

Structural, Thermal, and Electrical Characterization of Bis(ethylethylene)diammonium Dichloride Tetrachlorocadmate(II) with Perovskite-like Structure

A. Bonamartini Corradi,* M. R. Cramarossa, and T. Manfredini

Dipartimento di Chimica, University of Modena, 41100 Modena, Italy

J. Giusti

Dipartimento di Chimica, University of Firenze, 50100 Firenze, Italy

L. P. Battaglia

Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffattometrica del C.N.R., University of Parma, 43100 Parma, Italy

A. Sacconi and F. Sandrolini

Dipartimento di Chimica Applicata e Scienza dei Materiali, Facoltà di Ingegneria, University of Bologna, 40136 Bologna, Italy

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The synthesis, thermal and electrical characterization of a chlorocadmate(II) system with perovskite-like structure of formula $(\text{etenH}_2)_2[\text{CdCl}_4]\cdot\text{Cl}_2$ (etenH₂ = ethylethylenediamine dication) are described. The compound crystallizes in space group $P2_1/c$. The unit-cell dimensions are $a = 19.214(1) \text{ \AA}$, $b = 7.301(1) \text{ \AA}$, $c = 7.227(3) \text{ \AA}$, $\beta = 100.23(1)^\circ$, $V = 997.7(4) \text{ \AA}^3$, $Z = 2$. The final R value is 0.0486 ($R_w = 0.0497$). The crystal structure consists of inorganic layers of (CdCl_6) corner-sharing octahedra, organic dications intercalated between them and uncoordinated chloride ions. Only one end of the organic dications interact via hydrogen bonds with the inorganic layers, with the second end involved in hydrogen bonds with the free chloride ions. Furthermore a network of hydrogen bond interactions among the inorganic layers, the organic dications, and the uncoordinated chlorine atoms contribute to the crystal packing. The compound, thermally stable up to the melting point, behaves as an electrical insulator at low temperatures, approaching semiconductor values at higher ones.

Introduction

Polymeric bidimensional halometalates with perovskite-like structure, with general formula $(\text{R}-\text{NH}_3)_2\text{MX}_4$ and $(\text{NH}_3-\text{R}-\text{NH}_3)\text{MX}_4$ where R = organic group, M = divalent metal and X = halide, have received a great deal of attention for their structural phase transitions,¹ suitability as matrices for organic solid state reactions,² as crystalline models of lipid bilayers³ and similarity with intercalated compounds. Moreover the possibility of exploiting this type of compound in intercalation reactions with organic molecules has also been studied.⁴

Some structural differences and thermal properties are observed if the counterions are monoprotated or diprotated amines.¹ The nature of the organic counterions imparts flexibility to the crystal structure and permits the modulation of the distances between the layers.

Being particularly interested in the property of bidimensional chlorocadmate(II) systems,^{5,6} we report in this paper the synthesis and the structural, thermal and electrical characterization of a chlorocadmate(II) compound with a perovskite-like structure of formula $(\text{etenH}_2)_2[\text{CdCl}_4]\cdot\text{Cl}_2$ (etenH₂ = ethylethylenediamine dication). Within this class of compounds, this compound has an unusual Cd/Cl stoichiometric ratio.

The Cd(II) ion, which adopts a variety of coordination numbers and geometries, depending on crystal packing, hydrogen bonding and halide dimensions⁷ is a particularly suitable system for understanding structural properties and the correlation between the symmetry and the thermal and electrical behavior. The choice of the counterions derives from the fact that the presence of the ethyl substituent on one nitrogen atom of the organic cation may hinder this positively charged end from interacting with the inorganic layers, forcing the

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Table 1. Experimental Data for the Crystallographic Analysis

| | |
|---|---|
| formula | C ₈ H ₂₈ CdCl ₆ N ₂ |
| MW | 505.4 |
| space group | P2 ₁ /c |
| a, Å | 19.214(1) |
| b, Å | 7.301(1) |
| c, Å | 7.227(3) |
| β | 100.23(1) |
| U, Å ³ | 997.7(4) |
| Z | 2 |
| D _c | 1.682 |
| D _m | 1.70 |
| reflections for lattice parameters | number: 25 θ range: 10.6–16.0 |
| F(000) | 508 |
| temp, K | 294 |
| diffractometer | Enraf Nonius CAD4 |
| crystal size, mm | 0.16 × 0.46 × 0.56 |
| μ, cm ⁻¹ | 18.9 |
| radiation, λ, Å | Mo Kα, 0.7107 |
| scan speed, min ⁻¹ | 1.5–3.30 |
| scan width, deg | 1.3 + 0.35 tan θ |
| θ, range | 3–25 |
| h, range | –20, 20 |
| k, range | 0, 14 |
| l, range | 0, 19 |
| standard reflection | 412 |
| max intensity variation % | 4 |
| scan mode | ω–2θ |
| no. of reflections measured | 1964 |
| no. of reflections used in the refinement | 1509 |
| no. of refined parameters | 232 |
| R = Σ ΔF /Σ F _o | 0.0486 |
| R _w = [Σw(ΔF ²)/ΣwF _o ²] ^{1/2} | 0.0497 |
| k, g in w = k/[σ ² (F _o) + gF _o ²] | 1.0, 3.2 × 10 ⁻³ |
| max, min height in final ΔF map, e Å ⁻³ | –0.63, 0.31 |

organic diammonium cations to act as monoprotated amines.

The results are compared with those obtained for previously investigated structurally similar compounds, such as (enH₂)₂[CdCl₄] and (denH₃)₂[CdCl₅] (enH₂ = ethylenediamine dication; denH₃ = diethylenetriamine trication).^{5,6}

Experimental Section

Synthesis. The compound was separated by mixing the diprotonated amine and CdCl₂·2H₂O in concentrated hydrogen chloride solution (37%) in a 2:1 molar ratio and allowing the solution to stand several days at room temperature. By slow evaporation, white plate crystals, some of them suitable for X-ray single-crystal analysis, were obtained. The compound is stable in air at room temperature. Elemental analysis: (etenH₂)₂[CdCl₄]·Cl₂: Found: C, 18.98; H, 5.56; N, 11.08. Calcd for C₈H₁₆N₄CdCl₆: C, 18.99; H, 5.58; N, 11.07.

Physical Measurements. Thermogravimetric and differential scanning calorimetric analyses were performed with a TA instrument DSC10 system equipped with a mechanical cooler and an automatic data acquisition and computer system TA 2000. Carbon, hydrogen, and nitrogen were analyzed with a Carlo Erba Mod. 1106 elemental analyzer.

Crystal Structure Determination of the (etenH₂)₂[CdCl₄]·Cl₂ Compound. Intensity data for the compound were collected by mounting the crystal on the diffractometer in a random orientation; the resulting crystal data with other details inherent data collection and refinements are noted in Table 1. The structure was solved by the heavy-atom method and refinements were carried out by full-matrix least-squares and anisotropic thermal parameters for non-hydrogen atoms; hydrogen were introduced in the last refinement cycle, and an absorption correction (Walker and Stuart method, min, max correction 0.94–1.10) was applied.⁸ A small number of reflections, probably affected by counting errors, were excluded from the final refinement. The final atomic coordinates for non-

Table 2. Fractional Atomic Coordinates (×10⁴) for Non-Hydrogen Atoms in the (etenH₂)₂[CdCl₄]·Cl₂ (Esd's in Parentheses)

| atom | x/a (σ) | y/b (σ) | z/c (σ) |
|-------|---------|----------|----------|
| Cd | 0 | 0 | 0 |
| Cl(1) | 181(1) | 2068(2) | 3023(2) |
| Cl(2) | 1345(1) | –516(2) | 507(2) |
| Cl(3) | 3338(1) | 376(2) | 2380(2) |
| N(1) | 1295(3) | 5155(7) | 1014(9) |
| N(2) | 3266(2) | 4560(7) | 1637(6) |
| C(1) | 1987(3) | 4390(8) | 715(8) |
| C(2) | 2591(3) | 5381(9) | 1958(9) |
| C(3) | 3907(3) | 5467(10) | 2731(9) |
| C(4) | 4564(4) | 4520(13) | 2385(13) |

hydrogen atoms are quoted in Table 2. The atomic scattering factors were taken from the *International Tables*.⁹ All the calculations were carried out on a Gould 32/77 computer of the Centro di Studio per la Strutturistica Diffattometrica del C.N.R. di Parma using SHELX 76,¹⁰ SHELX86,¹¹ PARST,¹² and ORTEP¹³ programs.

Electrical Measurements. Samples were prepared for electrical measurements by cold pressing (up to a pressure of 0.3 kN/mm²) fine powders into the shape of disk 28 mm in diameter and up to 1 mm in thickness. Proper electrode configuration was obtained by gold or graphite evaporation under vacuum. Prior to any electrical measurements, samples were sintered at 140 °C. A three-terminal technique was used for both direct current (dc) and alternating current (ac) measurements, due to the rather low electrical conductivity exhibited by these compounds. The voltmeter–ammeter method in dc and a Schering bridge in ac measurements (2 × 10⁻² to 3 × 10⁵ Hz) according to ASTM D 150 and D 257 standards, respectively, were applied with cells and instrumentation elsewhere described.^{14,15}

Results and Discussion

Crystal Structure of the (etenH₂)₂[CdCl₄]·Cl₂ Compound. The crystal structure consists of inorganic layers of [CdCl₄]_n²⁻ anions, uncoordinated chloride ions and organic dications. The inorganic layers are composed of (CdCl₆) corner-sharing octahedra with the equatorial chlorine atoms sited in the Cd plane, shared by two different octahedra, and with the axial chlorine atoms positioned above and below the Cd plane (Figure 1). The octahedral geometry around the Cd(II) atom is slightly distorted and shows the typical axial compression, with the bridging Cd–Cl distances (2.627(1) Å) longer than the terminal ones (2.572(2) Å).

Bond distances and angles, reported in Table 3, are in good agreement with those previously found in other chlorocadmate(II) systems with perovskite-like structure.^{5,6,16}

Worthy of note is the presence of organic dications in their extended form, intercalated between the inorganic

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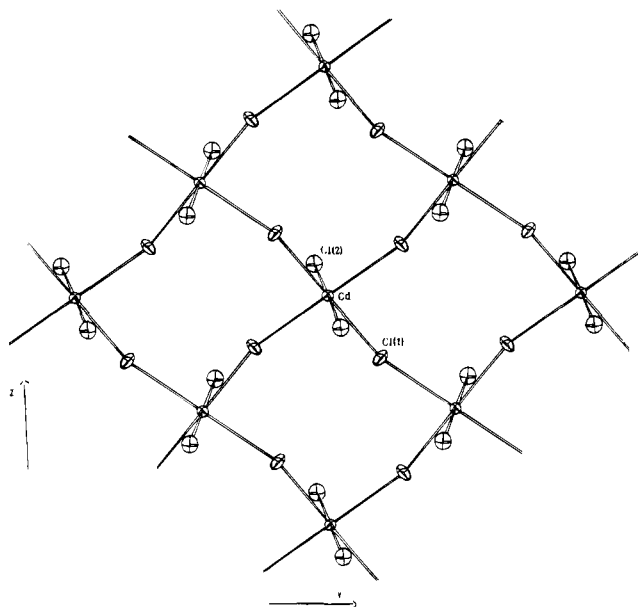


Figure 1. Inorganic layers in the $(\text{etenH}_2)_2[\text{CdCl}_4]\text{Cl}_2$ compound.

Table 3. Selected Distances (Å) and Angles (deg) for the $(\text{etenH}_2)_2[\text{CdCl}_4]\text{Cl}_2$ Compound (Esd's in Parentheses)

| | | | |
|------------------------------|----------|-----------------------------|-----------|
| Cd—Cd' | 5.137(1) | | |
| Cd—Cl(1) | 2.627(1) | Cd—Cl(2) | 2.572(1) |
| Cd—Cl(1) ^a | 2.631(1) | | |
| N(1)—C(1) | 1.493(8) | C(1)—C(2) | 1.519(8) |
| N(2)—C(2) | 1.484(8) | C(3)—C(4) | 1.498(11) |
| N(2)—C(3) | 1.494(8) | | |
| Cl(1)—Cd—Cl(2) | 89.11(4) | Cl(1)—Cd—Cl(1) ^a | 88.47(3) |
| Cl(1) ^a —Cd—Cl(2) | 88.30(4) | | |
| C(1)—N(2)—C(3) | 113.5(5) | N(2)—C(2)—C(1) | 108.2(5) |
| N(1)—C(1)—C(2) | 110.1(5) | N(2)—C(3)—C(4) | 110.3(5) |

$$^a x, \frac{1}{2} - y, z + \frac{1}{2}.$$

layers, with only one end ($\text{R}-\text{NH}_3^+$) directed toward the cavities of an octahedral inorganic site, interacting via hydrogen bonding with the coordinated chlorine atoms on a layer. The second positively charged end ($\text{R}-\text{NR}'\text{H}_2^+$) points in the opposite direction, resulting in hydrogen bonds with the uncoordinated chloride ions (Figures 2 and 3). In Table 4 the more relevant hydrogen bond distances and angles are reported. The distance between two adjacent inorganic layers (19.214 (1) Å) is nearly twice the length of the organic counterion, as is always found in perovskite alkylammonium chlorocadmates(II).¹⁷ The major difference between the present compound and the perovskite alkylammonium ones derives from the fact that in the alkylammonium ones the hydrophobic ends of the organic chains, directed towards the empty interlayer space, interact with each other through van der Waals forces, while in $(\text{etenH}_2)_2[\text{CdCl}_4]\text{Cl}_2$ the presence of a charged nitrogen atom interacting with an uncoordinated chloride ion avoids any type of contacts between the ammonium ends of the chains.

The organic chains lie in the a,c plane and their orientational angles with respect to the axes are $\varphi_a = 12.7(1)^\circ$, $\varphi_b = 89.8(1)^\circ$, $\varphi_c = 87.5(1)^\circ$.

Hydrogen bond interactions between the coordinated chlorine atoms of the inorganic layers and the unsub-

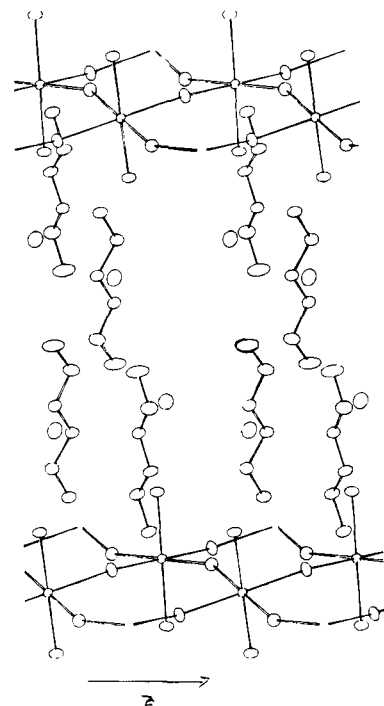


Figure 2. Perspective view of the $(\text{etenH}_2)_2[\text{CdCl}_4]\text{Cl}_2$ compound.

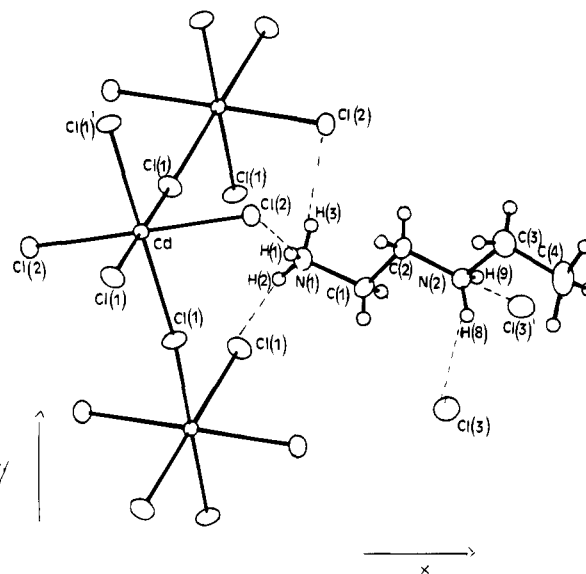


Figure 3. Network of hydrogen bonds interactions in the $(\text{etenH}_2)_2[\text{CdCl}_4]\text{Cl}_2$ compound.

stituted nitrogen atom are present in the so-called monoclinic configuration. In the perovskite type compounds two different schemes of hydrogen bonding interactions are found: the above-mentioned monoclinic configuration where the two $\text{NH}-\text{Cl}$ hydrogen bonds involve axial chlorine atoms and one $\text{NH}-\text{Cl}$ involves one equatorial chlorine atom, and the orthorhombic configuration in which two hydrogen bonds are involved with equatorial chlorine atoms and one with axial chlorine atoms.^{16,18}

The monoclinic scheme is found in the chlorocadmates(II) of diprotonated 1,2-ethylenediamine, diethylenetriamine and 1,5-pentanediamine compounds,^{5,6,16} but is also the most common scheme for the monopro-

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Table 4. Hydrogen Bond Distances (Å) and Angles (deg) for the (etenH₂)₂[CdCl₄]-Cl₂ Compounds (Esd's in Parentheses)

| | | | | | |
|-------------------------|----------|-------------------------|----------|------------------------------|---------|
| N(2)-Cl(3) | 3.101(5) | H(8)-Cl(3) | 2.22(10) | N(2)-H(8)-Cl(3) | 160(9) |
| N(1)-Cl(2) ^a | 3.242(7) | H(1)-Cl(2) ^a | 2.32(13) | N(1)-H(1)-Cl(2) ^a | 162(11) |
| N(2)-Cl(3) ^b | 3.104(5) | H(9)-Cl(3) ^b | 2.26(10) | N(2)-H(9)-Cl(3) ^b | 161(9) |
| N(1)-Cl(1) ^b | 3.200(5) | H(2)-Cl(1) ^b | 2.32(10) | N(1)-H(2)-Cl(1) ^b | 165(10) |
| N(1)-Cl(2) ^c | 3.185(5) | H(3)-Cl(2) ^c | 2.38(11) | N(1)-H(3)-Cl(2) ^c | 175(10) |

^a $x, -y + 1/2, z + 1/2$. ^b $x, -y + 1/2, z - 1/2$. ^c $x, y + 1, z$.

tonated amines with longest organic chains and is favored by steric factors.¹⁹

It is noteworthy that the lower crystallographic density of this compound with respect to other chlorocadmate(II) systems with similar structure implies structural differences. In fact, adjacent inorganic layers are at the edges of the crystal lattice, with only the organic chains intercalated between them, giving rise to holes between the chains.

Thermal Results. Generally chlorocadmates(II) with perovskite-like structures of general formula (NH₃(CH₂)_nNH₃)CdCl₄ ($n > 2$) and (R-NH₃)CdCl₄ undergo structural phase-transitions, and in some cases these are very complex.¹ Unlike the alkylammonium chlorocadmates(II), but like the ethylenediamine salt, the compound under study does not have structural phase transitions between -40 °C and its melting temperature (about 200 °C). A second-order phase transition, appearing as a very weak endothermic peak at about 30 °C ($\Delta H = 5.4$ cal/mol), may be associated with the activation of methyl group rotations. X-ray powder patterns recorded above and below this transition temperature show very little shift of some peaks, indicating a slight increase in the cell volume.

The strong anchoring of the organic cations, with one end involved in hydrogen bonding with an inorganic layer and the other with an uncoordinated chlorine atom, may hinder strong motions of the organic chain, making the thermal behavior of the diprotonated ethylethylenediamine more similar to that of the ethylenediamine than to that of the monoprotonated one.

Electrical Results. The electrical conductivity σ of the compound at 1 and 60 min after voltage application, in vacuo, is shown in Figure 4 as a function of the reciprocal absolute temperature, from -25 to 160 °C: up to this temperature conductivity values were found to be reproducible. Transient phenomena are present both as a function of time at constant temperature ($T \leq 60$ °C) and temperature at constant charging time (1 min) in the low temperature range (<25 °C). The compound shows insulating behavior at low temperatures, approaching semiconductor range as temperature increases with an apparent activation energy (calculated from 160 to 60 °C) of 55 kJ/mol. The absorption of a small amount of moisture (0.75 wt %) caused a strong increase in conductivity at room temperature (almost 2 orders of magnitude). The use of different types of electrodes (Au, C) gave negligible variations in conductivity and apparent activation energy values.

Figures 5 and 6 show the loss factor, ϵ' , and permittivity, ϵ'' , respectively, as a function of frequency at constant temperature: a relaxation process appears at temperature lower than 100 °C (activation energy of this process = 15 kJ/mol). A marked increase in loss factor values is found at all temperatures as frequency is

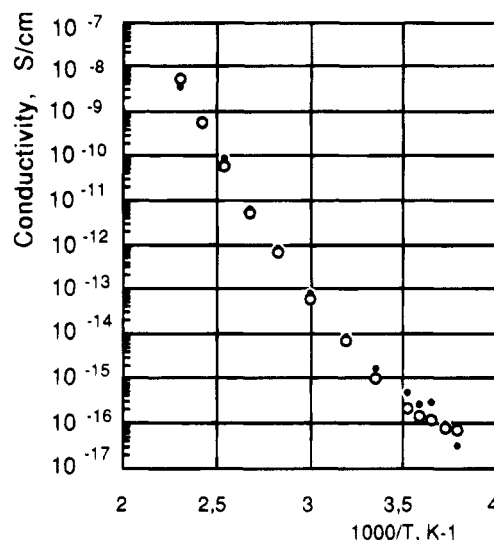


Figure 4. Electrical conductivity σ as a function of the reciprocal absolute temperatures at 1 (○) and 60 (●) minutes after the voltage applications.

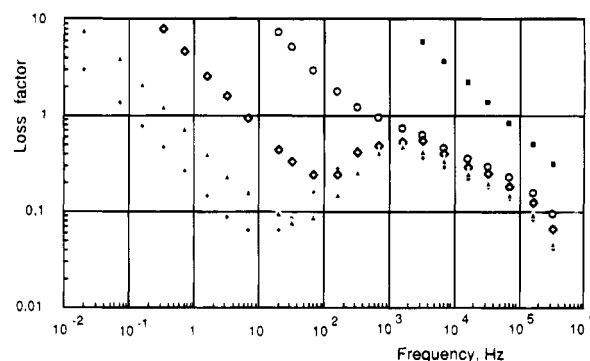


Figure 5. Loss factor ϵ' as a function of frequency at 25 (◆), 50 (▲), 75 (◇), 100 (○), and 150 (■) °C.

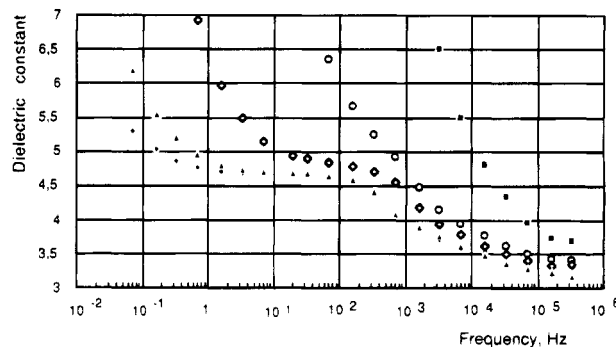


Figure 6. Dielectric constant ϵ'' as a function of frequency at 25 (◆), 50 (▲), 75 (◇), and 100 (○) and 150 (■) °C.

lowered, a phenomenon which prevents the detection of the relaxation process at high temperatures.

The relaxation process is related to the low temperature transition discussed in the DSC section. The same process is probably responsible for the transient phenomena found in dc measurements below 25 °C. The

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whole electrical behavior of the compound closely resembles that of other bidimensional chlorocadmates^{5,6} where an ionic mechanism of conduction, based on proton migration via hydrogen bonds, especially at high temperatures, has been proposed. The following data support this interpretation also in $(\text{etenH}_2)_2[\text{CdCl}_4]\cdot\text{Cl}_2$ compound: the independence of conductivity values and activation energy on electrode type, the strong increase in conductivity after a small moisture absorption, the strong increase in loss factor at low frequency, and the approach to unity of the slope of loss factor as a function of frequency in the log/log plot. The electrical conductivity is however lower than that of other chlorocadmates (by almost 2 orders of magnitude at room temperature and one order at 160 °C, owing to a somewhat higher activation energy, 55 vs 48 kJ/mol), on account of the increased difficulty of motion of protons, due to the structural complexity and to the presence of the counterions which require free chloride ions for electroneutrality reasons.

Summary

The unusual stoichiometry and structure of the $(\text{etenH}_2)_2[\text{CdCl}_4]\cdot\text{Cl}_2$ compound is a result of steric effects imposed by the alkyl substituent on the organic moiety. In fact, although the counterion belongs to the diammonium family, it acts as alkylammonium one, since for electroneutrality reasons the charged N(2) atom,

being directed away from the inorganic layers, requires the presence of one uncoordinated chloride ion.

From a thermal point of view the absence of structural phase transitions, as with the analogous ethylenediammonium compound, establishes for the $(\text{etenH}_2)_2[\text{CdCl}_4]\cdot\text{Cl}_2$ compound a behavior similar to that of the alkylenediammonium family.

Another peculiar characteristic of the $(\text{etenH}_2)_2[\text{CdCl}_4]\cdot\text{Cl}_2$ compound is the absence of any type of contacts among the faced ends of the organic chains. The electrical behavior of this compound resembles that of previously investigated chlorocadmates,^{5,6} the main charge carriers being protons involved in hydrogen bonds. A relaxation process appears at low temperatures, which is related to the order-disorder transition and which affect values of the dielectric constant, loss factor and conductivity at low temperatures. The structural complexity of the compound and the counterions, which require the presence of free chloride ions, leads to lower values of conductivity for this compound in comparison with other bidimensional chlorocadmates.

Acknowledgment. Financial support (60%) from the MURST is gratefully acknowledged.

Supplementary Material Available: Table of anisotropic and isotropic thermal parameters and atomic coordinates for hydrogen atoms (2 pages); list of observed and calculated structure factors for $(\text{etenH}_2)_2[\text{CdCl}_4]\cdot\text{Cl}_2$ compound (9 pages). Ordering information is given on any current masthead page.