and chlorine atoms are present. At this stage of the analysis the R index calculated as $R = \dfrac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$ was 0.16 and 0.17 for the observed reflections hk0 and 0kl respectively.

The refinement carried out by difference synthesis suggests that the molecule has mm symmetry and therefore we can define exactly the space group as Cmcm. Scattering factors for neutral nickel, chlorine, oxygen and carbon were from the compilation of Forsyth and Wells.[7]

At this point the three-dimensional intensity data became available and the refinement was therefore continued with these data. A structure factor calculation using the parameters from the two-dimensional work gave R = 0.14. The structure was refined by block diagonal least-square refinement with an Olivetti Elea 6001 computer. The isotropal least squares refinement was carried out with a program written by Panattoni *et al.*[8] The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. The weighting scheme used has been determined from an examination of the difference between observed and calculated structure factors as a function of the observed structure factor as suggested by Weisner and Lingafelter.[9] The curve plotted can be described by the equation $|\overline{\Delta F}| = 0.099\ F_o + 0.7$. Weights were assigned on the following basis: for unobserved reflections for which $F_c < F_{o\,min}$, $\sqrt{w} = 0$, for unobserved reflections with $F_c > F_{o\,min}$ and for observed reflections, $\sqrt{w} = 1/|\overline{\Delta F}|$, $|\overline{\Delta F}|$ being determined from the above equation. The resulting R was 0.117. For the anisotropic refinement the program used was that written by Panattoni *et al.*[8] and a change of weighting scheme has been made as suggested by R. L. Braun and E. C. Lingafelter.[10] The weighting scheme was $\sqrt{w} = \dfrac{1}{0.032\ F_o + 3.9}$ for all observed reflections. The final value of R was 0.097.

The final observed and calculated structure factors are listed in Table I.

Table I. Observed and calculated structure factors (×10) for $NiCl_2.2H_2O(N{-}N')$ [a]

L=0

H K	FO	FC
00+02+	0112*	0190+
00+04+	0201*	0071+
00+06+	1011+	0952+
00+08+	1034+	1057+
00+10+	0758+	0179+
01+01+	0774+	0748+
01+07+	1279+	1382+
01+09+	0254-	0235-
01+11+	0206-	0179-
01+13+	0294+	0270+
02+00+	2210+	2287+
02+02+	0263+	0142+
02+04+	1373-	1515-
02+06+	0463+	0511+
02+08+	0617+	0558+
02+10+	0351-	0345-
03+01+	0221+	0134+
03+03+	1918-	1938-
03+09+	0219-	0176-
03+11+	0723-	0730-
03+13+	0154+	0140+
04+00+	0621-	0397-
04+02+	0836-	0783-
04+04+	2058-	2346-
04+06+	0205-	0115-
04+10+	0895-	0834-
04+12+	0216-	0190-
05+01+	0412+	0436+
05+03+	1469-	1446-
05+05+	0383-	0403-
05+07+	0305+	0369+
05+09+	0289-	0258-
05+11+	0508-	0516-
06+00+	0970+	1011+
06+02+	0692-	0692-
06+04+	0808-	0811-
06+06+	0328+	0282+
06+08+	0370+	0317+
06+10+	0434-	0433-
06+12+	0130-	0117-
07+01+	1313+	1292+
07+03+	0324-	0340-
07+07+	1072+	1015+
07+09+	0135+	0130+
07+11+	0132-	0105-
08+00+	1294+	1330+
08+02+	0591+	0487+
08+06+	1061+	0978+
08+08+	0659+	0635+
08+10+	0142-	0105-
08+12+	0108+	0097+
09+01+	1098+	1082+
09+03+	0390-	0473-
09+07+	0690+	0672+
09+09+	0303+	0269+
09+11+	0233-	0198-
10+00+	0774+	0682+
10+04+	0301-	0268-
10+06+	0586+	0526+
10+08+	0296+	0282+
10+10+	0332-	0320-
11+03+	0946-	0872-
11+05+	0781-	0718-
11+07+	0249+	0299+
11+09+	0299-	0294-
11+11+	0293-	0296-
12+00+	0290+	0244+
12+02+	0819-	0816-
12+04+	0602-	0590-
12+06+	0088-	0097-
12+08+	0076-	0097-
12+10+	0409-	0449-
13+03+	0768-	0716-
13+05+	0568-	0543-
13+07+	0217+	0220+
13+09+	0218-	0233-
14+00+	0178+	0146+
14+02+	0100-	0112-
14+04+	0537-	0511-
14+06+	0184+	0195+
14+08+	0134+	0118+
15+01+	0610+	0579+
15+03+	0254-	0224-
15+05+	0387+	0327+
15+07+	0298+	0288+
16+00+	0525+	0462+
16+02+	0432+	0402+
16+04+	0179-	0137-
16+06+	0382+	0427+
17+01+	0478+	0465+
18+00+	0448+	0613+
18+02+	0118-	0095-

L=1

H K	FO	FC
00+02+	0260-	0512-
00+04+	0196+	0181+
00+06+	0992+	1249+
00+08+	0582-	0641-
00+12+	0442+	0441+
01+01+	1120-	1344-
01+03+	0270+	0201+
01+05+	0615+	0629+
01+07+	0378+	0372+
01+09+	0210+	0168+
01+11+	0350+	0342+
01+13+	0324+	0385+
02+02+	0983-	1005-
02+04+	0541+	0496+
02+06+	0566+	0523+
02+08+	0510-	0484-
02+10+	0319-	0317-
02+12+	0315+	0318+
03+03+	0945-	0990-
03+05+	0475+	0524+
03+07+	0250-	0220-
03+09+	0586-	0543-
03+11+	0169-	0188-
04+02+	1074-	1168-
04+04+	0546+	0519+
04+08+	0497-	0411-
04+10+	0554-	0554-
05+01+	0571-	0520-
05+03+	0710-	0675-
05+05+	0366+	0333+
05+07+	0343-	0282-
05+09+	0720-	0734-
05+11+	0137-	0117-
06+02+	0663-	0684-
06+04+	0300+	0261+
06+06+	0451+	0441+
06+08+	0363-	0267-
06+12+	0181+	0189+
07+01+	0519-	0598-
07+05+	0614+	0625+
07+09+	0264-	0278-
07+11+	0190+	0205+
08+02+	0415-	0491-
08+04+	0336+	0315+
08+06+	0607+	0530+
08+10+	0151+	0163+
09+01+	0316-	0350-
09+03+	0710+	0757+
09+07+	0237+	0197+
09+11+	0227+	0310+
10+02+	0341-	0456-
10+06+	0320+	0295+
11+01+	0370-	0529-
11+05+	0290+	0317+
11+09+	0301-	0362-
12+02+	0323-	0399-
12+04+	0201-	0180-
12+06+	0317-	0479-
13+01+	0359-	0371-
13+07+	0137-	0180-
14+02+	0348-	0364-

L=2

H K	FO	FC
00+02+	0961-	1067-
00+04+	0498-	0410-
00+06+	0656-	0591+
00+08+	0692-	0715-
01+03+	0585-	0493-
01+05+	0477-	0431-
01+07+	0623-	0635-
02+00+	1343-	1305-
02+04+	0394+	0458+
02+06+	0112-	0090-
02+08+	0218-	0234-
03+01+	0647+	0619+
03+03+	0526+	0654+
03+05+	0191+	0204+
03+09+	0336+	0354+
03+11+	0283+	0317+
04+00+	0818+	0811+
04+02+	0930+	0866+
04+04+	1107+	1310+
04+06+	0459+	0466+
04+08+	0230+	0277+
04+10+	0489+	0497+
05+01+	0210+	0088+
05+03+	0781+	0795+

L=2

H K	FO	FC
05+05+	0133+	0113+
05+07+	0182+	0178+
05+11+	0375+	0312+
06+00+	0382+	0321+
06+04+	0448+	0482+
06+06+	0141-	0119-
06+10+	0244+	0266+
07+01+	0844-	0846-
07+05+	0313-	0297-
07+07+	0446-	0440-
07+09+	0256-	0274-
08+00+	0709-	0796-
08+02+	0499-	0466-
08+04+	0478-	0528-
08+06+	0625-	0681-
08+08+	0388-	0413-
09+01+	0681-	0650-
09+07+	0498-	0543-
10+00+	0445-	0433-
10+04+	0183-	0204-
10+06+	0260-	0291+
11+03+	0545+	0550+
11+05+	0560+	0573+
11+09+	0228+	0226+
12+00+	0304+	0332+
12+02+	0505+	0513+
12+04+	0416+	0444+
12+08+	0193+	0248+
13+03+	0533+	0547+
13+05+	0334+	0322+
14+04+	0258+	0249+
15+01+	0388-	0383-
15+05+	0235-	0255-
16+00+	0381-	0381-
16+02+	0299-	0304-
17+01+	0360-	0335-

L=3

H K	FO	FC
00+02+	0508+	0636+
00+04+	0479-	0579-
00+06+	0482-	0566-
00+08+	0194+	0202+
00+12+	0524-	0503-
01+01+	0294+	0485+
01+03+	0143+	0125+
01+05+	0471-	0614-
01+07+	0274-	0296-
01+11+	0394-	0379-
01+13+	0291-	0254-
02+02+	0434+	0547+
02+04+	0186-	0183-
02+06+	0448-	0568-
02+08+	0451+	0548+
02+12+	0304-	0204-
03+01+	0901+	0881+
03+03+	0221+	0193+
03+07+	0195+	0151+
03+09+	0411+	0383+
04+02+	0690+	0685+
04+04+	0170-	0160-
04+06+	0184-	0166-
04+08+	0539+	0521+
04+10+	0452+	0362+
05+03+	0724+	0701+
05+05+	0323-	0319-
05+07+	0325+	0307+
05+09+	0613+	0632+
06+02+	0733+	0705+
06+04+	0488-	0520-
06+10+	0251+	0218+
06+12+	0243-	0262-
07+01+	0167+	0126+
07+03+	0404+	0297+
07+05+	0606-	0615-
07+09+	0329+	0267+
07+11+	0304-	0270-
08+02+	0409+	0317+
08+04+	0275-	0192-
08+06+	0542-	0522-
08+10+	0256-	0264-
09+01+	0652+	0643+
09+03+	0329-	0272-
09+05+	0517-	0464-
09+07+	0270-	0222-
09+11+	[illegible]	0191-
10+02+	0267+	0249+
10+08+	0465-	0418-

L=3

H K	FO	FC
10+08+	0325+	0299+
11+01+	0420+	0357+
11+03+	0126+	0078+
11+05+	0320-	0303-
11+09+	0315+	0286+
12+02+	0444+	0427+
12+08+	0266+	0291+
13+03+	0309+	0294+
13+07+	0208+	0179+
13+07+	0208+	0179+
14+02+	0342+	0295+
15+05+	0210-	0189-
16+04+	0236-	0178-

L=4

H K	FO	FC
00+02+	0809+	0914+
00+04+	0355-	0453-
00+06+	0706+	0946+
00+08+	0713+	0879+
01+01+	0543+	0660+
01+03+	0256-	0352-
01+05+	0252+	0311+
01+07+	0897+	0886+
01+11+	0294-	0262-
02+00+	1835+	1836+
02+02+	0383-	0311-
02+04+	0680-	0818-
02+06+	0306+	0295+
02+08+	0467+	0456+
02+10+	0274-	0233-
03+01+	0820-	0938-
03+05+	0495-	0529-
03+07+	0485+	0504+
03+09+	0519-	0487-
03+11+	0428-	0412-
04+02+	0863-	0953-
04+04+	1274-	1467-
04+06+	0268-	0210-
04+10+	0556-	0625-
05+01+	0359+	0327+
05+03+	1135-	1197-
05+05+	0204-	0179-
05+11+	0518-	0531-
06+04+	0886-	0982-
06+06+	0452+	0382+
06+08+	0351+	0268+
06+10+	0529-	0476-
07+01+	0963+	1048+
07+03+	0454-	0434-
07+05+	0330+	0247+
07+07+	0640+	0605+
07+09+	0362+	0295+
08+00+	1167+	1221+
08+02+	0257+	0249+
08+04+	0231+	0171+
08+06+	0824+	0748+
08+08+	0589+	0564+
09+01+	0821+	0781+
09+05+	0349-	0261-
09+07+	0801+	0881+
10+00+	0761+	0844+
10+02+	0309-	0256-
10+06+	0451+	0384+
10+08+	0144+	0208+
11+03+	0745-	0769-
11+05+	0601-	0556-
11+07+	0187+	0177+
12+00+	0211-	0178-
12+02+	0450-	0369-
12+04+	0701-	0723-
13+05+	0296-	0278-
14+00+	0215+	0174+
14+04+	0424-	0379-
15+01+	0491+	0447+
16+00+	0555+	0598+
16+02+	0179+	0169+

L=5

H K	FO	FC
00+02+	0475-	0555-
00+04+	0423+	0396+
00+06+	0631+	0673+
00+08+	0295-	0301-
00+12+	0894+	0458+

L=5

H K	FO	FC
01+01+	0478-	0587-
01+05+	0595+	0588+
01+07+	0268+	0279+
01+11+	0315+	0309+
02+02+	0537-	0599-
02+04+	0244+	0234+
02+06+	0541+	0513+
02+08+	0489-	0486-
02+10+	0218-	0206-
02+12+	0202+	0232+
03+01+	0555-	0609-
03+03+	0320-	0344-
03+05+	0281+	0244+
03+07+	0110-	0110-
03+09+	0454-	0424-
04+02+	0634+	0708+
04+04+	0263+	0213+
04+08+	0492-	0443-
04+10+	0385-	0388-
05+01+	0229-	0263-
05+03+	0553-	0578-
05+05+	0358+	0337+
05+07+	0243-	0242-
05+09+	0566-	0611-
06+02+	0596-	0627-
06+04+	0401+	0368+
06+06+	0175+	0168+
06+10+	0206-	0184-
07+01+	0331-	0284-
07+03+	0227-	0226-
07+05+	0558+	0568+
07+09+	0247-	0273-
07+11+	0159+	0208+
08+02+	0384-	0364-
08+04+	0213+	0195+
08+06+	0547+	0505+
08+10+	0203+	0185+
09+01+	0543-	0510-
09+05+	0490+	0501+
09+07+	0189+	0198+
10+02+	0400-	0327-
10+06+	0399+	0358+
10+08+	0226-	0239-
11+01+	0352-	0352-
11+05+	0315+	0315+
12+02+	0439-	0407-
12+08+	0205-	0271-
13+01+	0166-	0197-
13+03+	0251-	0231-
13+05+	0199+	0195+
13+07+	0121-	0143-
14+02+	0301-	0299-
15+01+	0151-	0159-
15+05+	0156+	0223+
16+02+	0115-	0171-

[a] Unobserved reflections and reflections affected by extinction are indicated with *.

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(6) R. G. Srivastava and E. C. Lingafelter, *Acta Cryst.*, *20*, 918 (1966).
(7) J. B. Forsyth and M. Wells, *Acta Cryst.*, *12*, 412 (1959).
(8) C. Panattoni *et al.*, private communication.
(9) I. R. Wiesner and E. C. Lingafelter, *Inorg. Chem.*, *5*, 1770 (1966).
(10) R. L. Braun and E. C. Lingafelter, *Acta Cryst.*, *22*, 780 (1967).

Table II. Data for $NiCl_2.2H_2O(N{-}N')$ Positional and Thermal Parameters.[a] Anisotropic Temperature Factors of the Form $\exp{-1/4}\,[B_{11}(a^*)^2h^2 + B_{22}(b^*)^2k^2 + B_{33}(c^*)^2l^2+2B_{12}a^*b^*hk+2B_{13}a^*c^*hl+2B_{23}b^*c^*kl]$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	1426 (2)	2500	190 (13)	194 (12)	238 (31)	0	0	0
Cl	1229 (2)	–125 (2)	2500	135 (12)	146 (14)	196 (44)	34 (11)	0	0
O	0	1406 (7)	4885 (12)	154 (34)	109 (36)	50 (102)	0	0	22 (34)
N	995 (2)	2868 (3)	2500	135 (15)	145 (16)	131 (40)	–21 (12)	0	0
C(1)	1628 (3)	2818 (4)	3862 (15)	171 (17)	222 (20)	187 (59)	–51 (15)	–49 (24)	29 (23)
C(2)	487 (6)	4064 (7)	2500	308 (49)	66 (34)	96 (88)	– 8 (33)	0	0
C(3)	986 (7)	5181 (9)	2500	295 (50)	150 (43)	148 (112)	–73 (37)	0	0
C(4)	482 (9)	6263 (9)	2500	437 (61)	194 (50)	182 (101)	5 (43)	0	0

[a] Positions are multiplied by 10^4. Temperature parameters are multiplied by 10^2. Estimated standard deviations are given in parentheses.

Table III. Observed and calculated structure factors (×10) for $NiBr_2.2H_2O(N{-}N')$[a]

H K	FO	FC
L=0		
02+00+	*383+	2302+
04+00+	1702-	1770-
06+00+	1231+	1222+
08+00+	2375+	2459+
10+00+	0533+	0292+
12+00+	0650-	0590-
14+00+	0750+	0568+
01+01+	1688+	1600+
03+01+	0893-	1020-
05+01+	0402-	0303-
07+01+	2313+	2298+
11+01+	0646-	0661-
13+01+	0348-	0263-
15+01+	1326+	1254+
00+02+	1172+	1520+
04+02+	2115-	2018-
06+02+	0612-	0498-
08+02+	1440+	1227+
10+02+	0441-	0316-
12+02+	1665-	1478-
16+02+	0924+	0906+
01+03+	0765+	0768+
03+03+	3023-	3072-
05+03+	2109-	2202-
07+03+	0669+	0616+
11+03+	1829-	1761-
13+03+	1075-	1036-
00+04+	1173+	1253+
02+04+	1550-	1465-
04+04+	3332-	3396-
06+04+	0633-	0657-
08+04+	1057+	0961+
10+04+	0654-	0491-
12+04+	1254-	1200-
01+05+	0782+	0849+
03+05+	0598-	0805-
05+05+	0718-	0709-
07+05+	0912+	0792+
09+05+	0549+	0453+
11+05+	1316-	1295-
13+05+	0807-	0805-
15+05+	0951+	0849+
00+06+	1954+	2068+
02+06+	0517+	0510+
04+06+	0937-	0887-
06+06+	0690+	0605+
08+06+	1585+	1708+
10+06+	0478+	0392+
12+06+	0477-	0448-
14+06+	0594+	0520+
16+06+	0789+	0863+
01+07+	1935+	1939+
03+07+	0483-	0497-
07+07+	1708+	1655+
09+07+	0975+	0991+
15+07+	0739+	0786+
00+08+	1401+	1485+
02+08+	0494+	0407+
04+08+	0602-	0655-
06+08+	0391+	0274+
08+08+	0981+	1038+
12+08+	0547-	0610-
14+08+	0293+	0301+
03+09+	0808-	0807-
05+09+	0683-	0630-
07+09+	0427+	0458+
11+09+	0712-	0718-
13+09+	0404-	0421-
00+10+	0655+	0702+
02+10+	0450-	0414-
04+10+	1078-	1350-
06+10+	0443-	0337-
10+10+	0604-	0561-
12+10+	0631-	0785-
03+11+	0923-	0903-
05+11+	0570-	0668-
11+11+	0495-	0568-
01+13+	0485+	0542+
07+13+	0379+	0515+
L=1		
01+01+	1154-	1340-
05+01+	0512-	0535-
07+01+	0501-	0617-
09+01+	0405-	0389+
11+01+	0600-	0542-
13+01+	0594-	0433-
02+02+	0923-	1033-
04+02+	1281-	1480-
06+02+	0547-	0687-
08+02+	0349-	0300-
10+02+	0614-	0534-
12+02+	0724-	0578-
14+02+	0403-	0334-
01+03+	0459+	0514+
03+03+	0911-	1120-
05+03+	0797-	0678-
07+03+	0261+	0162+
00+04+	0611+	0608+
02+04+	0486+	0551+
06+04+	0411+	0423+
08+04+	0637+	0661+
12+04+	0455-	0375-
12+04+	0455-	0375-
16+04+	0558+	0572+
01+05+	1013+	1060+
07+05+	0806+	0966+
09+05+	0830+	0924+
15+05+	0569+	0577+
17+05+	0447+	0381+
00+06+	1429+	1707+
02+06+	0627+	0430+
04+06+	0757-	0593-
06+06+	0464+	0442+
08+06+	0943+	0956+
12+06+	0784-	0258-
16+06+	0491+	0415+
01+07+	0604+	0544+
03+07+	0755-	0671-
05+07+	0735-	0693-
07+07+	0388+	0358+
09+07+	0351+	0343+
11+07+	0492-	0493-
13+07+	0443-	0399-
15+07+	0278+	0279+
02+08+	0586-	0592-
04+08+	1049-	0978-
06+08+	0344-	0237-
08+08+	0456+	0405+
10+08+	0346-	0324-
12+08+	1052-	0862-
01+09+	0807+	0572+
03+09+	0962-	0969-
05+09+	0949-	1001-
11+09+	0847-	0715-
13+09+	0713-	0585-
00+10+	0758+	0747+
04+10+	1171-	0957-
08+10+	0700+	0773+
12+10+	0449-	0539-
01+11+	0960+	0753+
05+11+	0331-	0295-
07+11+	0778+	0635+
09+11+	0680+	0585+
11+11+	0302-	0347-
00+12+	1065+	0972+
02+12+	0340+	0255+
04+12+	0390-	0401-
06+12+	0320+	0322+
08+12+	0957+	0832+
01+13+	0755+	0680+
03+13+	0659-	0597-
05+13+	0548-	0513-
07+13+	0751+	0618+
L=2		
02+00+	1041-	1263-
04+00+	1701+	1988+
08+00+	1656-	1714-
12+00+	1104+	1068+
16+00+	0940-	0892-
01+01+	0798-	0966-
03+01+	1707+	1702+
05+01+	0992+	0792+
07+01+	1806-	1625-
09+01+	1347-	1135-
11+01+	1036+	0892+
15+01+	1049-	1050-
L=2		
17+01+	0444-	0508-
00+02+	2124-	2359-
04+02+	2114+	2074+
08+02+	1488-	1317-
10+02+	0509+	0446+
12+02+	1302+	1218+
16+02+	0891-	0788-
01+03+	1488-	1256-
03+03+	1381+	1824+
05+03+	1489+	1440+
07+03+	0890-	0892-
09+03+	0601-	0525-
11+03+	1310+	1322+
13+03+	0831+	0873+
15+03+	0464-	0619-
00+04+	1871-	1540-
02+04+	0589+	0506+
04+04+	1894+	2305+
06+04+	0325+	0304+
08+04+	1246-	1327-
12+04+	0893+	0967+
16+04+	0523-	0582-
01+05+	1597-	1184-
03+05+	0958+	0884+
05+05+	0589+	0522+
07+05+	1041-	1103-
11+05+	1078+	1245+
17+05+	0458-	0413-
00+06+	2028-	1801-
04+06+	1408+	1217+
06+06+	0349-	0311-
08+06+	1259-	1393-
12+06+	0549+	0589+
14+06+	0437-	0371-
16+06+	0787-	0709-
01+07+	1545-	1157-
03+07+	0806+	0634+
05+07+	0810+	0568+
07+07+	1010-	1011-
09+07+	0865-	0816-
11+07+	0549+	0539+
15+07+	0770-	0641-
00+08+	1574-	1261-
04+08+	1076+	0916+
08+08+	0997-	0837-
12+08+	0805+	0678+
03+09+	1137+	0869+
05+09+	0649+	0491+
07+09+	0792-	0660-
11+09+	0845+	0865+
00+10+	0919-	0797-
04+10+	1173+	0936+
10+10+	0345+	0253+
12+10+	0647+	0657+
03+11+	0622+	0585+
07+11+	0387-	0402-
11+11+	0435+	0394+
00+12+	0453-	0494-
08+12+	0366-	0416-
01+13+	0408-	0394-
L=3		
01+01+	0328+	0339+
03+01+	0853+	0904+
09+01+	0516+	0542+
11+01+	0487+	0486+
00+02+	0417+	0343+
02+02+	0515+	0451+
04+02+	0644+	0761+
06+02+	0586+	0628+
12+02+	0469+	0527+
01+03+	0151-	0176-
03+03+	0359+	0342+
05+03+	0891+	0731+
09+03+	0394-	0400-
00+04+	1048-	0990-
02+04+	0274-	0179-
04+04+	0226+	0195+
06+04+	0670-	0634-
08+04+	0517-	0559-
12+04+	0252+	0257+
16+04+	0310-	0371-
01+05+	0963-	0860-
03+05+	0283+	0190+
07+05+	0837-	0859-
09+05+	0548-	0649-
L=3		
15+05+	0377-	0452-
00+06+	1164-	0915-
02+06+	0478-	0419-
04+06+	0407+	0348+
08+06+	0677-	0786-
10+06+	0357-	0318-
12+06+	0369+	0439+
16+06+	0435-	0497-
01+07+	0622-	0536-
03+07+	0721+	0646+
05+07+	0625+	0621+
07+07+	0350-	0370-
09+07+	0329-	0298-
11+07+	0419+	0487+
13+07+	0381+	0349+
15+07+	0305-	0260-
00+08+	0386-	0299-
02+08+	0617+	0558+
04+08+	1121+	1030+
08+08+	0603-	0465-
10+08+	0458+	0435+
12+08+	0625+	0641+
01+09+	0594-	0534-
03+09+	0722+	0849+
05+09+	0900+	0868+
09+09+	0330-	0276-
11+09+	0528+	0582+
13+09+	0510+	0567+
00+10+	0582-	0558-
04+10+	0785+	0752+
08+10+	0731-	0737-
12+10+	0445+	0553+
01+11+	0741-	0771-
03+11+	0408+	0450+
05+11+	0259+	0286+
07+11+	0649-	0701-
09+11+	0425-	0403-
00+12+	0801-	0691-
04+12+	0415+	0488+
06+12+	0273-	0280-
08+12+	0542-	0730-
01+13+	0545-	0508-
03+13+	0350+	0446+
05+13+	0430+	0840+
L=4		
02+00+	1679+	1640+
04+00+	0859-	0759-
08+00+	1660+	1879+
16+00+	0945+	1053+
01+01+	1198+	1348+
03+01+	0901-	0990-
07+01+	1754+	1840+
09+01+	1273+	1172+
15+01+	0955+	1050+
00+02+	2155+	1929+
04+02+	2046-	1986-
08+02+	1146+	1074+
12+02+	1159-	1075-
03+03+	1526-	1689-
05+03+	1735-	1671-
11+03+	1248-	1386-
13+03+	1023-	1049-
00+04+	0606+	0649+
02+04+	0999-	0801-
04+04+	2065-	2225-
06+04+	0783-	0701-
08+04+	0756+	0866+
12+04+	1043-	1114-
01+05+	1018+	1021+
03+05+	1163-	1055-
07+05+	0978+	1040+
11+05+	1050-	1196-
00+06+	1934+	1665+
04+06+	0978-	0844-
06+06+	0824+	0498+
08+06+	1404+	1420+
01+07+	1492+	1260+
07+07+	1246+	1045+
09+07+	0939+	1051+
00+08+	1770+	1346+
03+09+	1159-	0947-
L=5		
01+01+	0834-	0804-
03+01+	0759-	0686-
L=5		
05+01+	0335-	0394-
07+01+	0277-	0249-
09+01+	0558-	0471-
11+01+	0413-	0481-
13+01+	0242-	0227-
00+02+	0726-	0401-
02+02+	0587-	0630-
04+02+	1014-	0665-
06+02+	0588-	0631-
08+02+	0268-	0269-
10+02+	0413-	0275-
12+02+	0576-	0548-
14+02+	0338-	0329-
03+03+	0635-	0511-
05+03+	0831-	0838-
09+03+	0307+	0215+
11+03+	0223-	0162-
13+03+	0310-	0267-
00+04+	0675+	0750+
02+04+	0351+	0297+
06+04+	0615+	0485+
08+04+	0571+	0535+
01+05+	0737+	0877+
07+05+	0928+	0837+
09+05+	0546+	0706+
15+05+	0438+	0479+
00+06+	0912+	1021+
02+06+	0493+	0421+
04+06+	0374-	0265-
08+06+	0764+	0782+
10+06+	0308+	0284+
12+06+	0305-	0269-
01+07+	0437+	0451+
03+07+	0532-	0535-
05+07+	0519-	0534-
07+07+	0375+	0310+
09+07+	0282+	0268+
11+07+	0321*	0412-
13+07+	0281-	0318-
02+08+	0533-	0542-
04+08+	0826-	0924-
08+08+	0300+	0332+
10+08+	0424-	0385-
12+08+	0580-	0655-
01+09+	0385+	0382+
03+09+	0684-	0720-
05+09+	0717-	0846-
11+09+	0522-	0594-
00+10+	0477+	0505+
04+10+	0833-	0736-
08+10+	0594+	0818+
01+11+	0788+	0675+
07+11+	0555+	0610+
00+12+	0856+	0850+

[a] Unobserved reflections and reflections affected by extinction are indicated with *.

The final atomic coordinates, the temperature factor parameters and their estimated standard deviations are given in Table II.

$NiBr_2.2H_2O(N{-}N')$. A single crystal 0.25×0.1×0.1 mm was mounted about the [001] direction on an equi-inclination Weissenberg camera and used to collect intensity data with nickel-filtered CuK_α radiation (1.5418 Å). The layers hk0 through hk5 were collected on multiple-film packs, with a total of 374 independent reflections measured. The linear absorption coefficient for this crystal with CuK_α radiation is 88.6 cm^{-1}. No corrections were made for absorption or extinction. Integrated intensities were obtained with a Joyce Loebl Flying Spot Microdensitometer.

The coordinates of the atoms of the chloride isomer were taken for a three-dimensional structure factor calculation. The structure was refined with block diagonal least squares by minimizing the function $\Sigma w(|F_o|-|F_c|)^2$ including isotropic temperature factors for all atoms except nickel and bromine, which were refined with anisotropic temperature factors. The weights for observations were obtained in the same way as for the chloride isomer: $\sqrt{w}=0$ for unobserved reflections with $F_c<F_{\sigma\,\min}$, $\sqrt{w}=1/|\Delta F|$ for unobserved reflections with $F_c>F_{o\,\min}$ and for observed reflections. $|\Delta F|$ is definited from the equation $|\Delta F|=0.099\ F_\sigma+0.7$. The scattering atomic factors for Ni, Br, O, N, C were those of Forsyth and Wells.[7] The final R factor was 0.107.

In the Table III are indicated the final observed and calculated structure factors.

The final atomic coordinates, the temperature factor parameters and their estimated standard deviations are given in Table IV.

Table IV. Data for $NiBr_2.2H_2O(N{-}N')$ Positional and Thermal Parameters.[a] Anisotropic Temperature Factors of the Form $\exp{-1/4}\,[B_{11}(a^*)^2h^2 + B_{22}(b^*)^2k^2 + B_{33}(c^*)^2l^2+2B_{12}a^*b^*hk+2B_{13}a^*c^*hl+2B_{23}b^*c^*kl]$

Atom	x/a	y/b	z/c	B(A²)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	1481 (3)	2500		196 (20)	215 (18)	311 (46)	0	0	0
Br	1276 (1)	–132 (1)	2500		102 (8)	113 (8)	145 (30)	27 (5)	0	0
O	0	1440 (8)	4779 (12)	155 (37)						
N	998 (6)	2884 (8)	2500	115 (37)						
C(1)	1551 (8)	2855 (8)	3891 (15)	232 (41)						
C(2)	469 (7)	4058 (10)	2500	140 (38)						
C(3)	921 (11)	5174 (12)	2500	198 (52)						
C(4)	468 (11)	6215 (13)	2500	281 (60)						

[a] Positions are multiplied by 10^4. Temperature parameters are multiplied by 10^2. Estimated standard deviations are given in parentheses.

Results and Discussion

The structure of the isomorphous pair $NiCl_2 \cdot 2H_2O(N{-}N')$ (hereafter called NIC) and $NiBr_2 \cdot 2H_2O(N{-}N')$ (hereafter called NIB) consists of an octahedral configuration with two water molecules bonded to the nickel atom in the apical position. The metal atom, the chelate ligand and the two halogen atoms are coplanar and are situated in planes $z = 1/4, 3/4$. The molecular symmetry is mm.

A perspective drawing of the elementary cell is shown in Figure 1. Figures 2 and 3 show a perspective view of the octahedron of coordination and the molecular plane.

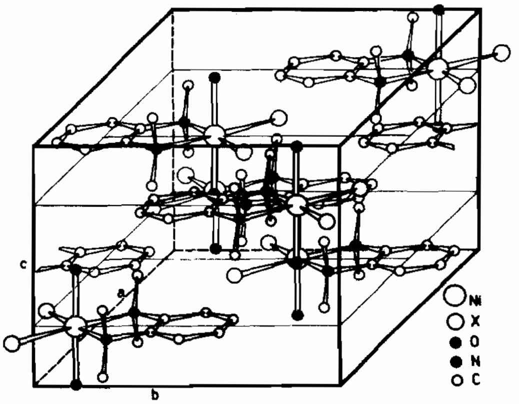

Figure 1. A perspective drawing of the elementary cell.

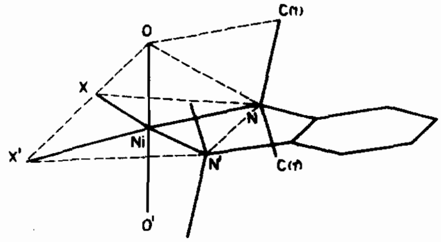

Figure 2. A perspective view of the octahedron of coordination.

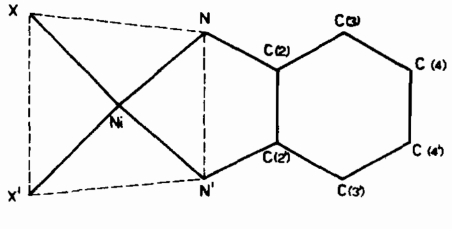

Figure 3. Molecular plane.

The bond lengths and angles of the two complexes are listed in Table V. The Ni–Cl and Ni–Br distances are 2.43 Å and 2.61 Å respectively. This indicates that in both compounds the nature of these bonds is more covalent that ionic (Pauling 1960).[11] Te Ni–N distances of 2.12 Å and 2.15 Å in NIC and NIB respectively agree with the Ni–N(en) bond lengths in $Ni(Me_4en)(NO_2)_2$ of 2.087 Å,[3] in $Ni(en)_3(NO_3)_2$ of 2.12 Å,[12] in $Ni(en)(H_2O)_4(NO_3)_2$ of 2.08 Å[13] and in $Ni(en)_2(NCS)_2$ of 2.10 Å.[14]

Table V. Interatomic Distances, Angles[a] and Errors

Distances, Å			
Ni—Cl	2.435 (9)	Ni—Br	2.606 (3)
Ni—O	2.123 (13)	Ni—O	2.036 (11)
Ni—N	2.118 (9)	Ni—N	2.151 (9)
Cl—Cl′	3.497 (3)	Br—Br′	3.754 (3)
Cl—N	3.288 (10)	Br—N	3.406 (9)
Cl—O	3.219 (9)	Br—O	3.282 (8)
Cl—C(1)	3.484 (8)	Br—C(1)	3.594 (10)
O—N	3.010 (12)	O—N	2.986 (11)
O—C(1)	2.928 (9)	O—C(1)	2.890 (13)
N—C(1)	1.511 (13)	N—N′	2.936 (18)
N—N′	2.831 (17)	N—C(1)	1.485 (14)
N—C(2)	1.494 (15)	N—C(2)	1.529 (14)
C(1)—C(1′)	2.494 (20)	C(1)—C(1′)	2.484 (19)
C(1)—C(2)	2.441 (14)	C(1)—C(2)	2.428 (15)
C(2)—C(2′)	1.386 (21)	C(2)—C(2′)	1.380 (21)
C(2)—C(3)	1.412 (18)	C(2)—C(3)	1.417 (18)
C(3)—C(4)	1.383 (20)	C(3)—C(4)	1.344 (21)
C(4)—C(4′)	1.371 (37)	C(4)—C(4′)	1.377 (32)
Ni—C(1)	3.025 (9)	Ni—C(1)	3.020 (12)
Angles, deg.			
Cl—Ni—Cl′	91.8 (1)	Br—Ni—Br′	92.1 (1)
Cl—Ni—O	89.6 (1)	Br—Ni—O	89.1 (2)
Cl—Ni—N	92.2 (3)	Br—Ni—N	90.9 (2)
O—Ni—N	90.4 (1)	O—Ni—N	90.9 (2)
N—Ni—N′	83.9 (4)	N—Ni—N′	86.0 (4)
Ni—N—C(2)	109.1 (6)	Ni—N—C(2)	106.4 (6)
Ni—N—C(1)	111.8 (4)	Ni—N—C(1)	111.0 (5)
C(1)—N—C(1′)	106.7 (8)	C(1)—N—C(1′)	113.6 (9)
C(1)—N—C(2)	108.7 (5)	C(1)—N—C(2)	107.3 (5)
N—C(2)—C(2′)	118.9 (8)	N—C(2)—C(2′)	120.6 (8)
N—C(2)—C(3)	120.9 (9)	N—C(2)—C(3)	121.4 (9)
C(3)—C(2)—C(2′)	120.7 (10)	C(3)—C(2)—C(2′)	118.0 (10)
C(2)—C(3)—C(4)	118.6 (11)	C(2)—C(3)—C(4)	122.3 (12)
C(3)—C(4)—C(4′)	121.2 (12)	C(3)—C(4)—C(4′)	119.7 (13)

[a] Standard deviations in the least significant digits are shown in parentheses.

The sum of the nickel(II) octahedral radius (1.39 Å) and the single bond covalent radius for nitrogen (0.70 Å) (Pauling 1960)[11] gives an octahedral nickel(II)-nitrogen bond length of 2.09 Å which is in agreement with the measured values for these compounds.

The N–C(2) distances of 1.49 Å (NIC) and 1.53 Å (NIB) are not significantly different from a single bond length.

The increased distance between N–N′ (from 2.83 Å (NIC) to 2.93 Å (NIB)) with consequent deformation of the angles of the chelate ring could be explained on the basis of the stronger interaction of the bromine atom with the methyl group. This causes a decrease in the symmetry around the nitrogen atom with increasing *p* character in the Ni–N bond.

All other distances in the base plane are normal.

The bond distances $Ni{-}OH_2$ are 2.12 Å in NIC and 2.04 Å in NIB respectively.

We conclude from the $Ni{-}OH_2$ distances in the two complexes that the water molecules are coordinated to the Ni.

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(11) L. Pauling, "The Nature of the Chemical Bond", 3rd edn., Ithaca, Cornell Univ. Press (1960).

(12) L. N. Swink and M. Atoji, *Acta Cryst.*, *13*, 639 (1960).

(13) G. Simmons, private communication to Prof. E. C. Lingafelter.

(14) B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, *16*, 753 (1963).

Whe have also examined the electronic spectra of these complexes in the solid state (by reflectance) and in methanol solution. Figure 4 shows the band maxima of the solutions. They are the same as those found in the corresponding solids indicating that the octahedral structure is mantained in solution.

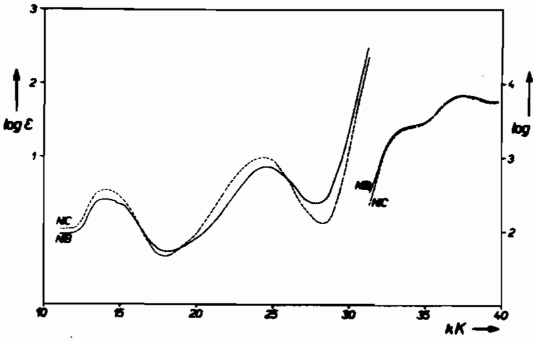

Figure 4. Spectra of NIC and NIB in methanolic solutions.

Moreover, these solution spectra are similar to those of other nickel(II) complexes[15] and, particularly the pattern of absorption of $NiX_2 . 2H_2O(N-N')$ is strikingly similar to that of $Ni(H_2O)_6{}^{2+}$. In fact the chromophores $Ni^{II}N_2O_2X_2$ have, effectively, O_h-micro-symmetry and the spectrochemical effect of (N+Br)/2 is known to be very similar to that of oxygen.[16,17]

No assignements can be made for bands of higher energy and higher intensity as they occur in a region where the organic ligand shows pronunced absorption.

As can be seen from Figure 4, the d–d transitions in NIC and NIB differ in intensity. This effect can be attributed to the difference in Ni–O bond-distance in NIC and NIB[18] and explained in terms of molecular orbital theory.

The d–d bands are mainly determined by the $t_{2g} \rightarrow e_g$ transitions; now, if we do not consider the π ligand effect, the $t_{2g}(xy,zx,zy)$ molecular orbitals are all 3d atomic orbitals, while $e_g(z^2,x^2-y^2)$ m.o.'s are for the most part 3d a.o.'s, but with a small contribution of the σ ligand's orbitals.[19] It is known that the intensity of a d–d type band increases as the ligand contribution increases. Therefore NIC seems to have a greater σ mixing than NIB. Keeping in mind that the t_{2g} and e_g m.o.'s are antibonding orbitals, it appears that the σ ligand operates more in NIB than in NIC in the bonding m.o.'s.

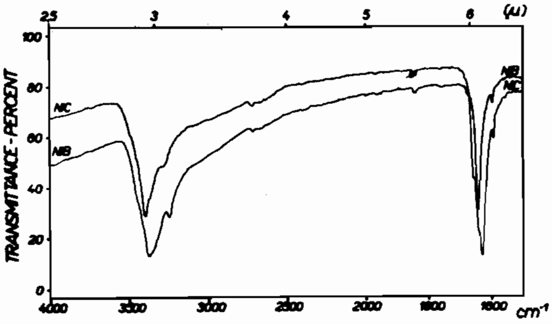

Figure 5. Infrared spectra of NIC and NIB

Table VI. Frequencies of IR spectra of NIC, NIB, and H_2O (gas)[20]

Compound	O–H Stretching frequencies, cm^{-1}	O–H Bending frequencies, cm^{-1}
H_2O (gas)	3756, 3657	1595
NIC	3395, 3285	1640
NIB	3370, 3240	1627

A parallel study of the infrared spectra of the two solids in a Nujol mull is shown in Figure 5. Table VI shows the values of the frequencies of the band maxima of Figure 5, together with the corresponding frequencies of water in the gas state. It can be seen that the OH stretching modes of the water molecules in NIC and NIB are shifted down (with respect to water gas) and the bending modes are shifted up indicating that hydrogen bonds exist in the solide state in these compounds. Their most probable locations are between the oxygen atoms of the water molecules and the halogen atoms of molecules, related by the c-glide plane, as shown in Figure 6.

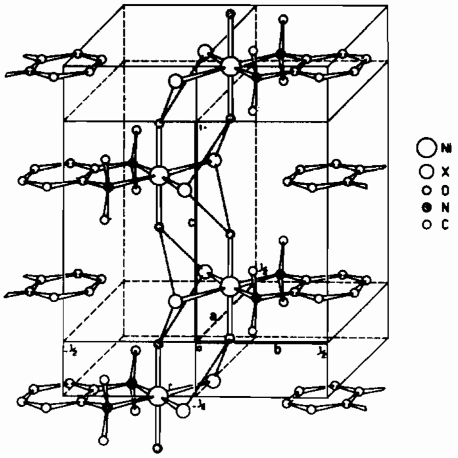

Figure 6. A perspective view of the molecules which are believed to be involved in weak hydrogen bond (broken lines).

In fact from X-ray analysis we have found the following intermolecular contact: H_2O---Cl 3.26 Å and the corresponding H_2O---Br 3.40 Å, showing that the contact is made between the oxygen and halogen atoms.

In addition there is a diffuse positive density in the final difference-synthesis in the oxygen-halogen intermolecular approach direction, at a distance from the oxygen atom which could be consistent with the presence of a hydrogen atom, if it is assumed that the oxygen of the coordinated water is in sp^3 hybridization state.

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(15) C. K. Jørgensen, "Orbitals in atoms and molecules", Academic Press, London (1962).
(16) C. E. Schäffer and C. K. Jørgensen, *Mat. fys. Medd. Dan. Vid. Selsk.*, *34*, n. 13 (1965).
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(18) C. K. Jørgensen, private communication.
(19) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press Oxford (1964).

(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", J. Wiley & Sons, New York (1962).

Hence the structure of the two complexes may be described in terms of hydrogen-bonded chains parallel to the c axis. The stability of these structures is shown by the relatively high density of the crystals and by the fact that the anhydrous crystals quickly revert to the hydrate on exposure to air.

Acknowledgments. The authors wish to express their thanks to Professor C. K. Jørgensen for the interesting discussions and for his valuable suggestions. Thanks are also due to Dr. B. Crociani for infrared spectra. The authors are indebted to the Consiglio Nazionale delle Ricerche for financial support and to Computer Center of Padova University, for allowing computing facilities on the Olivetti Elea 6001 computer.