

Layered Ni(II)Alkylphosphonates: Hybrid Inorganic/Organic Weak Ferromagnets

Said A. Ibrahim* and Mohamed R. Mahmoud Department of Chemistry ,University of Assiut, Assiut, EGYPT

Abstract

Ni(II)methyl- and octadecylphosphonates were synthesized and characterized by elemental and thermogravimetric analyses as well as spectroscopic (uv-visible and IR) methods. The crystal structure of the compounds was determined from X-ray powder diffraction "*ab initio*" and refined by the Rietveld method as orthorhombic space lattices. Methyl derivative was found to obey the Curie-Weiss law at temperature above 50K with $\Theta = -32K$. The negative charge indicates an antiferromagnetic exchange coupling between the near neighboring Ni(II) ions. Ni(II)-octadecylephosphonate is lamellar and the structure consists of alternating inorganic and inorganic layers. The magnetic properties follows Curie-Weiss law and the critical temperature has been located at the onset of the χ vs T plot and was found to be T_N= 21K. The magnetization vs field plots, measured at different temperatures, provide the indication that the compound is a weak ferromagnet below T_N.

Keywords:Ni(II)- Phosphonates, layered compounds, weak ferromagnet

1.Introduction

Metal(II)phosphonates, $M^{II}[RPO_3].nH_2O$ (M is a divalent metal, Cd, Mn, Fe, Ni, Co, Zn; and R is an alkyl/aryl group), represent an important class of *low-dimensional magnetic materials*.[1] In general these compounds are lamellar, made of inorganic and organic layers with the metal ions and phosphonate oxygen atoms laying in puckered sheets. The inorganic network is interspersed by two organic layers and van der Waals contacts are established between single organic unities (**Scheme 1**). The length of the organic *R*-group determines the interlamellar distance, depending on the number of carbon atoms.

An attractive feature of many metal(II) phosphonates is the two-dimensional character of the lattice, in which the metal containing layers are separated by the organic sheets. It has been shown that the structure of the divalent metal phosphonates tends to comprise zig-zag layers with the metal ion six-coordinated in a distorted octahedral symmetry. Moreover several paramagnetic metal(II) phosphonates [M(II)(O3PR)(H2O)] (M(II) = Fe, Cr, Ni; R = alkyl or phenyl) features magnetic

long-range ordering at low temperatures and have provided interesting examples of lowdimensional magnets[2]. They are generally prepared by direct reaction of metal salts with the corresponding phosphonic acid in aqueous solutions. Often only crystalline powders or poorly crystalline samples can be obtained excluding the possibility of structure determination by Single Crystal X-ray analysis. Furthermore, the first example of polymorphism of a M(II) phosphonate i.e. Fe(II) methyl-

phosphonate, has been reported [3]. These facts could perhaps explain the lack of detailed information on the crystal structure and the magnetic properties of the two nickel(II) alkyl phosphonates, i.e. methyl and octadecyl phosphonate.

In this work we present the preparation, X-ray diffraction powder crystallographic studies and magnetic behaviour of the new *two*-dimensional inorganic-organic layered Ni(II)octadecyl-phosphonate, $Ni^{II}[CH_3(CH_2)_{17}PO_3].H_2O$. The long-chain organic

substituent was chosen in order to study the influence of a more hindered alkyl group on the structure and the magnetic properties.

*corresponding author, Address: Department of Chemistry, Faculty of Science, Assiut University, Assiut 71516, Egypt; e-mail saidibrahim7@yahoo.com



Scheme1

2.Materials and Methods. 2.1 Synthesis

Methylphosphonic acid $(CH_3PO_3H_2)$ was of analytical grade (Aldrich) an was used without further purification. The octadecylphosphonic acid CH_3 - $(CH_2)_{17}$ -PO₃H₂ was prepared according to the literature methods [4]and its purity was checked by elemental analysis.

 $[Ni(CH_3PO_3)H_2O]$ and $Ni^{II}[CH_3(CH_2)_{17}PO_3]$. H₂O, were prepared by reaction of NiCl₂ and methyl-, octadecylphosphonic acids in water in the presence of urea according to the following equations for example:

 $NiCl_2 + CH_3(CH_2)_{17}PO_3H_2 + H_2NCONH_2 + H_2O (t=80°C, 7 days) \rightarrow$

 $Ni^{II}[CH_3(CH_2)_{17}PO_3] + 2 NH_4Cl + CO_2$

3.Results and Discussion

3.1Chemical-physical Characterization

FT-IR spectra of Ni(II)mthylphosphonates and Ni(II)octadecyl-phosphonate (**Figs.1**,2) revealed the presence of coordinated water [3430 cm^{-1} ; 3396 cm^{-1} (*sh*); 1660 cm⁻¹ (*str*)] together with some other absorptions due to specific groups. The two intense peaks found at 2954 cm⁻¹ and 2870 cm⁻¹ can be assigned to the asymmetric [v_{as} (CH₃)] and symmetric [v_{s} (CH₃)] methyl stretching, while the strong bands at 2916 and 2848 cm⁻¹ are typical for the asymmetric and symmetric stretches of an extended

methylene chain in *all-trans* conformation. This conformation of the octadecyl chain is confirmed by the presence of some specific methylene bending modes (1150-1400 cm⁻¹). The $[PO_3]_2$ - group generates specific asymmetric (1096 cm⁻¹) and symmetric (1066-962 cm⁻¹) stretching modes. The vs(PO₃)₂- stretches are split, as a result of the lower local symmetry of the phosphonate groups.



Fig.1.



Fig.2

3.2. TGA measurements

Of Ni^{II}[CH₃(CH₂)₁₇PO₃].H₂O (**Fig. 3**) showed one mass loss between 50 and 100°C (2.3 weight%) due to the water of crystallisation or absorbed water. The compound eliminates one coordinated water molecule from 130°C till 270°C .The observed

weight loss at this stage is5.2%, a value that corresponds to one water molecule per formula unit. The calculated weight loss for a water molecule is 4.4%. Above 280°C the Ni(II) octadecyl-phosphonate starts to decompose and stops at 570°C, loosing 52.89% of the weight corresponding to the aliphatic chain of the ligand.



Fig.3

3.3. Structural Characterization

The X-ray powder diffraction spectra of the compounds were solved "ab initio" and refined by the Rietveld method (Fig.4 shows the XRD pattern of the methylcompound. On the other hand Ni(II)octadecyl-phosphonate prevented the determination of the full crystal structure; however it was possible to obtain a useful refinement by structureless Le Bail fitting.[5] Ni_{II}[CH₃(CH2)₁₇PO₃].H₂O crystallises in the orthorhombic space group Pmn21 with the following unit-cell parameters: a=5.478(7) Å, b=42.31(4) Å, c=4.725(3) Å. The compound is lamellar and the octadecyl groups fill the space between the inorganic layers showing *all-trans* conformation. A tilt angle of 48.2° between the chain axis and the (ac) plane could be estimated (Scheme 2).



Scheme 2.

3.4. Magnetic Properties

Static magnetic susceptibility measurements were made on a polycrystalline sample with an applied magnetic field of 200 Oe in the temperature range of 5 - 270K and in zero and field cooled modes.

The temperature dependence of the molar magnetic susceptibility $(1/\chi \text{ vs. T}, \text{ Fig. 5})$ is linear above 150 K and the plot obeys the Curie-Weiss law. The calculated C-value of 1.25 cm³·K·mol⁻¹ corresponds to that one expected for Ni(II) ion with d^8 (S=1)

electronic configuration. The Weiss constant is negative, $\theta = -24$ K, thus indicating *anti*-ferromagnetic nearest neighbour exchange interactions. Zero-field (*zfc*) and field-cooled (*fc*) magnetization experiments were made under an applied field of 10 Oe (**Fig. 6**). A bifurcation point at T = 21 K was found between the two graphs. The *zfc* and *fc* plots behave differently on decreasing the temperature. One can than assume that the Ni-*octadecyl* phosphonate is magnetically ordered below T_N = 21 K.

The hysteresis loop measured at T = 5K (**Fig. 7**) does not show the typical field dependence of a ferromagnetically ordered system. The magnetization reveals no saturation at 3 Tesla. The data obtained at that field corresponds to 18% the value expected for a fully aligned moment in Ni2+ containing materials (*i.e.* 11170 cm3·Oe·mol-1). This behaviour is characteristic for *weak ferromagnets* and is due to "*spin-canting*".[6]

The remnant magnetization, *Mremn*, and the *coercive* field, Hc, can be obtained from the plot and are 220 cm³·Oe·mol-1 and 516Oe, respectively. From the equation $M(H,T) = Ms(T) + \chi(T) \cdot H$ (if we assume: $Ms(OK) \approx Mremn(5K)$) a canting angle of ca. 1° can be estimated.



Fig.5.



Fig.6



Fig.7

Conclusions

 $Ni^{II}[CH_3PO_3].H_2O$ and $Ni^{II}[CH_3(CH_2)_{17}PO_3].H_2O$ have been prepared and characterized (*IR*, *TGA*, *X-Ray etc.*). The compounds show a layered structure, the aliphatic chain retains an *all-trans* conformational order. The magnetic properties of Ni(II)*octadecyl*-phosphonate are typical of a *weak-ferromagnet*, the phenomenon is generated by "*spin-canting*". This result is different from that found in Ni^{II}*methyl*-phosphonate, where only antiferromagnetic interactions are present with no long-range magnetic ordering down to the lowest measured temperature (*i.e.* 5K).

Acknowledgment

The authors are grateful for the technical assistance of C. Bellitto and E.M. Bauer and for the Istituto di struttura della materia, CNR, Roma, Italy in the magnetic measurements using SQUID magnetometer.

References

[1] Alberti,G. in Lehn, J.M. ed. ' Comprehensive supramolecular chemistry', Pergamon Press, Oxford, 1996, 151-85.

[2] Bellitto,C., Altomare, A., Federici,F. Rizzi, R. and Ibrahim,S.A., Synthesis, X-ray powder structure and magnetic properties of the new weak ferromagnet Fe(II)phenylphosphonate., Inorg. Chem.,2000, 39, 1803-12.

[3] Altomare, A. Bellitto, C. Ibrahim, S.A., Mahmoud, M.R. and Rizzi, R. Fe(II)-phosphonates: A new series of molecule based weak ferromagnets J.Chem. Soc. Dalton Trans., 2000, 3913-24.

[4] See for example, structure and mechanism of organophosphorus chemistry, Academic Press, New York, 1965.

[5] Le Bail, A., Duroy, H., Fourquet, J.L., AB-initio structure determination of LiSbWO₆ by X-ray powder diffraction, Mater. Res. Bull., 1988, 23, 447-52.

[6] Bellitto, C., Bauer, E.M., Collapietro, M., Ibrahim, S.A., Mahmoud, M.R., Righini,G., Layered hybrid organic-inorganic Co(II) alkylphosphonates: synthesis, crystal structure and magnetism of the series $[Co(CH_3PO_3)H_2O]$ and $[Co(C_2H_5PO_3)H_2O]$ J. Solid State Chem. 2006, 179, 389-94.

Figure Captions.

Scheme1. Schematic representation of the 2D lattice.

Fig.1. FTIR spectrum of Ni(II)-methylposphonate.

Fig.2 FTIR spectrum of Ni(II)-octadecylphosphonate.

Fig.3 TGA of NiII[CH3(CH2)17PO3]•H2O

Fig. 4. X-ray powder diffraction pattern of Ni(II)-methylphosphonate.

Scheme 2. Packing model for $Ni^{II}[CH_3(CH_2)_{17}PO_3] \cdot H_2O$

Fig.5. $1/\chi$ vs. T plot.

Fig.6 Zero-field (zfc), field-cooled (fc)and irreversible magnetization.

Fig.7 Hysteresis loop of NiII[CH3(CH2)17PO3]•H2O measured at T=5K.