Stabilization of High-Spin Five-Coordinate Nickel(II) Complex Anions by Appropriate Counterions

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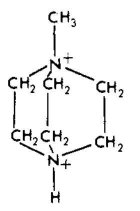
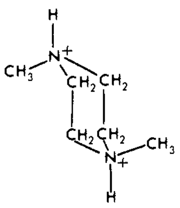
Abstract: This paper reports the preparation and structural investigation of the five-coordinate anionic chloro complexes of nickel(II), of the formulas $[Ni_2Cl_8]^{4-}$ and $[NiCl_4(ROH)]^{2-}$ (R = CH_3 and C_2H_5), which have been found to be stable in ionic crystals with large divalent counterions.

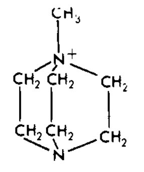
Previous work has shown that the stability of neutral five-coordinate transition metal complexes containing positively charged ligands depends to a large extent on lattice energy and hydrogen bonding.[1] A similar effect has been observed for the five-coordinate Cu(II) complex anion, $[CuCl_5]^{3-}$, which appears to be stabilized in ionic crystals by large counterions,[2,3] for example, $[M(NH_3)_6]^{3+}$. On the basis of these observations it appeared worthwhile to extend our studies on five-coordination and explore if other five-coordinate anionic complexes of the transition metal ions could be stabilized in the crystalline state by suitable noncoordinating cations. The reaction of Ni(II) halides with the halides of univalent and divalent organic cations with varied structures and sizes was investigated under different experimental conditions. Two divalent cations, protonated N-methyldabconium (I) and diprotonated N,-N′-dimethylpiperazinium (II), were found to stabilize five-coordinate anionic chloro complexes of nickel(II).



I = $[C_7H_{16}N_2]^{2+}$



II = $[C_6H_{16}N_2]^{2+}$



III = $[C_7H_{15}N_2]^{+}$

Results and Discussion

Nickel(II) chloride reacts with the chlorides of the cations I and II, under the conditions described in the Experimental Section, to yield compounds of stoichiometry: $(I)NiCl_4$, $(II)NiCl_4 \cdot ROH$, and $(II)_2NiCl_6 \cdot ROH$ (where R = C_2H_5 or CH_3). These compounds are deep purple, paramagnetic, crystalline substances, moderately stable to heat. They are insoluble in nonpolar solvents or in polar organic solvents such as alcohols, and decompose on contact with water and other solvents of good donor properties. The magnetic moments and d–d electronic absorptions of these compounds are listed in Table I.

It is well known[4] that the chlorides of univalent as well as divalent cations generally react with $NiCl_2$ to form ionic compounds containing either the deep blue, mononuclear, tetrahedral $[NiCl_4]^{2-}$ anion,[5] or the reddish yellow, polynuclear, octahedral $[NiCl_3^-]_n$ anion,[6,7] both with a high-spin electron configuration. For the Ni(II) compounds containing the cations I and II, and having stoichiometry $(I)NiCl_4$, $(II)NiCl_4 \cdot ROH$, and $(II)_2NiCl_6 \cdot ROH$, the values of the magnetic moments still indicate a high-spin electron configuration of the metal ion, but the intense purple colors immediately suggest a stereochemistry other than tetrahedral or octahedral, thus adding interest to the structural investigation of these compounds.

For the compound of stoichiometry $(I)NiCl_4$, the vibrational spectrum in the 4000–300-cm^{-1} region is virtually identical with that of the dichloride and of the tetrachlorocobaltate(II) of cation I. The differences in the N^+–H stretching region (3100–2400 cm^{-1}) undoubtedly arise from different extents of hydrogen bonding in the crystal lattice, as commonly observed for substituted ammonium salts of different anions.[8] Thus, in the purple compound of stoichiometry $(I)NiCl_4$, the cation I is unchanged and the nickel(II) must then be present as part of a complex chloro anion. Since the d–d electronic spectrum of the compound (Figure 1a) cannot be reconciled with either a tetrahedral or an octahedral stereochemistry of Ni(II) complexes, but closely resembles the spectra of high-spin Ni(II) complexes known from X-ray studies to be five-coordinate,[9–11] it is logical to formulate this complex chloro anion as a dimer, $[Ni_2Cl_8]^{4-}$, in which each Ni(II) attains five-coordination through a "double Cl bridge." According to this formulation, a strong infrared absorption centered at about 250 cm^{-1} in the vibrational spectrum of the compound $(I)_2[Ni_2Cl_8]$ is assigned to a Ni–Cl stretching mode involving terminal ligands. (The Ni–Cl modes involving bridging Cl ligands usually occur[12] below the limit of

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(1) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, **8**, 2331 (1969).

(2) G. C. Allen and N. S. Hush, *ibid.*, **6**, 4 (1967); M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Jap.*, **34**, 245 (1961).

(3) F. Basolo, *Coord. Chem. Rev.*, **3**, 213 (1968).

(4) For a listing of examples, see "Gmelins Handbuch der Anorganischen Chemie," Teil B, "Nickel," Lieferung 3, Verlag Chemie, Weinheim/Bergstr., 1966, pp 1080–1083, 1095, 1102.

(5) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959); N. S. Gill, *ibid.*, 3512 (1961).

(6) R. W. Asmussen and O. Bostrup, *Acta Chim. Scand.*, **11**, 745 (1957); O. Bostrup and C. K. Jørgensen, *ibid.*, **11**, 1222 (1957).

(7) R. D. Willett, *J. Chem. Phys.*, **45**, 3737 (1966); G. D. Stucky, *Acta Cryst.*, **B24**, 330 (1968); G. D. Stucky, S. D'Agostino, and G. McPherson, *J. Am. Chem. Soc.*, **88**, 4828 (1966).

(8) P. Sauvageau and C. Sandorfy, *Can. J. Chem.*, **38**, 1901 (1960), and references therein.

(9) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

(10) L. Sacconi, "Transition Metal Chemistry," Vol. **4**, Marcel Dekker Inc., New York, N. Y., 1968, pp 199–298.

(11) G. D. Stucky and F. K. Ross, *Inorg. Chem.*, in press.

Table I. Some Properties of Five-Coordinate Complex Anions of Nickel(II)

Stoichiometry of salt[a]	Complex anion	Color	μ_{eff}, BM	d–d electronic absorptions, kK[b]					
(I)$NiCl_4$	$[Ni_2Cl_8]^{4-}$	Deep purple	3.35	7.14	9.6	11.9	15.3	17.2	19.2
(II)$NiCl_4 \cdot C_2H_5OH$ $(II)_2NiCl_6 \cdot C_2H_5OH$	$[NiCl_4(C_2H_5OH)]^{2-}$	Red-purple	3.50	7.3	9.8	12.1	15.6	17.4	20.0
(II)$NiCl_4 \cdot CH_3OH$ $(II)_2NiCl_6 \cdot CH_3OH$	$[NiCl_4(CH_3OH)]^{2-}$	Red-purple	3.52	7.3	9.8	12.1	15.4	17.4	20.0

[a] I = protonated N-methyldabconium, $[C_7H_{16}N_2]^{2+}$; II = diprotonated N,N′-dimethylpiperazinium, $[C_6H_{16}N_2]^{2+}$. [b] From hexachlorabutadiene mull spectra (absorption maxima of reflectance spectra are coincident, but mull spectra show better resolution).

the instrument used in this work.) The frequency of the Ni–Cl (terminal) stretching mode in $[Ni_2Cl_8]^{4-}$ is intermediate between the frequencies generally observed for the Ni–Cl stretching vibrations of tetrahedral and octahedral chloro complexes,[12] and appears to be characteristic of five-coordinate Ni(II).[1]

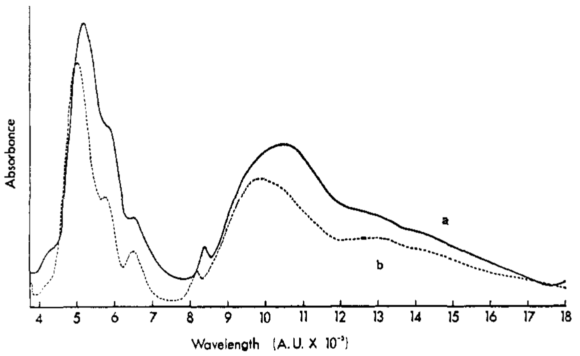
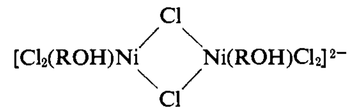


Figure 1. The d–d electronic absorption spectra (reflectance) of five-coordinate complexes of Ni(II): (a, solid line) the square-pyramidal $[Ni_2Cl_8]^{4-}$; (b, dashed line) $[NiCl_4(C_2H_5OH)]^{2-}$, stereochemistry unknown.

For the compounds of stoichiometry (II)$NiCl_4 \cdot ROH$ and $(II)_2NiCl_6 \cdot ROH$ (where R = C_2H_5 or CH_3), the infrared vibrational spectra show the characteristic absorptions of cation II, virtually identical with those of its dichloride and tetrachlorocobaltate(II), and indicate that Ni(II) is present in these compounds as a complex chloro anion. The vibrational spectra of these compounds also contain two additional absorptions. A strong band centered at about 250 cm^{-1}, similar to that present in the spectrum of $(I)_2[Ni_2Cl_8]$, is assigned to a Ni–Cl (terminal) stretching mode; a medium, broad band occurring at 3400–3380 cm^{-1} is assigned to the OH stretching mode of the coordinated alcohol molecule.[13] Direct evidence for the presence of one molecule of ethanol or methanol in the compounds of stoichiometry (II)$NiCl_4 \cdot ROH$ and $(II)_2NiCl_6 \cdot ROH$ was obtained by heating the compounds at 145° in an evacuated system. Under these conditions the compounds turned slowly from purple to blue, with a decrease in weight corresponding to the loss of one molecule of the alcohol; the vapor evolved, collected in a cold trap and examined by nuclear magnetic resonance, was found to consist totally of the respective alcohol. The blue compound obtained by elimination of the alcohol from the compounds (II)$NiCl_4 \cdot C_2H_5OH$ and (II)$NiCl_4 \cdot CH_3OH$ was identified from its analytical data and its vibrational and d–d electronic spectra as the complex salt (II)$[NiCl_4]$, containing the tetrahedral tetrachloronickelate(II) anion. Similarly, the blue compound obtained by elimination of the alcohol from the compounds of stoichiometry $(II)_2NiCl_6 \cdot C_2H_5OH$ and $(II)_2NiCl_6 \cdot CH_3OH$ was identified as the "double salt," $(II)_2Cl_2$-$NiCl_4$, again containing the tetrahedral $[NiCl_4]^{2-}$ ion. In the absorption spectra of these blue complex salts, the medium intensity band at 3400–3390 cm^{-1} is no longer present, thus confirming its assignment as the OH stretching vibrations of the alcohol molecule present in the original purple compounds.

The structural formulation of the Ni(II) anionic complexes present in the compounds of stoichiometry (II)$NiCl_4 \cdot ROH$ and $(II)_2NiCl_6 \cdot ROH$ is based essentially on their d–d electronic spectra (Figure 1b) which are identical with one another and very closely resemble that of the $[Ni_2Cl_8]^{4-}$ anion, except for a slight shift to higher energies. This shift indicates a somewhat higher average ligand field about the central Ni(II), and is consistent with the replacement of a chloro ligand by an oxygen-donor ligand. Thus the alcohol-containing complexes may logically be assigned the structural formulas (II)$[NiCl_4(ROH)]$ and $(II)_2Cl_2[NiCl_4(ROH)]$, with the complex anion $[NiCl_4(ROH)]^{2-}$ having a five-coordinate mononuclear structure. The possibility of a chloro-bridged dimeric structure of the type



seems rather unlikely, as halogen bridges usually form to fulfill the coordinating requirement of the metal ion, and are unnecessary in compounds such as $(II)_2Cl_2[NiCl_4(ROH)]$, which contain "free" Cl^- ions in the crystal lattice.

It should be observed that the electronic d–d spectra of the $[Ni_2Cl_8]^{4-}$ and $[NiCl_4(ROH)]^{2-}$ anions, while clearly indicating that Ni(II) has coordination number five, do not allow one to assign with confidence the geometrical arrangement of the ligands. In fact the energies of the observed transitions (Table I) do not show a satisfactory agreement, for any reasonable value of μ, with the energies calculated from the available energy level diagrams of either trigonal-bipyramidal or square-pyramidal Ni(II).[9] However, the overall pattern of the d–d electronic spectra of the $[Ni_2Cl_8]^{4-}$ and $[NiCl_4(ROH)]^{2-}$ ions is similar to that of the $[Ni(L^+)(H_2O)Cl_3]$ complex (where L^+ = N-methyldabconium

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(12) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 4, 350 (1965); R. J. H. Clark and C. S. Williams, *Chem. Ind.* (London), 1317 (1964).

(13) V. Imhof and R. S. Drago, *Inorg. Chem.*, 4, 427 (1965).

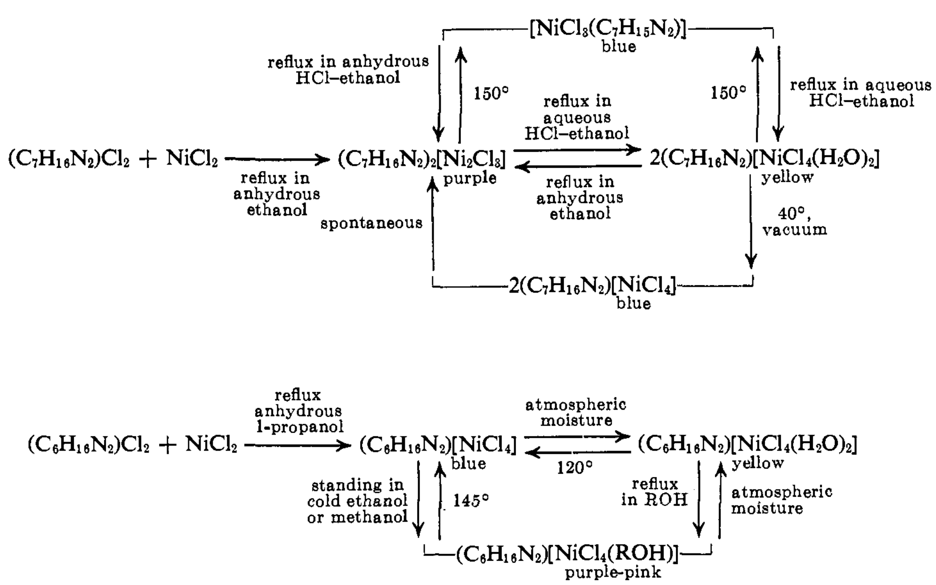

Figure 2. Correlation chart of four-, five-, and six-coordinate chloronickelate(II) anions.

cation-ligand, III) which has an essentially trigonal-bipyramidal stereochemistry.[11] On this basis, it might have been tempting to attribute a similar geometry also to the $[Ni_2Cl_8]^{4-}$ and $[NiCl_4(ROH)]^{2-}$ ions. The fact that an almost undistorted square-pyramidal geometry has been established by Stucky and Ross[14] for the environment of Ni(II) in $(Ni_2Cl_8)^{4-}$ points out that, at the present stage of knowledge, great caution should be exercised in making assignments for five-coordinate high-spin Ni(II) solely on the basis of d–d electronic spectra.

It was mentioned that the compounds (II)$[NiCl_4(ROH)]$ and $(II)_2Cl_2[NiCl_4(ROH)]$ lose alcohol on heating at about 145°, forming the corresponding blue salts of the tetrahedral $(NiCl_4)^{2-}$ anion. The compound $(I)_2[Ni_2Cl_8]$ also decomposes on heating. In this case hydrogen chloride is evolved, and the deep blue crystalline solid which remains is identified from its analytical and spectral properties as the previously reported[15] pseudotetrahedral nonionic complex $[Ni(L^+)Cl_3]$ (where L^+ = N-methyldabconium cation-ligand, III). Thus, the coordinating tendency of this cation-ligand is sufficiently marked to favor this mononuclear, nonionic species rather than an ionic structure involving noncoordinated N-methyldabconium cations III, and the polymeric, octahedral $[NiCl_3^-]_n$ anions.

The salts of the $[Ni_2Cl_8]^{4-}$ and $[NiCl_4(ROH)]^{2-}$ anions are very sensitive to moisture. The alcohol complexes, (II)$[NiCl_4\,(ROH)]$ and $(II)_2Cl_2[NiCl_4\,(ROH)]$, if exposed to the atmosphere even in the presence of their alcohol mother liquor, slowly lose the coordinated alcohol molecule and take on two molecules of water, forming bright yellow crystalline compounds of the stoichiometry (II)$NiCl_4 \cdot 2H_2O$ and $(II)_2NiCl_6 \cdot 2H_2O$, respectively. Similarly, the purple complex $(I)_2[Ni_2Cl_8]$ slowly turns yellow when exposed to moist air or when heated with an ethanol solution containing a small quantity of concentrated hydrochloric acid. The yellow product obtained by exposure to moist air has the stoichiometry (I)$NiCl_4 \cdot 3H_2O$, whereas the one formed in acidic ethanol has the stoichiometry (I)$NiCl_4 \cdot 2H_2O$. The vibrational absorption spectra of all these yellow compounds indicate that the cations I and II are unaltered, and that the water is coordinated. Also, the magnetic moments and the electronic spectra, which are virtually identical for all hydrated compounds cited above, show that Ni(II) has a tetragonally distorted octahedral stereochemistry.[16] The energies of the observed d–d electronic absorptions agree with those expected for Ni(II) in an environment of four Cl and two O ligating atoms; the yellow compounds are therefore formulated as the salts of the complex anion *trans*-$[NiCl_4(H_2O)_2]^{2-}$. It is noteworthy that when heated at 100°, all these yellow compounds containing the octahedral $[NiCl_4(H_2O)_2]^{2-}$ anion readily lose water to form the tetrahedral $[NiCl_4]^{2-}$, whereas the five-coordinate $[NiCl_4(ROH)]^{2-}$ anions lose alcohol to form the tetrahedral $[NiCl_4]^{2-}$ only when heated above 145°.

An interesting phenomenon occurs when the yellow (I)$[NiCl_4(H_2O)_2]$ is dehydrated *in vacuo* at 30–40°. The color of the solid changes gradually from yellow to bright blue, and then more slowly from blue to the deep purple of $(I)_2[Ni_2Cl_8]$. The intermediate blue compound is identified, from its d–d electronic spectrum, as the tetrahedral tetrachloronickelate(II) of the cation I. Thus, the complex salt of stoichiometry (I)$NiCl_4$ exists as two isomeric crystalline forms, differing in the structure of the complex Ni(II) anions. The crystalline form containing the tetrahedral monomeric $[NiCl_4]^{2-}$ anion is metastable with respect to the form containing the five-coordinate dimeric $[Ni_2Cl_8]^{4-}$ anion. This is a very unusual example of monomer–dimer isomerism for a simple halometalate complex ion. Figure 2 shows a correlation chart including these and the other complex salts studied in the investigation.

The $[Ni_2Cl_8]^{4-}$ and $[NiCl_4(ROH)]^{2-}$ complex anions represent, to our knowledge, the first five-coordinate halonickelate(II) complexes to be reported. Undoubtedly the large lattice energy characteristic of these salts of dipositive cations and di- or tetranegative anions is the principal factor responsible for the stabilization in the solid state of the unusual five-coordinate anionic

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(14) G. D. Stucky and F. R. Ross, unpublished data.

(15) J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Am. Chem. Soc.*, in press.

(16) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 788 (1964); D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **6**, 1092 (1967).

complexes. Hydrogen bonding between the N^+–H groups of the cations and the neighboring chloro ligands or chloride ions in the crystal lattice should also contribute appreciably to the stabilization of these systems. Our failure to obtain the corresponding five-coordinate anionic complexes of Ni(II) with bromo and iodo ligands may be attributed at least in part to the lack of extra-stabilization resulting from the much weaker hydrogen bonding of these heavier halides. Thus it appears that a rather special set of conditions—an appropriate charge, size, and shape of the counterion, and a particularly favorable network of hydrogen bonding throughout the crystal—is required to stabilize the five-coordinate $(Ni_2Cl_8)^{4-}$ more than the common tetrahedral $(NiCl_4)^{2-}$ and octahedral $(NiCl_3^-)_n$. In fact, even such closely related divalent cations as diprotonated and dimethylated dabconium failed to form the five-coordinate Ni(II) complex anion. Similar considerations hold for the five-coordinate $[NiCl_4(ROH)]^{2-}$ anions in the presence of the diprotonated N,N′-dimethylpiperazinium counterion. As yet, only Ni(II), a d^8 system, has been observed to form these five-coordinate complex anions; it is possible, however, that with an appropriate choice of cations and under suitable preparative conditions similar complex anions of other transition metal ions could be formed.

Experimental Section

Starting Materials. To prepare N,N′-dimethylpiperazinium dichloride, $[C_6H_{16}N_2]^{2+}(Cl^-)_2$, anhydrous HCl gas was passed through an ethanol solution of N,N′-dimethylpiperazine (Aldrich Chemical Co.) until the solution became strongly acidic (pH 2). The white crystals which formed were filtered off, washed with acetone, and dried *in vacuo*. *Anal.* Calcd for $C_6H_{16}N_2Cl_2$: N, 14.97; Cl, 37.89. Found: N, 14.7; Cl, 38.1. Protonated N-methyldabconium dichloride, $[C_7H_{16}N_2]^{2+}(Cl^-)_2$, was prepared in a similar manner, using N-methyldabconium chloride,[15] $(C_7H_{15}N_2)^+Cl^-$, as the starting material. *Anal.* Calcd for $C_7H_{16}N_2Cl_2$: N, 15.18; Cl, 38.46. Found: N, 15.0; Cl, 38.3. All solvents used were Reagent or Spectra grade, and anhydrous.

Preparation of the Complexes. The Blue (II)[NiCl$_4$]. An ethanol solution of $NiCl_2$ (10 mmoles) and a 1-propanol solution of N,N′-dimethylpiperazinium dichloride, (II)Cl_2 (8 mmoles), were dehydrated by refluxing for several minutes with a small quantity of triethyl orthoformate. The hot $NiCl_2$ solution was then added, with stirring, to the solution of the organic salt. A bright blue precipitate (fine needles) began to form at once. The mixture was stirred at 80° for 10 min and filtered while still hot. The precipitate was washed quickly with 1-propanol containing some triethyl orthoformate and dried *in vacuo*.. *Anal.* Calcd for $(C_6H_{16}N_2)NiCl_4$: Cl, 44.78; Ni, 18.54. Found: Cl, 44.9; Ni, 18.3. The vibrational and electronic d–d spectra of the compound agreed with those expected for the tetrahedral tetrachloronickelate(II) of cation II.

The Red-Purple (II)[NiCl$_4$(ROH)]. The crystalline blue (II)-$NiCl_4$ was suspended in anhydrous ethanol containing about 5% of triethyl orthoformate, and the suspension was allowed to stand at room temperature. After several hours the original blue solid completely changed to red-purple crystals. These were filtered in a drybox, washed once with cold anhydrous ethanol, and dried in *vacuo* for 10 min. *Anal.* Calcd for $(C_6H_{16}N_2)NiCl_4(C_2H_5OH)$: Cl, 39.19; Ni, 16.19; C_2H_5OH, 12.69. Found: Cl, 39.6; Ni, 16.4; C_2H_5OH, 13.0. A similar red-purple complex was obtained by suspending the blue (II)$NiCl_4$ in an anhydrous methanol solution of $NiCl_2$ (about 1 mmole for 10 mmoles of the blue complex). If some excess of $NiCl_2$ is not present, the blue complex partly decomposes when suspended in methanol, with the separation of some N,N′-dimethyliperazinium dichloride. *Anal.* Calcd for $(C_6H_{16}N_2)NiCl_4(CH_3OH)$: Cl, 40.66; Ni, 16.64; CH_3OH, 9.19. Found: Cl, 41.0; Ni, 16.5; CH_3OH, 10.1. The percentage of alcohol was determined by heating a sample of the complex at 150° under vacuum and measuring the loss of weight. The vapor evolved was collected in a cold trap at −80°, and the condensate was identified as ethanol, or methanol, from its nmr spectrum.

The Red-Purple (II)$_2$Cl$_2$[NiCl$_4$(ROH)]. An anhydrous ethanol solution of $NiCl_2$ was added dropwise to an excess of a saturated solution of N,N′-dimethylpiperazinium dichloride, (II)Cl_2, in boiling anhydrous ethanol. A blue precipitate formed immediately, which slowly changed to red-purple as the solution cooled to room temperature. The red-purple crystalline product was filtered in a drybox, washed with anhydrous ethanol, and dried *in vacuo*. *Anal.* Calcd for $(C_6H_{16}N_2)_2NiCl_6(C_2H_5OH)$: N, 10.19; Cl, 38.69; Ni, 10.68; C_2H_5OH, 8.37. Found: N, 10.0; Cl, 38.8; Ni, 10.9; C_2H_5OH, 8.5.

An analogous red-purple methanol complex was prepared in a similar manner, using methanol as the solvent. In this case cooling was not necessary since the purple complex formed directly in the boiling solution. *Anal.* Calcd for $(C_6H_{16}N_2)_2Cl_2 \cdot NiCl_4(CH_3OH)$: N, 10.45; Cl, 39.71; Ni, 10.95; CH_3OH, 5.98. Found: N, 10.3; Cl, 39.5; Ni, 10.9; CH_3OH, 6.1.

The blue compound first formed upon addition of $NiCl_2$ to the hot ethanol solution of (II)Cl_2 was identified as the double salt (II)$_2Cl_2NiCl_4$ from its analysis (*Anal.* Calcd for (II)$_2Cl_2NiCl_4$: Cl, 42.20; Ni, 11.66. Found: Cl, 42.4; Ni, 11.3) and its vibrational and d–d electronic spectra. This latter showed the characteristic absorptions of the tetrahedral $(NiCl_4)^{2-}$ ion.

The Deep Purple (I)$_2$[Ni$_2$Cl$_8$]. One gram of protonated N-methyldabconium dichloride, (I)Cl_2, was suspended in 40 ml of boiling anhydrous ethanol; a hot ethanol solution containing 0.65 g of anhydrous $NiCl_2$ was then added dropwise. The hot heterogeneous mixture reacted slowly to yield a deep purple precipitate (square tablets) which was filtered in a drybox, washed with anhydrous ethanol, and dried *in vacuo*. *Anal.* Calcd for $(C_7H_{16}N_2)_2Ni_2Cl_8$: N, 8.58; Cl, 43.20; Ni, 17.85. Found: N, 8.6; Cl, 43.2; Ni, 17.9.

The Blue (I)NiCl$_4$. A weighed sample of the yellow (I)[$NiCl_4(H_2O)_2$] (see below) was placed in a wide-mouthed vessel in a desiccator, and gently warmed to 30–40° with a lamp, under continuous pumping. The color of the solid gradually changed from yellow to bright blue (weight loss with respect to the yellow compound: Calcd: 9.87. Found: 10.1). The bright blue complex, whose electronic spectrum was characteristic of the tetrahedral $(NiCl_4)^{2-}$ anion, had the tendency to transform spontaneously into the purple (I)$_2Ni_2Cl_8$ without weight change. The transformation was slow at room temperature and in the absence of an external disturbance; heating above 50°, grinding, scratching, or the addition of a liquid such as ethanol, greatly accelerated the change from the blue to the purple isomer. The blue (I)$NiCl_4$ was stable indefinitely when stored in a sealed vial below 20°.

Complexes Containing the Yellow [NiCl$_4$(H$_2$O)$_2$]$^{2-}$ Anion. When the red-purple (II)$NiCl_4$(ROH) is allowed to stand in alcohol exposed to a moist atmosphere, the molecule of coordinated alcohol is replaced by two molecules of water, and well-formed yellow crystals of (II)$NiCl_4(H_2O)_2$ form slowly. *Anal.* Calcd for $(C_6H_{16}N_2)NiCl_4(H_2O)_2$: Cl, 40.21; Ni, 16.64; H_2O, 10.21. Found: Cl, 40.4; Ni, 16.3; H_2O, 10.4 (determined as loss of weight to form the blue (II)$NiCl_4$). The yellow complex is paramagnetic with μ_{eff} = 3.28 BM. The infrared spectrum shows the expected absorptions arising from coordinated H_2O molecules. The d–d electronic spectrum (reflectance and hexachlorobutadiene mull) is characteristic of Ni(II) in a pseudo-octahedral field of D_{4h} symmetry; the observed absorptions with their respective assignments follow: a broad weak band with maxima at 5.7 and 7.0 kK ($^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, split in D_{4h} symmetry): a medium band at 12.1 kK ($^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$); and a relatively intense band at 22.6 kK ($^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$). In a similar manner, the red-purple double salt (II)$_2$-Cl_2NiCl_4(ROH) forms the yellow (II)$_2Cl_2NiCl_4(H_2O)_2$ (Calcd: N, 10.39; Cl, 39.40; Ni, 10.89. Found: N, 10.30; Cl, 39.5; Ni, 10.3), whose vibrational and electronic spectra are identical with those of (II)$NiCl_4(H_2O)_2$.

The corresponding complex salt of cation I was obtained as follows. The crystalline purple (I)$_2Ni_2Cl_8$ was suspended in ethanol containing about 5% of concentrated aqueous hydrochloric acid, and the mixture was refluxed for 1 hr. The color of the suspended solid slowly changed from purple to bright yellow. The yellow compound was filtered, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd for $(C_7H_{16}N_2)NiCl_4(H_2O)_2$: Cl, 38.90; Ni, 16.10; H_2O, 9.87. Found: Cl, 39.3; Ni, 16.0; H_2O = 10.0 (determined as weight loss to re-form the purple (I)$_2Ni_2Cl_8$).

A yellow powdery complex, whose electronic spectrum is very similar to that of (I)$NiCl_4(H_2O)_2$, is formed when either the solid blue (I)$NiCl_4$ or the solid purple (I)$_2Ni_2Cl_8$ is exposed to moist air.

(This change is very rapid for the blue isomer, but relatively slow for the purple isomer.) The weight gained in the formation of the yellow complex, which is identical with the weight loss when the yellow complex is dehydrated to re-form the original blue or purple complexes, corresponds to three molecules of water per Ni(II) ion (Calcd: 14.11. Found: 13.9). This yellow complex can be tentatively formulated as (I)$NiCl_4(H_2O)_2 \cdot H_2O$. It is significant that in the vibrational spectrum of this complex, the water absorptions are more intense and much broader than those observed in the complex formed in ethanol solution, (I)$NiCl_4(H_2O)_2$, which contains two molecules of coordinated water only.

Characterization of the Complexes. The complexes prepared were characterized by analysis, visible and infrared spectra (30,000–250 cm^{-1}), and magnetic susceptibility measurements. For details, see ref 15.

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Electronic Energy Levels in Hexahalotellurate(IV) Complexes

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Abstract: The electronic spectra of the octahedral $TeCl_6^{2-}$ and $TeBr_6^{2-}$ complexes are reported and assigned. The s → p transition $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ gives rise to three spin-allowed bands in $TeCl_6^{2-}$ (32,880; 34,480; 35,680 cm^{-1}) and $TeBr_6^{2-}$ (28,470; 29,730; 30,850 cm^{-1}). These data are taken as evidence that the excited singlet states are distorted to lower symmetry, probably C_{2v}. The lowest allowed halide → Te(IV) charge transfer transitions are at 44,170 cm^{-1} and somewhat higher than 52,000 cm^{-1} in $TeCl_6^{2-}$; analogous transitions appear at 37,000 and 42,600 cm^{-1} in $TeBr_6^{2-}$. The observed spectral data indicate that the "inert" $5s^2$ Te(IV) electrons, which reside in the $a_{1g}\sigma^*$ level, are partially delocalized to the halide ligands.

The elucidation of electronic structure in hexahalo complexes of post-transition metals through electronic spectroscopic means has primarily been directed at the d^{10} systems represented by the central metals Sn(IV) and Sb(V).[1,2] Of the relatively few studies on the interesting complexes of $d^{10}s^2$ metals, a recent investigation[1] has shown that the interpretation of absorption spectra of halo complexes of Sb(III) and Bi(III) is complicated by uncertainties in the structure of the species under investigation. Furthermore, the most extensive spectral studies[3] on halo complexes of Se(IV) and Te(IV) have been in aqueous media where hydrolysis is a serious problem.[4,5]

We have begun an investigation of the electronic spectra and structures of TeX_6^{2-} complexes. This choice of $d^{10}s^2$ systems is appropriate because the complexes can be studied in media where sufficient structural information is at hand to allow a detailed interpretation of the results. In particular, the anions $TeCl_6^{2-}$ and $TeBr_6^{2-}$ in various solid samples have been shown from X-ray diffraction,[6,7] infrared,[4,5,8] Raman,[4,5] and nuclear quadrupole resonance[9] studies to possess regular octahedral structures. Furthermore, two independent Raman spectral studies[4,5] are in agreement that these anions retain octahedral structure in acetonitrile solution. In the present paper we report absorption spectra of $TeCl_6^{2-}$ and $TeBr_6^{2-}$ as thin films (n-Bu_4N^+ salts) and in various nonaqueous solvents, in an effort to establish a basis for serious discussion of their electronic structures.

Experimental Section

Preparation of Compounds. $(NH_4)_2[TeCl_6]$**.** This compound was prepared by a modification of a method due to Fernelius.[10] Tellurium dioxide, freshly prepared from 99.999% tellurium, was dissolved in hot, concentrated hydrochloric acid. A saturated solution of ammonium chloride in hydrochloric acid was added, and yellow crystals of the complex formed immediately. The solution was evaporated down to about one-third its original volume and cooled. The crystals were collected on a sintered glass filter and washed with hydrochloric acid. The complex was recrystallized from concentrated hydrochloric acid, washed thoroughly, and dried under vacuum.

$(NH_4)_2[TeBr_6]$**,** $[n\text{-}Bu_4N]_2[TeCl_6]$**, and** $[n\text{-}Bu_4N]_2[TeBr_6]$**.** These compounds were prepared by methods analogous to the above.

Solvents. Acetonitrile was distilled eight times off phosphorus pentoxide and fractionated; the fraction boiling at 82.0° was collected. Precautions were taken to prevent access of moisture at all stages in handling the solutions. Dichloromethane was washed with dilute sulfuric acid and sodium carbonate solution, dried over calcium chloride, and fractionated; the fraction boiling at 39.6° was collected.

Spectral Measurements. Absorption spectra were recorded on Beckman DK-2A, Cary 14CMRI, and Cary 15 spectrophotometers. Thin films were prepared by evaporating dichloromethane solutions of tetra-n-butylammonium salts of $TeCl_6^{2-}$ and $TeBr_6^{2-}$

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