



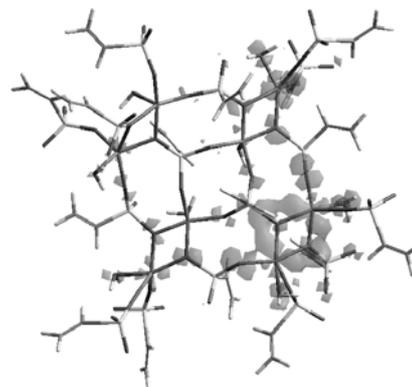
ELECTRONIC PROPERTIES OF Cu^{2+} VINYLPHOSPHONATE ESTIMATED BY PM3 SEMIEMPIRICAL METHOD

Aurelia VISA, Bianca MARANESCU* and Mircea MRACEC

Institute of Chemistry Timișoara of the Roumanian Academy, 24 M. Viteazul Ave, Timișoara – 300223, Roumania

Received September 12, 2013

The network was built using the basic unit $[\text{Cu}(\text{C}_2\text{H}_3\text{PO}_3)_4 \cdot \text{H}_2\text{O}]^{6-}$. Its geometry is best described by a distorted tetragonal pyramid: the five ligands are oriented as follows: an oxygen atom from a vinyl phosphonic group is oriented in axial position and four equatorial positions are occupied by three atoms of oxygen derived from the phosphonate group and the fourth by a water molecule. The fundamental vibration for all compounds proves that the geometries obtained by calculation are stable structures. The C=C bond lengths estimated by calculation are around 1.32 Å being comparable with RX experimental data. Bond lengths of $\text{Cu}-\text{O}_w$ are underestimated compared with experimental data and other Cu-O bonds are comparable with experimental data. LUMO and HOMO energy gap is 2.933 eV for VP-3Cu and can explain the semiconductor behavior of these metal organic networks.



INTRODUCTION

Phosphonate metal-organic frameworks (MOFs) are a very important class of porous materials with strategic applications in various fields.¹⁻⁵ These applications depend on the structure of these materials. Therefore, control of the synthesis parameters and ligand structures is crucial in the formation of new structures. The self-assembly of phosphonate metal organic frameworks depends on numerous structural factors such as: the nature of incorporated metal, geometry of the phosphonic acid, presence of other coordinating moieties on the phosphonate backbone, protonation degree and synthetic parameters related to the reaction conditions: pH, pressure, temperature, reagent molar ratio, reaction time.⁶⁻⁸

In recent years, several researchers have used the hydrothermal method to synthesize a variety of phosphonate metal organic frameworks starting from

divalent transition metals (Co, Ni, Zn, Cu, Cd, Mn, Fe, Pb) with unsaturated phosphonic acids (vinylphosphonic acid, phenylvinylphosphonic acid).⁹

Unsaturated phosphonic ligands are particularly important because of their conjugated π -bonded systems that usually favor the absorption of UV light, with the extent of conjugation determining the wavelength of the absorption maximum. These materials can act almost as an antenna for the absorption of light energy. This energy can then excite electronic transitions in neighboring metal atoms, giving rise to the observation of luminescent properties as well as electrical properties.

Various research groups¹⁰⁻¹² were studied using semiempirical quantum chemistry methods as AM1, PM3 and PM6 models in order to predict the structures of metal organic frameworks and to calculate the geometric and crystallographic properties.

The influence of different counterion for the copper salt used as the Cu(II) source with

* Corresponding author: biancamaranescu@yahoo.com

unsaturated phosphonic acid, on the structure and crystallinity of the final product was studied in our research group.¹³ To the best of our knowledge, phosphonate metal organic frameworks with copper ion and vinylphosphonic ligand have so far not been investigated by theoretical calculations. Calculations of cobalt and nickel ion with vinylphosphonic ligand have been performed in our previous work.^{14,15}

In this paper, we describe the theoretical studies and characterization of copper vinylphosphonate at PM3 semiempirical level to calculate the geometric properties (bond lengths, bond angles, torsion angles) and electronic properties (energetic levels, charges, heats of formation, ZPE, v_{\min} , v_{\max}) and to compare with X-ray experimental results.

METHODS

Gas phase equilibrium geometry of conformers was obtained by semi-empirical PM3-RHF calculations using the Polak-Ribiere conjugate gradient algorithm for geometry optimization.¹⁶⁻²⁰ Stop criteria were: SCF convergence of 10^{-5} and RMS gradient of 10^{-2} kcal/A·mol.^{20,21} For the structures with $\frac{1}{2}$ spin number we used half electron approximation. Calculations have been performed with HyperChem7.52 package.²¹

RESULTS AND DISCUSSION

The network was built using the basic unit $[\text{Cu}(\text{C}_2\text{H}_3\text{PO}_3)_4\cdot\text{H}_2\text{O}]^{6-}$ made experimentally in the group led by D.A. Knight.²² Its geometry is best described by a distorted tetragonal pyramid: the five ligands are oriented as follows: the axial is occupied by an oxygen atom belonging to a vinyl phosphonic group and the four equatorial positions are occupied by oxygen atoms coming from the phosphonate group and the fourth of a molecule of water. The other two oxygen atoms remaining free will bind Cu^{2+} atoms in equatorial position and will contribute to the network formation. The vinyl group from vinyl phosphonic acid will contribute to the formation of the hydrophobic part of the two-dimensional network. Two ions contribute to the formation of vinyl phosphonic connection with one oxygen atom, the other two oxygen atoms are linked by a new Cu^{2+} ion and will contribute to the network extension. The copper vinylphosphonate

network has two types of cycles (holes). A cycle consists of four atoms from the two copper and two oxygen atoms of two phosphonates, and the second hole is composed of two symmetrical units (-Cu-O-P-O-) a total of eight atoms.

In Fig. 1 the first four elements forming the network are shown.

Likewise was built model: $[\text{Cu}_8(\text{C}_2\text{H}_3\text{PO}_3)_{16}\cdot 8\text{H}_2\text{O}]^{16-}$ shown in Fig. 2 that has all the elements of an infinite supramolecular network where you can see holls constituted by 8 respectively 4 atoms, which give various practical applications. The size of this cycles is very important and can conduct the research in the direction of gas storage.

The numbering of atoms is given in Fig. 3, representing the model with eight Cu^{2+} ions coordinate eight water molecules and 16 phosphonate $[\text{Cu}_8(\text{O}_3\text{PCH}=\text{CH}_2)_{16}\cdot 8\text{H}_2\text{O}]^{16-}$. For simplicity only the atoms belonging to the central ion and the second Cu^{2+} ion are numbered. The hydrogen atoms are omitted.

The atom numbering is shown in Fig. 3 for the most complex model VP-8Cu. It can be seen that VP-8Cu model presents a squared structure. In order to have a unitary numbering for each model we used the following rule: one central Cu atom is numbered as Cu_1 . The following copper ions are numbered in clockwise direction. The phosphorus atoms from vinylphosphonates are numbered with $\text{P}_{\text{copper number phosphorus atom number}}$ (ex. P_{11}). The P atoms attached to central copper ion are all considered as belonging to the central ion and are numbering in the clockwise direction. The other phosphorus atoms are numbered starting for the attached the Cu^{2+} . The water oxygen atoms are numbered as $\text{O}_{\text{copper number}}$ (ex $\text{O}_{\text{w}1}$ attached to Cu_1). Oxygen atoms attached to phosphorus are numbered as $\text{O}_{\text{oxygen atom number P copper number}}$ (ex. $\text{O}_{1\text{P}11}$). The carbon atoms are numbered in a similar way as oxygen atoms.

From the three oxygen atom belonging to phosphonate group two are having negative charge, are sp^3 hybridized and are contributed with an lone electron pair to P-O-Cu formation and the third oxygen is sp^2 hybridized and forms a P=O bond.

In this paper the geometric properties (bond lengths, bond angles, torsion angles) shown in Tables 1-4 and electronic properties (energetic levels, charges, heats of formation, ZPE, v_{\min} , v_{\max}) from semi-empirical PM3 calculation and X-ray experimental data were compared.

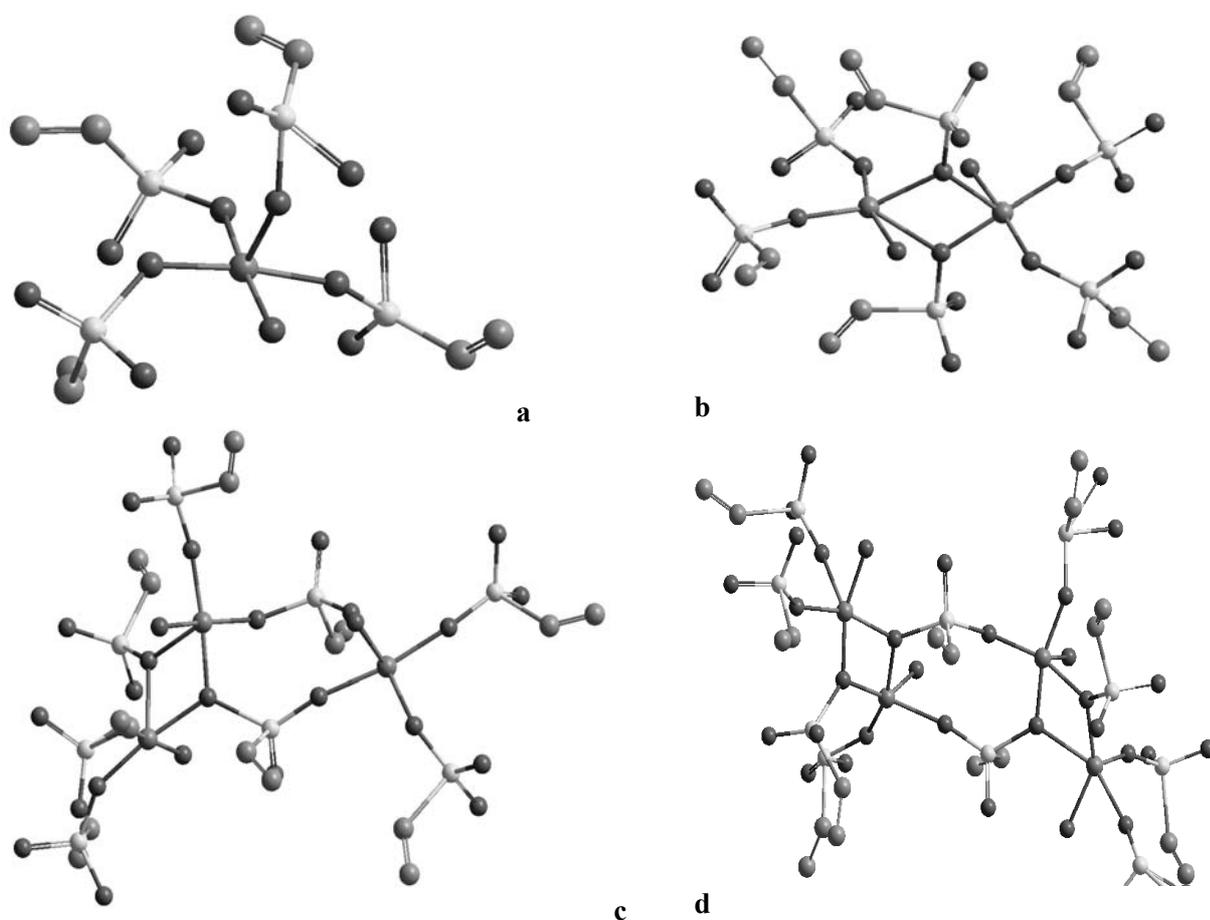


Fig. 1 – The network elements: **a**) $[\text{Cu}(\text{C}_2\text{H}_3\text{PO}_3)_4 \cdot \text{H}_2\text{O}]^{6-}$; **b**) $[\text{Cu}_2(\text{C}_2\text{H}_3\text{PO}_3)_6 \cdot 2\text{H}_2\text{O}]^{8-}$; **c**) $[\text{Cu}_3(\text{C}_2\text{H}_3\text{PO}_3)_8 \cdot 3\text{H}_2\text{O}]^{10-}$, **d**) $[\text{Cu}_4(\text{C}_2\text{H}_3\text{PO}_3)_{10} \cdot 4\text{H}_2\text{O}]^{12-}$. Color code: green-Cu, yellow-P, red-O, turquoise-C.

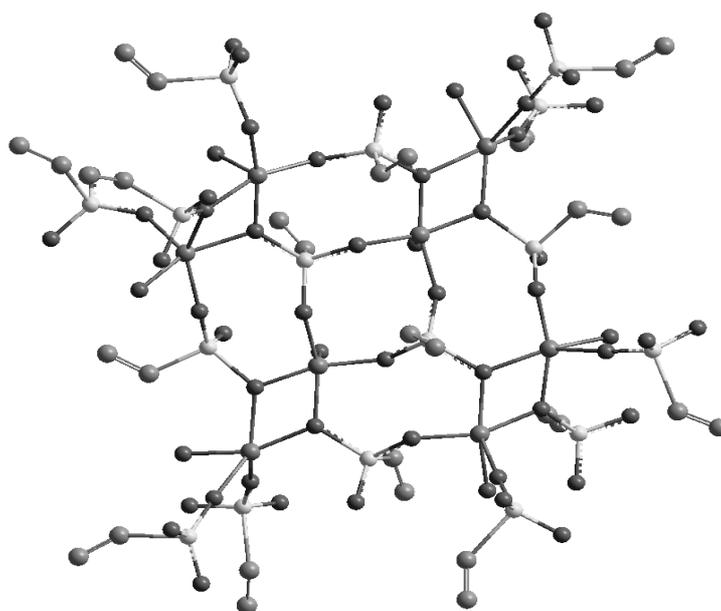


Fig. 2 – The $[\text{Cu}_8(\text{C}_2\text{H}_3\text{PO}_3)_{16} \cdot 8\text{H}_2\text{O}]^{16-}$ which highlights supramolecular infinite character. Color code: green-Cu, yellow-P, red-O, turquoise-C.

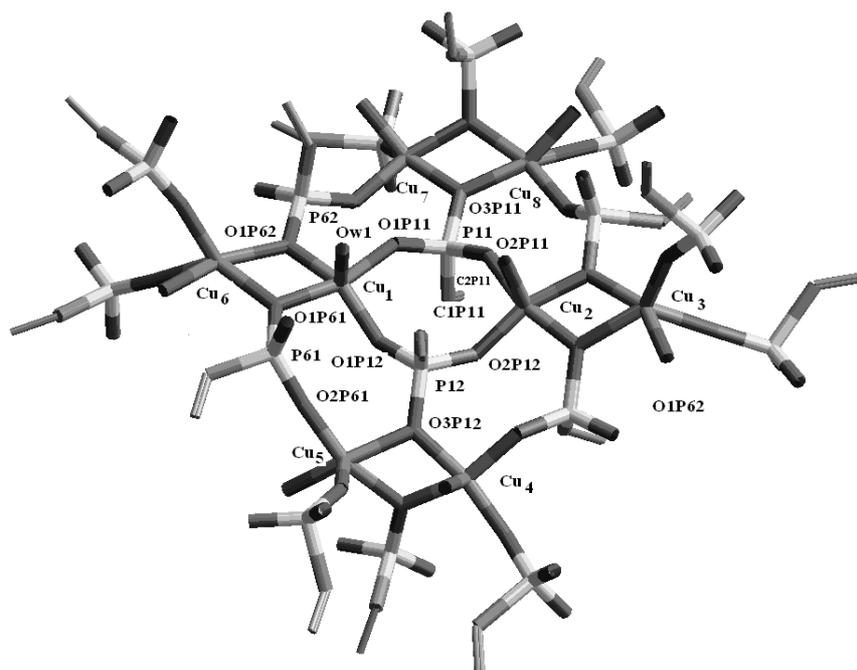
Fig. 3 – Numbering of atoms in a compound network $[\text{Cu}_8(\text{O}_3\text{PCH}=\text{CH}_2)_{16}\cdot 8\text{H}_2\text{O}]^{16-}$.

Table 1

Bond length for central Cu^{2+} ion and attached vinylphosphonate atoms

Model/ Bond length	$\text{Cu}_1\text{-O}_{\text{w}1}$	$\text{Cu}_1\text{-O}_{\text{IP}11}$	$\text{Cu}_1\text{-O}_{\text{IP}12}$	$\text{Cu}_1\text{-O}_{\text{IP}61}$	$\text{Cu}_1\text{-O}_{\text{IP}62}$	$\text{P}_{11}\text{-O}_{\text{IP}11}$	$\text{P}_{11}\text{-O}_{2\text{P}11}$	$\text{P}_{11}\text{-O}_{3\text{P}11}$	$\text{P}_{11}\text{-C}_{\text{IP}11}$	$\text{C}_{\text{IP}11}\text{-C}_{2\text{P}11}$
VP- Cu	1.8896	1.8905	1.8105	1.8367	2.0148	1.7527	1.4392	1.6657	1.8066	1.3216
VP-2Cu	2.0326	1.878	1.8688	1.8971	2.0955	1.7242	1.5454	1.5565	1.9694	1.3239
VP-3Cu	1.9184	1.879	1.8694	1.9015	2.0586	1.7167	1.5577	1.5461	1.9499	1.3234
VP-4Cu	2.0443	1.9652	1.9804	1.9801	2.0182	1.8663	1.535	1.5339	1.9265	1.3202
VP-8Cu	2.0652	1.9082	1.8857	1.8908	1.8879	1.6793	1.6853	1.6253	1.7800	1.3214
RX	2.306	1.961	1.978	1.932	2.001	–	–	–	–	–

Table 2

Bond angles for central Cu^{2+} ion and attached vinylphosphonate atoms

Model/ Angle	$\text{O}_{\text{IP}11}\text{-Cu}_1\text{-O}_{\text{w}1}$	$\text{O}_{\text{IP}11}\text{-Cu}_1\text{-O}_{\text{IP}12}$	$\text{O}_{\text{IP}12}\text{-Cu}_1\text{-O}_{\text{IP}61}$	$\text{O}_{\text{IP}61}\text{-Cu}_1\text{-O}_{\text{IP}62}$	$\text{Cu}_1\text{-O}_{\text{IP}62}\text{-P}_{11}$	$\text{O}_{\text{IP}11}\text{-P}_{11}\text{-C}_{\text{IP}11}$	$\text{Cu}_1\text{-O}_{\text{IP}61}\text{-Cu}_6$
VP- Cu	76.156	98.717	90.5868	91.6086	149.121	112.262	–
VP-2Cu	92.2242	92.2986	92.1152	74.7766	137.522	104.774	107.921
VP-3Cu	92.8574	91.3737	92.4416	69.4496	139.196	105.694	115.385
VP-4Cu	75.0854	101.906	95.6468	60.7794	147.541	101.653	114.467
VP-8Cu	76.5114	96.0457	98.375	66.9867	139.414	112.285	116.949

Table 3

Torsion angles for central Cu^{2+} ion and attached vinylphosphonate atoms

Model/ Torsion angle	$\text{P}_{11}\text{-O}_{\text{IP}11}\text{-Cu}_1\text{-O}_{\text{w}1}$	$\text{O}_{\text{w}1}\text{-Cu}_1\text{-O}_{\text{IP}12}\text{-P}_{12}$	$\text{O}_{\text{IP}11}\text{-Cu}_1\text{-O}_{\text{IP}12}\text{-P}_{12}$	$\text{O}_{\text{IP}12}\text{-Cu}_1\text{-O}_{\text{IP}61}\text{-Cu}_{\text{retea}}$	$\text{O}_{\text{w}1}\text{-Cu}_1\text{-O}_{\text{IP}61}\text{-Cu}_{\text{retea}}$	$\text{C}_{\text{IP}11}\text{-P}_{11}\text{-O}_{\text{IP}11}\text{-Cu}_1$	$\text{C}_{2\text{P}11}\text{-C}_{\text{IP}11}\text{-P}_{11}\text{-O}_{\text{IP}11}$
VP- Cu	-165.226	123.587	-25.920	–	–	72.111	-139.202
VP-2Cu	-106.346	116.641	-31.280	-121.879	77.442	73.153	-171.961
VP-3Cu	-111.711	127.833	-60.874	-160.551	66.949	69.139	-178.924
VP-4Cu	-130.199	123.364	-17.922	-133.954	126.903	79.205	-155.696
VP-8Cu	-142.102	120.365	-75.2834	-125.549	94.207	71.551	-116.959

Table 4

Calculated electronic and thermodynamic properties

Model/Electronic properties	ΔH_{form} [Kcal/mol]	ν_{min} [cm ⁻¹]	ν_{max} [cm ⁻¹]	ZPE [Kcal/mol]	HOMO [eV]	LUMO [eV]	LUMO-HOMO [eV]
VP- Cu	-490.436	13.78	3642.93	150.9312	-9.0060	-5.6751	3.3309
VP-2Cu	44.883	13.30	3890.81	231.2733	13.2727	16.4049	3.1321
VP-3Cu	-134.206	5.38	3845.27	314.419	15.2981	18.2316	2.9334
VP-4Cu	-526.293	7.56	3904.46	401.3139	15.9780	19.7694	3.7909
VP-8Cu	-1630.308	4.97	3922.52	686.5871	19.1091	22.2595	3.1503

The ν_{min} (fundamental vibration) for all compounds is positive proving that the calculated geometries are stable structures, are stationary states no transition states.

The C = C double bond lengths estimated by calculation are pointed around 1.32 Å are comparable to RX data described in the literature.²²

Bond lengths (Table 1) for Cu-O_w are underestimated compared with the experimental data described in the literature and other Cu-O bonds are comparable with experimental X-ray data described by D. A. Knight and coauthors²². The bond angles and torsion angles calculated with PM3 semiempirical method are presented in Tables 2 and 3.

The LUMO-HOMO energetic difference is 2.933 eV for VP-3Cu (Table 4). This difference may explain the semiconductor behavior of these metal organic networks. In Fig. 4 the small difference between HOMO and LUMO allows the

transition of one electron from the top layer in the conduction band.

From the orbital analysis it can be observed that the highest occupied levels are positive and the lowest occupied levels are negative.

From the orbital components analysis (Fig. 5) it can be observed that from VP-Cu models in HOMO level are involved σ bonds of the organic functionalities. The d orbitals are implied in HOMO level in case of VP-2Cu, VP-3Cu, VP-4Cu and VP-8Cu models.

The semiconducting behavior of metal organic frameworks depends on these small energy gaps between HOMO and LUMO, typically less than 3eV.²³ The semiconducting materials are of particular interest, because these materials possess advantageous electrical, optoelectronic and processing properties for design and fabrication of novel class of electronic devices.

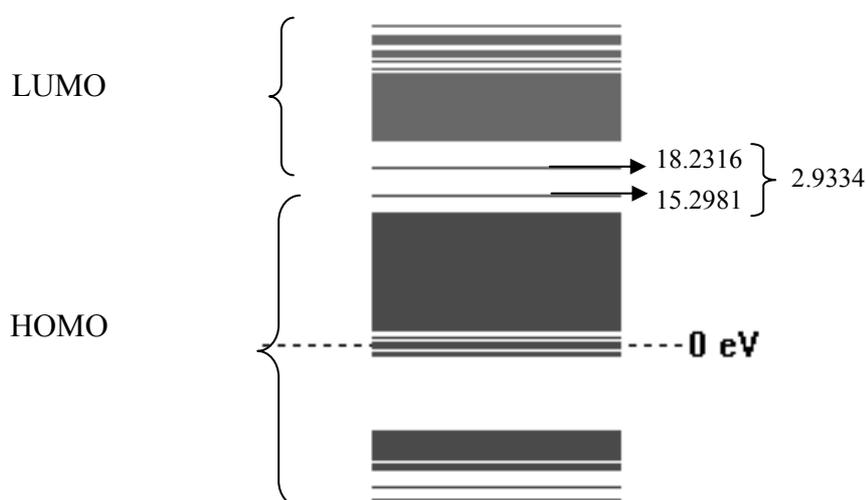


Fig. 4 – Orbital distribution for VP-3Cu model.

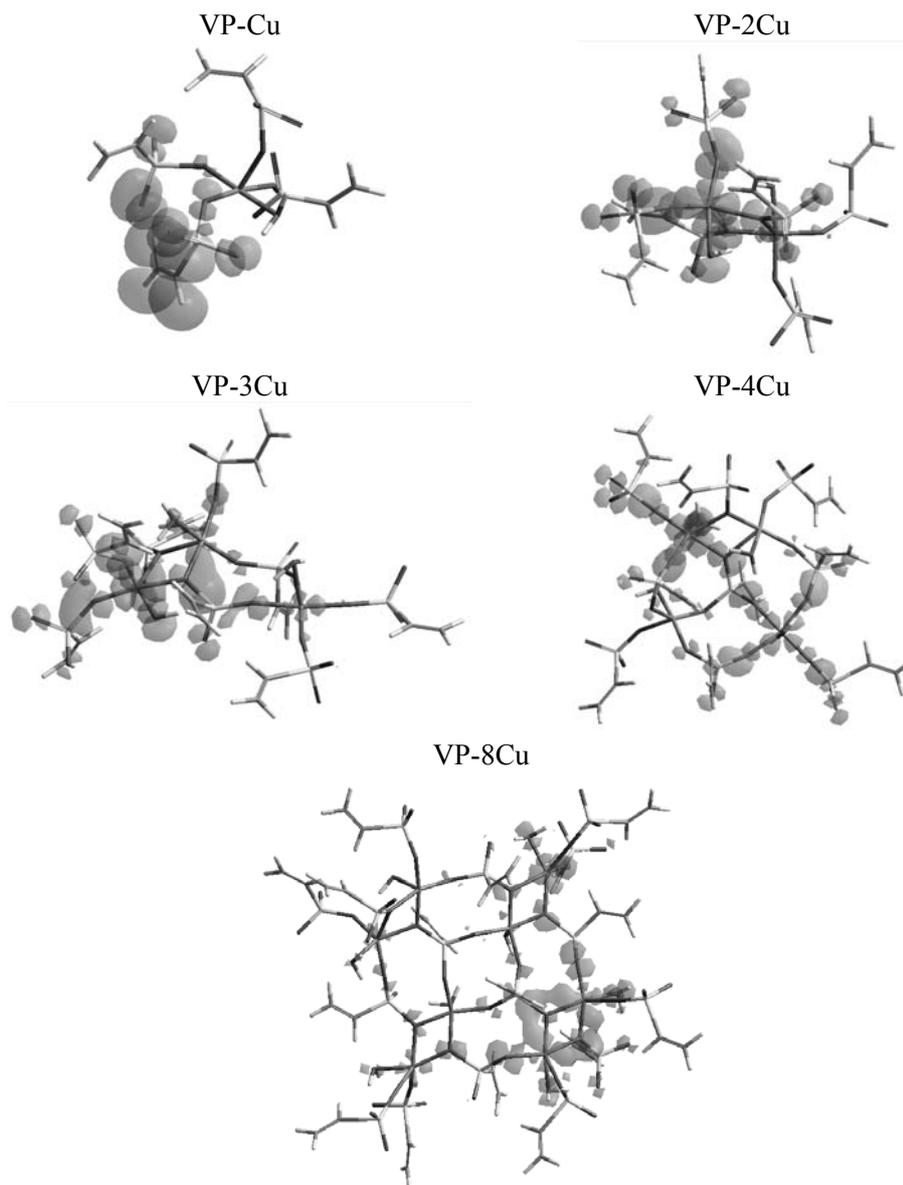


Fig. 5 – The HOMO orbital components.

CONCLUSIONS

The semiempirical quantumchemical methods were used to predict the geometry of copper vinylphosphonate. The PM3 semiempirical models were used and the comparison of the theoretical and experimental cell parameters suggests that the PM3 models are suitable for predicting X-ray structures with good accuracy. This was confirmed by the detailed comparison of the Cu–O distances in the X-ray and theoretical structures. Also, the fundamental vibration for all compounds is positive proving that the calculated geometries are stable structures. The calculated thermodynamic data make clear the metal organic network formation tendency.

The σ bonds are implied in HOMO level in case of VP-Cu model. For all the other models in HOMO level are involved d orbitals.

Acknowledgments: This work was supported by a grant of the Roumanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2011-3-0092.

REFERENCES

1. N.W. Ockwig, O. Delgado-Friedrichs, M. O’Keeffe and O.M. Yaghi, *Acc. Chem. Res.*, **2005**, *38*, 176-182.
2. S.M. Neville, B. Moubaraki, S.K. Murray and C.J. Kepert, *Angew. Chem. Int. Ed.*, **2007**, *46*, 2059-2062.
3. C.L.Cahill, D.T.de Lill and M. Frisch, *Cryst. Eng. Commun.*, **2007**, *9*, 15-26.

4. M. Dinca, A. Dailly, Y. Liu, C.M. Brown, D.A. Neumann and J.R. Long, *J. Am. Chem. Soc.*, **2006**, *128*, 16876-16883.
5. P. Horcajada, C. Serre, M. Vallet-Regi, M. Sebban, F. Taulelle and G. Férey, *Angew. Chem. Int. Ed.*, **2006**, *45*, 5974-5978.
6. W. Quelling, M.H. Yu, C.J. O'Connor and Zubieta J., *Inorg. Chem.*, **2006**, *45*, 7628-7641.
7. B.K. Tripuramallu, S. Mukherjee and S.K. Das, *Cryst. Growth Des.*, **2012**, *12*, 5579-5597.
8. W. Quelling, M.H. Yu, C.J. O'Connor and J. Zubieta, *Inorg. Chem.*, **2006**, *45*, 3224-3239.
9. R.M. Colodrero, A. Cabeza, P. Olivera, D. Choquesillo, A. Turner, G. Ilia, B. Maranescu, K. Papathanasiou, G.B. Hix, K.D. Demadis and M.A. Aranda, *Inorg. Chem.* **2011**, *50*, 11202-11211.
10. C.A.F. de Oliveira, F.F. da Silva, I. Malvestiti, V.R. dos S. Malta, J.D.L. Dutra, N.B. da Costa Jr., R.O. Freire and S.A. Junior, *J. Solid State Chem.*, **2013**, *197*, 7-13.
11. X.F. Wang, G.X. Liu and H.Zhou, *Inorg. Chim. Acta*, **2013**, *406*, 223-229.
12. G. Accorsi, N. Armaroli, B. Béatrice Delavaux-Nicot, A. Kaeser, M. Holler, J.F. Jean Nierengarten and A. Alessandra Degli Esposti, *J. Molec. Struct: THEOCHEM*, **2010**, *962*, 7-14.
13. A. Visa, B. Maranescu, A. Bucur, S. Iliescu and K.D. Demadis, *Phosphorus Sulfur Silicon Relat. Elem.*, **2013**, DOI: 10.1080/10426507.2013.843004.
14. B. Maranescu, A. Visa, M. Mracec, G. Ilia, V. Maranescu, Z. Simon and M. Mracec, *Rev. Roum. Chim.*, **2011**, *56(5)*, 473-482.
15. B. Maranescu, A. Visa, S. Iliescu, A. Popa, G. Ilia, V. Maranescu, Z. Simon and M. Mracec, *Rev. Roum. Chim.*, **2011**, *56(12)*, 1133-1141.
16. M.J.S. Dewar, E.G. Zebisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc.*, **1985**, *107*, 3902-3909.
17. J.J.P. Stewart, *J. Comput. Chem.*, **1989**, *10*, 209-220.
18. J.J.P. Stewart, *J. Comput. Chem.*, **1991**, *12*, 320-334.
19. J.J.P. Stewart, *J. Mol. Model.*, **2004**, *10*, 155-164.
20. I.N. Levine, "Quantum Chemistry", 5th Edition, Prentice Hall, Inc., Upper Saddle River, New Jersey 07458 2000, Chap. 15, Chap. 17.
21. ** HyperChemTM, Release 7.52 for Windows, Copyright **2003**, Hypercube, Inc, 1115 NW 4th Street, Gainesville, FL 32601, US.
22. D.A. Knight, V. Kim, R.J. Butcher, B. Harper and T.L. Schull, *J. Chem. Soc., Dalton Trans.*, **2002**, 824-826.
23. M.A.M. El-Mansy, M.M. El-Nahass, N.M. Khusayfan and E.M. El-Menyawy, *Spectrochim Acta A*, **2013**, *111*, 217-222.

