

Structural Properties and Vibrational Spectra of the Ethylenediammonium Family of Perovskite Layer-Type Crystals: $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3][\text{MCl}_4]$, $M = \text{Ni, Pd, Cu, Cd, Mn}$

STEEN SKAARUP AND ROLF WILLESTOFTE BERG*

Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark

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A new compound, $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)\text{NiCl}_4$, has been prepared and investigated. Magnetism and powder X-ray diffraction photographs in combination with electronic and vibrational spectra indicate a weakly paramagnetic structure containing two-dimensional perovskite-type layers of tetragonally distorted corner-sharing NiCl_6 octahedra. The unit cell dimensions are: $a = 8.441 \pm 0.001$, $b = 6.995 \pm 0.001$, $c = 6.943 \pm 0.001$ Å, $\beta = 92.925 \pm 0.002^\circ$, in space group $P2_1/c$ (C_{2h}^2), $Z = 2$. It is shown that this compound and the corresponding Pd compound belong to an isostructural family of crystals: $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)\text{MCl}_4$, $M = \text{Ni, Pd, Cu, Cd, Mn}$. The vibrational spectra of these compounds are discussed in relation to the structure.

1. Introduction

Simple ligand field theory predicts that four-coordinate complexes with d^8 electronic configuration should be square planar and diamagnetic. This rule is normally followed by Pd(II) and Pt(II) complexes, but in Ni(II) compounds, ligand-ligand repulsion or other effects sometimes dominate with resulting paramagnetic tetrahedral or six-coordinate octahedral structures. This is the case with discrete NiX_4^{2-} , $X = \text{Cl, Br}$, which forms blue, tetrahedral complexes with magnetic moments of ca 3.8 B.M. in solution, in melts, and in the solid state (1). In some solids, normally orange in color and with magnetic moments of ca 2.9 B.M. or lower, Ni(II) adopts a more or less regular (NiX_6) octahedral or tetragonal configuration (2, 3).

Having studied the structure and spectral

* Author to whom correspondence should be addressed.

¹ *en* is shorthand notation for $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 = 1,2$ diaminoethane.

properties of square planar $(en\text{H}_2)\text{PdCl}_4$ ¹ (4, 5), it was decided to determine the effect of substituting the metal on the structure of both the organic cation (*trans* or *gauche* conformation) and the inorganic anion.

In the present paper, it is shown that the structures of $(en\text{H}_2)\text{MCl}_4$ for both $M = \text{Ni}$ and Pd can be interpreted as two-dimensional perovskite-like layer structures with characteristic planes of corner-sharing octahedra analogous to those known from a number of Cu(II) (6), Cd(II) (7), and Mn(II) (8) compounds. Because the layer structure provides a model for two-dimensional Heisenberg ferromagnetic interaction, the similar di(alkylammonium) compounds have been extensively studied by a wide variety of experimental methods (9-26). The compounds $(en\text{H}_2)\text{CuCl}_4$, $(en\text{H}_2)\text{CdCl}_4$, and $(en\text{H}_2)\text{MnCl}_4$ were therefore included here as well, and it is shown that all of these $(en\text{H}_2)\text{MCl}_4$ compounds form a separate family of perovskite-layered crystals.

2. Experimental

2.1. Preparation

The new compound, $(enH_2)NiCl_4$, was prepared by dissolving $NiCl_2 \cdot 6H_2O$ and $(enH_2)Cl_2$ in concentrated hydrochloric acid. The olive-green solution was slowly evaporated at about $80^\circ C$ until the reddish-brown microcrystals formed. The hygroscopic precipitate was dried under vacuum; it turned yellow-green on exposure to air during a few hours or days, depending on the humidity. The brown compound is regained by heating. The purity was checked by elemental analysis (calculated percentages from $C_2Cl_4H_{10}N_2Ni$ in parentheses): C, 9.03 (9.15); Cl, 54.10 (54.00); H, 3.94 (3.84); N, 10.58 (10.67). Attempts at making larger single crystals were unsuccessful—a microcrystalline solid always resulted. The only solvents found for $(enH_2)NiCl_4$ were dimethyl sulfoxide and water, both of which coordinate to Ni. Nitromethane, a useful solvent for tetrahedral $NiCl_4^{2-}$ alkylammonium compounds (1), does not dissolve $(enH_2)NiCl_4$. The compound shows no color change upon heating to $140^\circ C$ for several days.

$(enH_2)CuCl_4$, $(enH_2)CdCl_4$, and $(enH_2)MnCl_4$ were prepared by dissolving $(enH_2)Cl_2$ and the metal chloride hydrates in water and evaporating the solvent. The Cu and

Cd compounds were checked by comparing X-ray powder photographs with calculated patterns from literature data (27, 28), while the Cl content of the manganate was confirmed by titration.

2.2. X-ray Investigation

Since no single crystals of $(enH_2)NiCl_4$ sufficiently large for Weissenberg photographs could be made, powder diffraction patterns were recorded instead, using Fe-filtered $CoK\alpha$ radiation (1.78892 Å). The diffraction pattern was readily indexed by assuming prominent features to have the same indices as similar patterns of $(enH_2)CuCl_4$ and $(enH_2)CdCl_4$ (27–29). Reflections with $h0l, l = \text{odd}$ and $0k0, k = \text{odd}$ were missing, as required by the $P2_1/c$ symmetry. All 76 observed lines could be indexed, but only 30 lines corresponding to single reflections were used in the least-squares fitting of unit cell dimensions, in order to achieve optimum accuracy. The obtained lattice constants are compared with Pd, Cu, Cd, and Mn results in Table I.

The microcrystalline nature of $(enH_2)NiCl_4$ also made it difficult to measure the density accurately: $d_{\text{obs}} = 2.11\text{--}2.16 \text{ g/cm}^3$ (flotation); $d_{\text{calc}} = 2.130 \text{ g/cm}^3$.

2.3. Vibrational Spectroscopy

The infrared and far-infrared absorption spectra (Table II and Fig. 2) were recorded on

TABLE I
UNIT CELL DIMENSIONS^a OF $(enH_2)MCl_4$; SPACE GROUP $P2_1/c$ (No. 14, C_{2h}^2);
 $Z = 2$

<i>M</i>	<i>a</i>	<i>b</i>	<i>c</i>	β	Reference
Ni	8.441(1)	6.995(1)	6.943(1)	92.925(2) ^o	This work
Pd	7.91 (2)	7.66 (2)	7.34 (2)	91.90 (1) ^o	5
Cu	8.110(6)	7.366(6)	7.187(6)	92.46 (6) ^o	27
Cd	8.59	7.36	7.27	92.40 ^o	28
	8.67	7.20	7.15	92.5 ^o	29
Mn	8.609(2)	7.192(2)	7.130(2)	92.685(24) ^o	8

^a In some of the references the naming of the axes differs from the one used here: second setting with $a > c$. The estimated standard deviations of the last digits are given in parentheses.

TABLE II
 INFRARED AND RAMAN FREQUENCIES OF $(en\text{H}_2)\text{MCl}_4$ (cm^{-1})

$M = \text{Ni}(\text{normal})$	Ni(C-deuterated)	Pd[4]	Cu	Cd	Mn	Assignments
Infrared						
1574		1569	1579	1580	1580	NH def
		1488				NH def
1059		1059	1064	1061	1064	CN stretch, CH def
1013		1000	1009	1018	1022	NH def
784		784	782	800	803	CH def
315	302	308	316	320	323	CN tors
268	269	336 319	283	227	237	$M\text{Cl}$ layer mode
		183		193	196	$M\text{Cl}$ layer mode
~180	~180		~190			$M\text{Cl}$ layer mode + CCN def
		162		164	~160	CCN def
129	130	130	147	135	122	} Translatory modes + CC tors
123	121	105	121	126	110	
			112			
98	95	94	94	103	98	
Raman						
463	454			464	460	} $(en\text{H}_2)$ mode
454	448			456	452	
226	227	313	285	213	207 ^a	} $M\text{Cl}$ layer modes
		294	248		177 ^a	
		278	193		142 ^a	
			179		124 ^a	

^a Obtained using Ar^+ line at 514.5 nm.

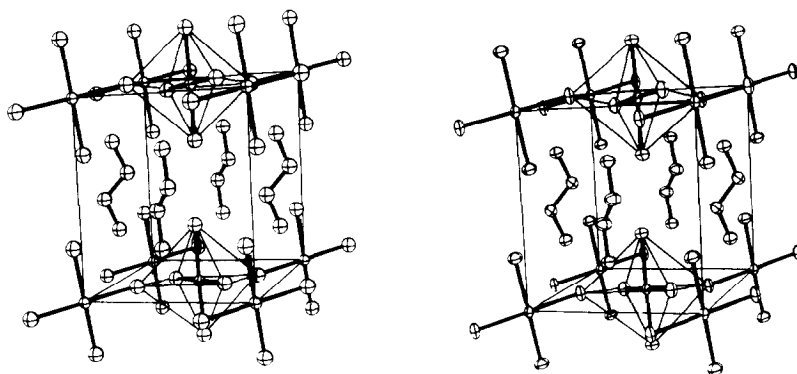


FIG. 1. Unit cells of $(en\text{H}_2)\text{CuCl}_4$ (left) and $(en\text{H}_2)\text{PdCl}_4$ drawn by the ORTEP program using the data of (27) and (5). a -axis vertical; c -axis horizontal. One octahedron in each perovskite layer is indicated. The atoms in the left drawing are shown as spheres of arbitrary size, whereas the thermal ellipsoids (right) contain 50% of the charge density.

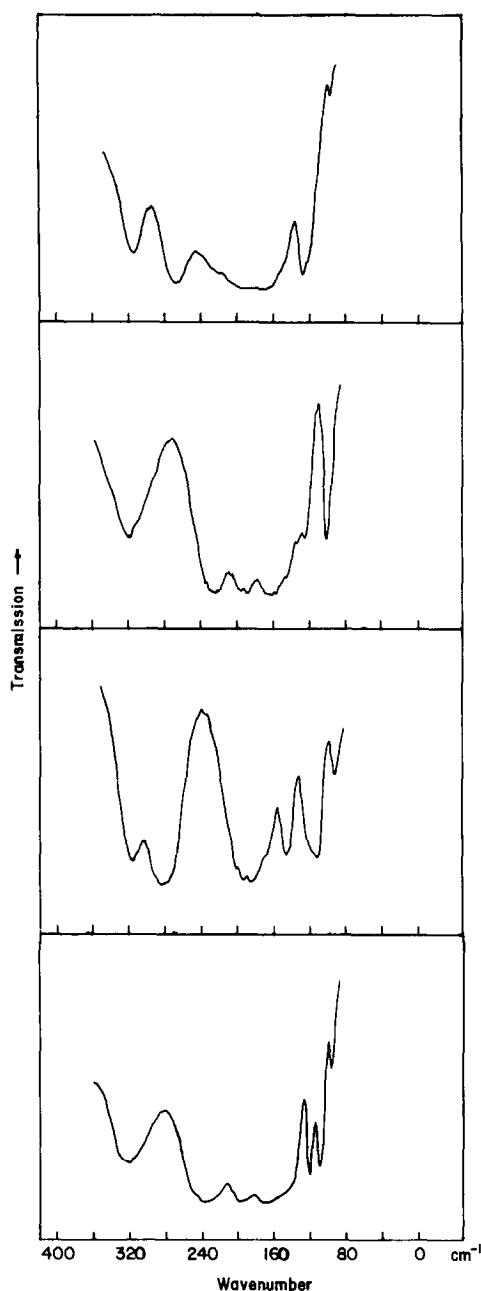


FIG. 2. Far infrared spectra of $(enH_2)MCl_4$. $M = Ni$ (top), Cd, Cu, and Mn.

Beckman IR-20 and RIIC-FS-720/FTC-300 spectrometers, as in (4) (finely ground powder samples in Nujol mulls or polyethylene disks).

The Raman spectra were obtained using a

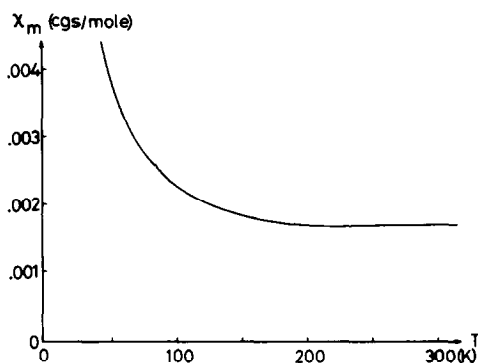


FIG. 3. Temperature dependence of the average molar magnetic susceptibility of polycrystalline $(enH_2)NiCl_4$. Field, 12 kG; corrected for diamagnetism. The graph shown is unsmoothed and represents 349 points.

JEOL JRS-400D spectrometer using Kr^+ laser excitation (647.1 nm) (4).

2.4. Magnetism and Electronic Spectrum

The molar magnetic susceptibility was determined (i) for two powdered samples of paramagnetic $(enH_2)NiCl_4$, in one case as a function of temperature in the range 45 to 317°K (Fig. 3) and (ii) for the diamagnetic $(enH_2)PdCl_4$. The data were collected using the Faraday method (30).

The absorption spectrum of $(enH_2)NiCl_4$ powder dispersed in a pressed polyethylene disk was recorded using a Cary 14 spectrophotometer equipped with a liquid nitrogen cryostat. The spectrum is reproduced in Fig. 4.

3. Results and discussion

3.1. Structure

The lattice constants in Table I show great similarities among the five compounds. The space group and the number of formula units per primitive cell require both the MCl_4^{2-} and the enH_2^{2+} ions to occupy sites with inversion. This implies (i) either planar or octahedral coordination of the metal (though the bond lengths are not necessarily all equal), ruling out tetrahedral coordination, and (ii) that the ethylenediammonium cation must have the *trans* conformation. The lack of single crystals

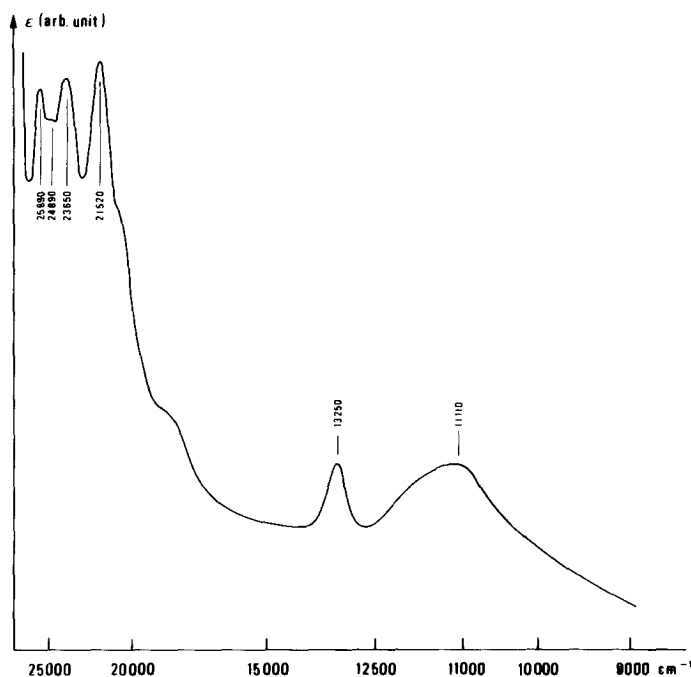


FIG. 4. Electronic absorption spectrum of $(enH_2)NiCl_4$ at $77^\circ K$.

of $(enH_2)NiCl_4$ made a quantitative structural determination impossible. However, detailed structures are available for the Pd and Cu compounds. Figure 1 shows the remarkably close similarity (considering the twinning problems) between the two *independently* determined structures, and undoubtedly the Ni, Cd, and Mn compounds have closely similar structures (cf. Table I).

The diamagnetic Pd compound has been reasonably interpreted (5) as containing discrete, nearly square planar anions. Instead, in the light of this work, the structure can be described as consisting of infinite, two-dimensional perovskite-like layers of distorted corner-sharing $PdCl_6$ octahedra. The distinction between these two models is a quantitative one, depending on the relative lengths of the short and long bridging PdCl bonds in the layer. In $(enH_2)PdCl_4$ the lengths are 2.300 and 3.062 Å and in $(enH_2)CuCl_4$ 2.292 and 2.882 Å, and undoubtedly Cl atoms <3 Å away are definitely bonded to Cu (6). The *terminal* M-Cl bonds (nearly perpendicular to

the layer) are slightly longer than the short *in-layer* bonds, 2.323 (Pd) and 2.298 Å (Cu). This trend is reversed in the corresponding bis-propylammonium compounds (31, 32). In the Cd compounds with known perovskite-like layer structures, the two in-layer bond lengths are nearly equal and the terminal CdCl distance is about 0.1 Å shorter (33, 34). Mn compounds show great structural similarity to Cd (19).

The new Ni compound is probably quite similar to the Pd and Cu compounds (Fig. 1)—with one of the in-layer bond lengths considerably larger than the other and with nearly equal terminal and short bridging bonds. Thus, $(enH_2)NiCl_4$ and $(enH_2)PdCl_4$ might be considered tetragonally six-coordinate, i.e., intermediate between rigorous square planar and octahedral. The weak paramagnetism of the Ni compound is also consistent with this belief (3).

It has recently been suggested that a *b*-axis of ca 8.0 Å and a nonbonded PdCl distance of 3.2 Å is a characteristic of the planar PdCl

framework alone and should provide evidence for significant repulsive interactions between Pd and Cl (31). This idea is to some extent supported by the structure of $(enH_2)PdCl_4$, but both distances are here considerably shorter (7.66 and 3.06 Å).

The $(enH_2)MCl_4$ family can be thought of as derived from the K_2NiF_4 lattice (35), the ethylenediammonium ion replacing two potassium ions. Since the ammonium terminals behave as two (connected) cations, the structure is more comparable to K_2NiF_4 than to $TlAlF_4$, which has the same ABX_4 stoichiometry as enH_2MCl_4 , and which also has perovskite layers. If the enH_2^{2+} "terminal ion radius" is taken to be that of the NH_4^+ ion, the structures fit into a general relationship (35) between structures of ternary A_2BX_4 compounds and the radii of the cations.

In $(enH_2)MCl_4$, the voids between the MCl_6 octahedral layers contain the $-NH_3^+$ groups of the cations, which form $N-H \cdots Cl$ hydrogen bonds, and successive layers are held together through the covalent backbone of C-C and C-N bonds. In contrast to this, the layers in the monovalent alkylammonium compounds are linked only by van der Waals forces of the hydrocarbon chains instead of covalent bonds.

The corresponding bromine compounds probably have similar structures, as verified by unit cell determination in the case of $(enH_2)CuBr_4$ (36) and by spectroscopy for $(enH_2)PdBr_4$ (4). The same structural similarities can be expected for higher alkylenediammonium MCl_4 salts of Cd (29, 37), Cu (11), Mn (8), and Fe (19); members of the propylenediammonium family are already known. The change from an even to an odd number of carbon atoms replaces the inversion center with a mirror plane and doubles the unit cell perpendicular to the layers, and the space group symmetry goes from monoclinic to orthorhombic or tetragonal.

3.2. Vibrational Spectra

The infrared bands above 400 cm^{-1} , being nearly anion independent, are internal vib-

rations of enH_2^{2+} (4). The CH_2 rocking frequency at about 800 cm^{-1} was claimed (38) to be sensitive to the cation conformation: *trans* and *gauche* ions should have frequencies below 820 and above 830 cm^{-1} , respectively. The five *trans*-compounds, $(enH_2)MCl_4$, have frequencies from 782 to 803 cm^{-1} , but a frequency of 809 cm^{-1} was reported for *gauche* $[enH_2]_2[CoCl_4]Cl_2$ (39), so the correlation is *not* safe.

The far-ir spectra contain internal vibrations of both the enH_2^{2+} ions and the MCl_6^{2-} layers as well as external (rotatory and translatory) lattice modes. It has been suggested (9, 40) that the far-ir spectra of $(RNH_3)_2MCl_4$, $R = \text{alkyl}$, $M = \text{Cu, Cd}$, show only bands of the perovskite-type layers and are independent of the organic cation. Our results do not support this belief: The band at $\sim 315\text{ cm}^{-1}$ shifts 13 to 14 cm^{-1} in Pd and Ni compounds when deuterated at the *carbon* atoms, and additional enH_2^{2+} vibrations involving the alkylene group are expected at lower frequencies (41). Hence, the organic ions do contribute to the far-ir spectrum, and we see no reason to expect other organic cations to behave differently. In any case, deuteration studies are necessary to prove the "layer-only" approximation of Stoelinga *et al.* (9, 40).

The main far-ir features (aside from CN bond torsion) are: (i) a strong band above 200 cm^{-1} due to MCl stretching, (ii) two or one (broad) bands between 160 and 200 cm^{-1} due to $ClMCl$ and CCN deformations, (iii) lower frequency bands difficult to assign, and (iv) a sharp band near 100 cm^{-1} (CC torsion?). All the spectra are closely related, the Cd and Mn cases being most alike.

The NiCl stretching frequency is 15 to 20 cm^{-1} lower than for tetrahedral geometry (42-44). This suggests slightly weaker (longer) NiCl bonds in our tetragonal complex. The CuCl stretching frequency at 283 cm^{-1} is very close to the 281 cm^{-1} band of the yellow high-pressure phase of bisisopropylammonium tetrachlorocuprate, which has a "planar" $CuCl_4^{2-}$ stereochemistry (45). Similar values

have been found in other cases (46, 47). The CdCl and MnCl stretches are 30 to 40 cm^{-1} lower than the tetrahedral values (42), the Mn value being close to that observed in $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ (21).

The Raman spectra are not as similar as the infrared ones. In a useful approximation involving small changes in the positions of the chlorine atoms, the layers have an idealized structure of D_{4h} symmetry, with the fourfold axis perpendicular to the layer. Thus, a vibrational analysis using two-dimensional plane groups and a unit cell containing two MCl_4^{2-} ions leads to four Raman active MCl stretching vibrations—two of A_{1g} symmetry and two of B_{2g} symmetry (48), involving in-phase and out-of-phase combinations of terminal and bridging bond stretches. $(\text{enH}_2)\text{CuCl}_4$ does have four Raman band stretches of comparable intensities at 285, 248, 193, and 179 cm^{-1} , close to the values reported for $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ (48). $(\text{enH}_2)\text{MnCl}_4$ also has four Raman bands near positions where $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ has bands, assigned to layer internal modes (15, 16). The Ni and Cd Raman spectra consist of only one strong band plus minor features at the limit of detectability. The strong line is assigned to symmetrical MCl stretch and has a frequency of 226 cm^{-1} in $(\text{enH}_2)\text{NiCl}_4$ and 213 cm^{-1} in $(\text{enH}_2)\text{CdCl}_4$. We note that the Raman active, symmetrical NiCl stretch of discrete tetrahedral NiCl_4^{2-} has the considerably higher frequency of 271 cm^{-1} (9), whereas the CdCl stretch found here is identical to that observed in $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ (15).

3.3. Magnetism and Electronic Spectrum

The $(\text{enH}_2)\text{NiCl}_4$ compound is weakly paramagnetic at room temperature with $\mu^{\text{eff}} = 2.04$ B.M. (corrected for diamagnetism). The temperature dependence does not follow a Curie-Weiss law, since the susceptibility is essentially constant at room temperature (Fig. 3). We shall not attempt to explain the magnetic behavior, but low values of μ^{eff} also

TABLE III
ELECTRONIC ABSORPTION SPECTRUM OF
 $(\text{enH}_2)\text{NiCl}_4$ AT 77°K; ASSIGNMENTS ARE
QUOTED IN OCTAHEDRAL NOTATION

Assignment	Band (cm^{-1})
${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	— ^a
$\rightarrow {}^3T_{1g}(F)$	~11,110
$\rightarrow {}^1E_g(D)$	13,250
$\rightarrow {}^1T_{2g}(D)$	~18,000
$\rightarrow {}^3T_{1g}(P)$	~21,000–26,000

^a Outside range examined.

have been observed in other compounds of tetragonal Ni(II) (3).

The $d-d$ electronic absorption spectrum of $(\text{enH}_2)\text{NiCl}_4$ at 77°K is in accordance with what would be expected from Ni(II) in an approximately octahedral crystal field (2). The absorption maxima are listed in Table III. The lowest spin-forbidden transition should be relatively independent of the crystal field strength and hence give a sharp weak band. Such a band (${}^3A_{2g} \rightarrow {}^1E_g(1D)$ in O_h notation) is seen at ca 13 250 cm^{-1} .

We believe that the magnetism and electronic spectrum taken together indicate that the Ni coordination is in effect tetragonal, somewhat similar to the coordination in $(\text{enH}_2)\text{PdCl}_4$.

4. Conclusion

The family of perovskite-type layer structures of ethylenediammonium tetrachlorometallate(II) complexes has been examined and extended by the addition of $(\text{enH}_2)\text{NiCl}_4$ and $(\text{enH}_2)\text{PdCl}_4$. Although very similar in structure, two distinct types of compounds may be discerned. One is the 4 + 2 coordinate (tetragonal or nearly "square planar") type, comprising the Ni, Pd, and Cu compounds, in which the terminal bonds are very close to one set of bridging bonds, the other pair of bridging bonds being considerably (0.5–1.0 Å) longer. The other ("octahedral") type is found in Cd

and Mn (and Fe?) compounds, which probably have two nearly equal sets of bridging bonds with the terminal bonds being somewhat (~ 0.1 Å) shorter. In their infrared spectra, the "octahedral" type is characterized by: (i) two lines at about 1000 cm^{-1} instead of one; (ii) a CH deformation at about 800 cm^{-1} instead of about 785 cm^{-1} ; (iii) an MCl stretch frequency below 250 cm^{-1} .

The fact that compounds of a number of divalent metals with different electronic configurations are able to form closely related perovskite-type layer structures clearly shows that this kind of structure is favored more by packing efficiency and hydrogen bonding (50) than by ligand field energies of the isolated anions. Square (or nearly square) planar structures are a limiting case of both octahedral and tetrahedral configurations; there is no sharp borderline as the octahedra become tetragonally distorted and the tetrahedra become flattened. An operational definition of square planarity in Ni(II) compounds is provided by the paramagnetism of octahedral and tetrahedral configurations versus the diamagnetism of square planar complexes (51). Hence, paramagnetic $(enH_2)NiCl_4$ with $\mu^{eff} \sim 2.04$ B.M. at room temperature is not square planar, but the low value of μ makes it an example of tetragonally six-coordinate "nearly planar" tetrachloronickelate. This is in accordance with the electronic spectrum.

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Note added in proof

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