



*Dedicated to the memory of
Dr. Henry V. Kehiaian (1929–2009)*

LAMELLAR Co^{2+} VINYLPHOSPHONATE METAL ORGANIC FRAMEWORK. PM3 SEMI-EMPIRICAL ANALYSIS OF STRUCTURAL PROPERTIES**

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Phosphonates metal organic frameworks (MOF) are a very important class of compound with special properties. In order to predict the special properties (electrical properties, conductivity) and to compare the calculated and experimental geometric properties of the Co^{2+} vinylphosphonate metal organic framework we performed a PM3 semi-empirical analysis of structural properties. For this reason five octahedral models were calculated: three arising from constructed geometries and two from experimental RX data. For the PM3 semi-empirical results the calculated bond lengths are lower than the experimental ones. The bond angles are comparable and the torsion angles are lower or comparable with the experimental results. From the charge densities the negative value of the central Co ion of the 3x3 Co network (VP-9Co) predict the special electric proprieties of the Co^{2+} vinylphosphonate metal organic framework. The LUMO-HOMO energetic difference decreases from the TriVP-Co to the VP-9Co reaching to a value of 1.465 eV. This very small difference could explain the semiconductive proprieties of VP-9Co metal organic network. The small difference allows one electron transition from the superior level into a conduction band.

INTRODUCTION

Metal organic frameworks are a class of synthetic porous materials that have become an area of interest in the last decade not only because of the fascinating structures of these compounds¹⁻⁴ but due to possible applications in areas of gas storage⁵⁻⁷ heterogeneous catalysis,^{8,9} separation,^{10,11} ion exchange,¹² magnetism,¹³ sensors,¹⁴ etc. Most networks are based on metal organic dicarboxylic derivatives that form a uniform structure with transition metal ions. Metalphosphonates don't have a very well defined geometric structure due to

the variable coordination mode of the phosphonate group. Generally, metal phosphonates possess layered solid state structures, where the octahedrally coordinated metal cation is inside the polymeric layer and is linked to the phosphonic acid (with tetrahedral coordinated phosphorus atom).¹⁵ An interesting class of metalphosphonates is the one that use a phosphonic derivative containing a double bond. Thus, Co^{2+} vinylphosphonate was obtained by the reaction of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ vinyl phosphonic acid (VP) in echimolecular ratio and hydrothermal conditions.^{16,17}

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For the cobalt atom (with electronic structure [Ar] $4s^2 3d^7, ^4F_{9/2}$) it loses $2e^-$ ($4s^2$) and d levels splits in an octahedral field into three T_{2g} levels and two E_g levels.^{18,19} Through complexation results an octahedral system complete occupied with e^- ($7e^-$ from Co^{2+} and $12e^-$ from ligands, filling the 3d, 4s and 4p levels) with a free electron placed on the 5s higher level. In order to predict potential coordination capacity, geometric and electronic structures for several models of the octahedral structure calculations were made:

An octahedral model with three methylphosphonic acids $[Co(O_3PCH_3)_3]^{4-}$ (TriVP-Co), which simulates an octahedral structure involving oxygen atoms participation as follows: a phosphonate ion participate with two oxygen atoms in the equatorial plane, and the others two oxygen atoms are one in the equatorial plane and the other in the axial plane (Fig. 1a).

An octahedral model with four vinylphosphonate acids and a water molecule $[Co(O_3PCH=CH_2)_4 \cdot H_2O]^{6-}$ (TetraVP-Co), which simulates an octahedral structure involving oxygen atoms as follows: an phosphonate ion participate with two oxygen atom in the equatorial plane, while the other three oxygen atoms participate with the phosphorus oxygen double bound, two in the equatorial plane and the third in the axial plane. The pair of non-participant electrons from the water molecules is shared in the axial plane (water oxygen is sp^3 hybridized) (Fig. 1b).

An octahedral model with two Co^{2+} ions coordinated with two water molecules and seven phosphonate $[Co_2(O_3PCH=CH_2)_7 \cdot 2H_2O]^{10-}$ (VP-2Co), which simulates an octahedral structure with the participation of oxygen atoms in the following way: two oxygen atom from phosphonate participate in the equatorial plane, while the other three oxygen atoms comes from the phosphorus-oxygen double bound, two in the equatorial plane and the third in the axial plane. The pair of non-participant electrons from the water molecules is shared in the axial plane (water oxygen is sp^3 hybridized) (Fig. 1c).

Two octahedral models from experimental RX structures,¹⁷ which simulate the lamellar Co^{2+} vinylphosphonate metal organic framework:

(i) An octahedral model with seven Co^{2+} ions coordinated with seven water molecules and fourteen phosphonate $[Co_7(O_3PCH=CH_2)_{14} \cdot 7H_2O]^{14-}$ (VP-7Co), which simulates an octahedral structure. For the Co^{2+} central ion the phosphonates participate with the oxygen atoms coming from phosphorus-oxygen

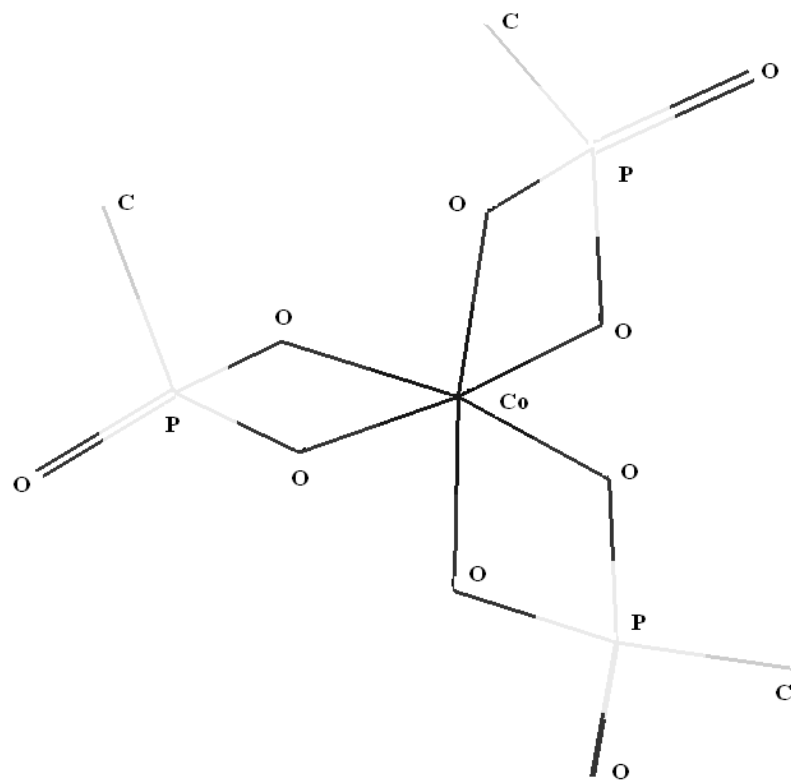
single bond in the equatorial plane and with the phosphorus-oxygen double bond in axial plane. At four Co^{2+} ions located on the network outside (two on the left side and two on the right side) is a P=O-Co bond situated in the equatorial plane. The pair of non-participant electrons from the water molecules is shared in the axial plane (water oxygen is sp^3 hybridized) (Fig. 2).

(ii) An octahedral model with nine Co^{2+} ions coordinated with nine water molecules and sixteen phosphonate $[Co_9(O_3PCH=CH_2)_{16} \cdot 9H_2O]^{14-}$ (VP-9Co), which simulates an octahedral structure. For the Co^{2+} central ion the phosphonates participate with the oxygen atoms coming from phosphorus-oxygen single bond in the equatorial plane and with the phosphorus-oxygen double bond in axial plane. The pair of non-participant electrons from the water molecules is shared in the axial plane (water oxygen is sp^3 hybridized) (Fig. 2).

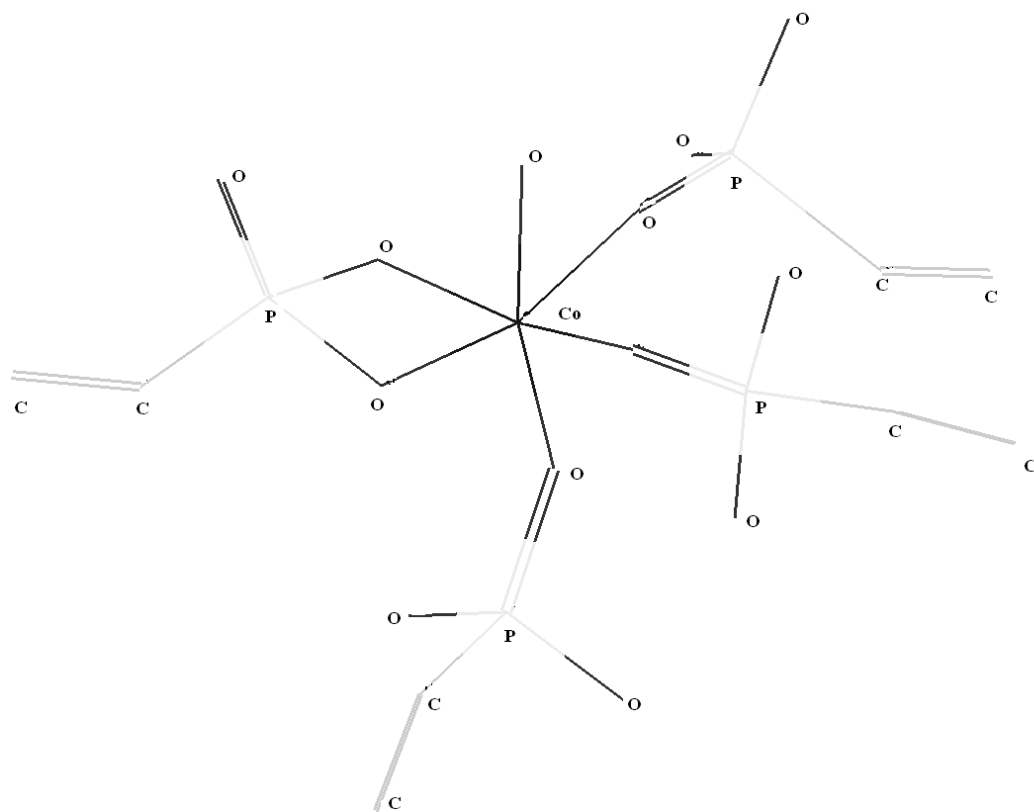
The atom numbering is shown in Fig. 2 and is given for the most complex model VP-9Co. From Fig. 2 it can be seen that VP-9Co model represent 3×3 Co^{2+} squared structure. For simplification only the atoms attached to the Co^{2+} central ion and the one attached to an exterior Co^{2+} ion were numbered. The hydrogen atoms were omitted for clarity.

In order to have a unitary numbering for each model we used the following rule: the central Co atom is numbering as Co_1 . The following cobalt ions are numbering in clockwise direction. The phosphorus atoms from vinylphosphonates are numbered with $P_{cobalt\ number\ phosphorus\ atom\ number}$ (ex. P_{11}). The P atoms attached to central cobalt ion are all considered as belonging to central ion and are numbering in the clockwise direction. The other phosphorus atoms are numbering starting for the attached the Co^{2+} . The water oxygen atoms are numbering as $O_{w\ cobalt\ number}$ (ex O_{w1} attached to Co_1). Oxygen atoms attached to phosphorus are numbered as $O_{oxygen\ atom\ number\ P\ cobalt\ number}$ (ex. O_{1P11}). The carbon atoms are numbered in the similar way as oxygen atoms.

The phosphorus atom (electronic structure [Ne] $3s^2 3p^3, ^4S_{3/2}$) from vinylphosphonate is tetrahedral hybridized (pentavalent tetracoordinated).²⁰ Two oxygen atoms from phosphonate have negative charge, are sp^3 hybridized and participate to the P-O-Co bond with a pair of non-participant electrons. The third oxygen atom is sp^2 hybridized form a phosphorus-oxygen double bond and can participate to a P=O-Co double bond.



a



b

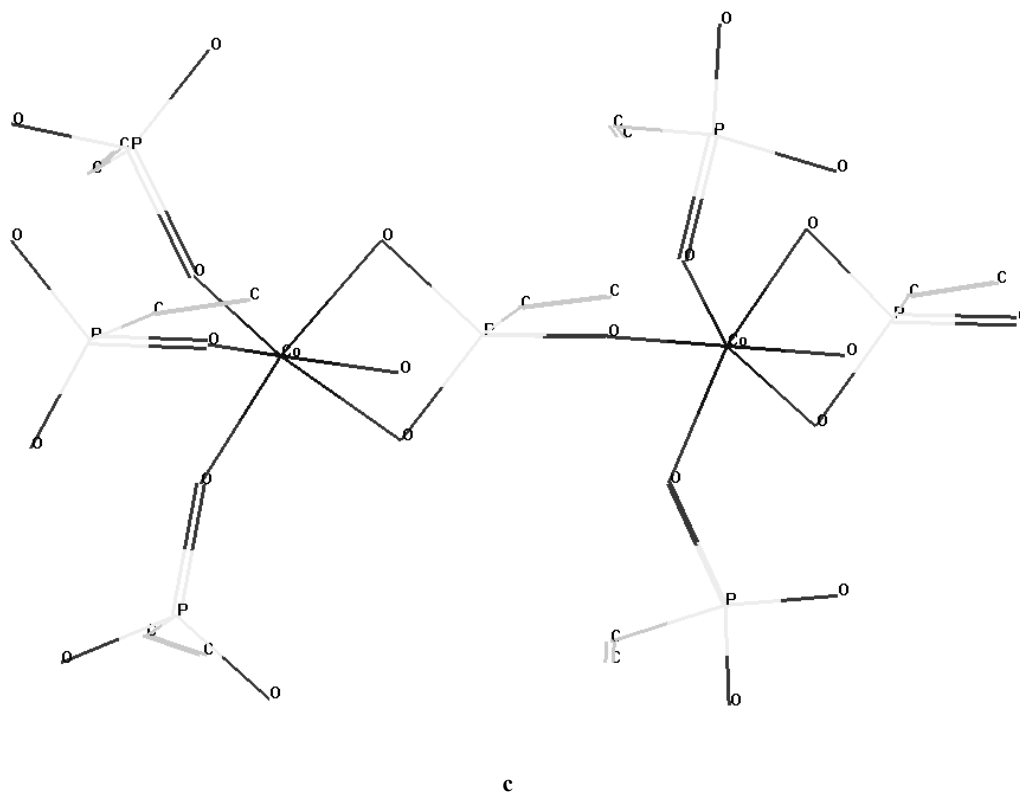


Fig. 1 – The TriVP-Co (a), TetraVP-Co (b) and VP-2Co (c) models representation.

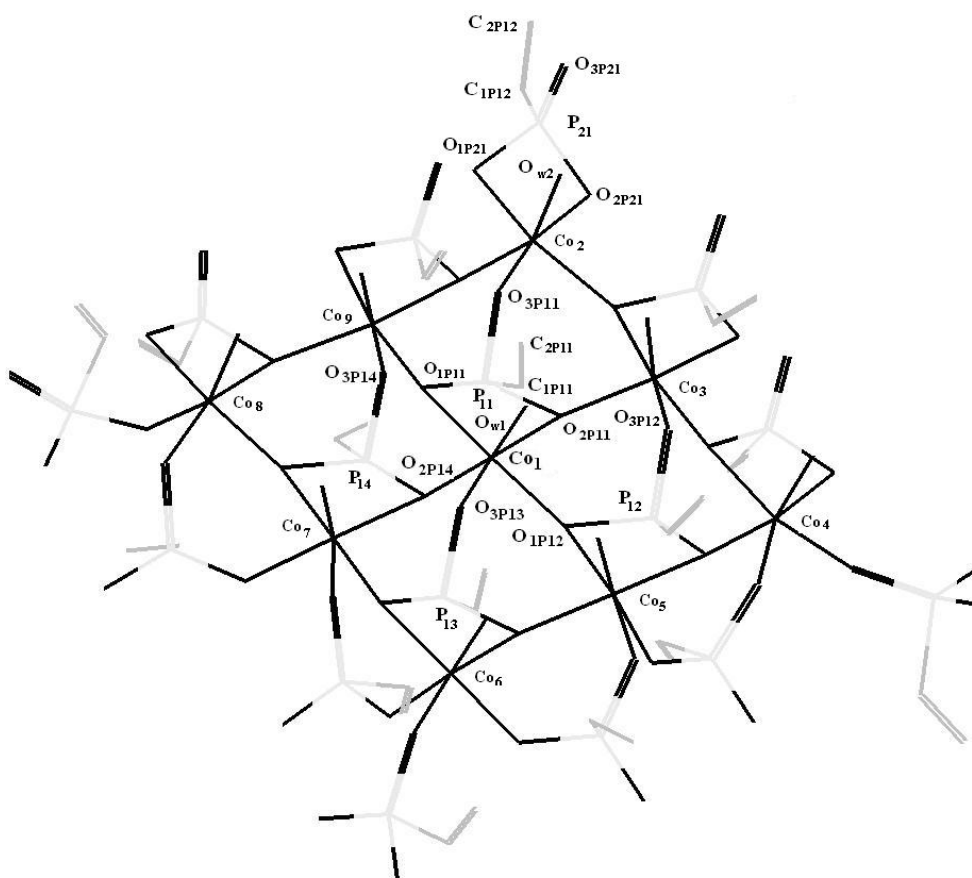


Fig. 2 – $[\text{Co}_9(\text{O}_3\text{PCH}=\text{CH}_2)_{16} \cdot 9\text{H}_2\text{O}]^{14+}$ atom numbering.

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

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.^{21,22} Stop criteria were: SCF convergence of 10^{-5} and RMS gradient of 10^{-2} kcal/A·mol.^{22,23} for the structures with $\frac{1}{2}$ spin number we used half electron approximation.^{21,22} Calculations have been performed with HyperChem7.52 package.²³

RESULTS AND DISCUSION

In Table 1 the bond lengths for the proposed models in comparison with the experimental results are presented. From $\text{Co}_1\text{-O}_{w1}$ axial bond the lengths are with 11% shorter and for $\text{Co}_1\text{-O}_{2P14}$ axial bonds are 5% shorter than experimental values, respectively. For equatorial oxygen atoms belonging to the same phosphorus atom the calculated and the experimental data are similar.

The calculated values for P-O and P-C bonds are higher than the experimental RX data for the central ion. Experimental values for P-O and P-C bonds of 1.54 and 1.79 Å, respectively, are in accordance with the measured values for the outer phosphonate ion. The calculated C=C bond length is similar with the experimental RX data around 1.32 Å (see supplementary materials Table 1).

The calculated bond lengths are similar with the experimental RX data (Table 2).

Torsion angles of VP-7Co and VP-9Co are lower than experimental data (Table 3). Torsion angles of TetraVP-Co and VP-2Co models are higher in the case of axial oxygens, $\text{P}_{13}\text{-O}_{3P13}\text{-Co}_1\text{-O}_{w1}$ torsion angle make an exception. The torsion angles formed by equatorial oxygen atoms and C=C bond have similar values with the experimental results.

The estimated values of the net charges are presented in Table 4. The central Co^{2+} ion form VP-7Co and VP-9Co models have negative values. The net charges of cobalt ion in TriVP-Co, TetraVP-Co and VP-2Co models are positive. Positive charges are observed for outer cobalt ions in the network models (see supplementary materials Table 2).

All net charges of both equatorial and axial oxygen atoms have negative values. The phosphorus has positive values of the net charges around 1.8 for built models and 1.4 for VP-7Co and VP-9Co models. The central Co_1 ion becomes negative in the network models (VP-7Co and VP-9Co) due to the charge transfer from oxygen atoms to cobalt ion. This negative value can explain the gas storage, heterogeneous catalysis, separation, ion exchange, magnetism, sensors properties of the Co^{2+} vinylphosphonate.

The negative heats of formation for the studied compounds in comparison with the heat of formation of Co^{2+} are presented in Table 5 and these values prove the strong tendency of metal organic framework formation.

The v_{\min} (fundamental vibration) for all compounds is positive proving that the calculated geometries are stable structures, are stationary state but not transition state.

Table 1

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

Model/ Bond length	$\text{Co}_1\text{-O}_{w1}$	$\text{Co}_1\text{-O}_{1P11}$	$\text{Co}_1\text{-O}_{2P11}$	$\text{Co}_1\text{-O}_{1P12}$	$\text{Co}_1\text{-O}_{3P13}$	$\text{Co}_1\text{-O}_{2P14}$	$\text{P}_{11}\text{-O}_{1P11}$	$\text{P}_{11}\text{-O}_{2P11}$	$\text{P}_{11}\text{-O}_{3P11}$	$\text{P}_{11}\text{-C}_{1P11}$
TriVP-Co	-	1.8598	1.9317	1.8904	1.8978	1.9652	1.6466	1.6450	1.5512	1.9505
TetraVP-Co	1.9944	1.8835	1.9010	1.9134	2.0237	1.9700	1.7182	1.7192	1.5826	1.7509
VP-2Co	1.9839	1.9168	1.9428	2.0008	1.9143	1.9464	1.5456	1.5543	1.6768	2.3820
VP-7Co	1.9445	1.9236	2.0265	2.1491	1.9461	1.9602	1.8327	1.7636	1.7066	1.9248
VP-9Co	1.9890	1.9648	2.0240	2.0438	1.9567	1.9232	1.9544	1.7740	1.8025	2.0348
RX	2.2300	2.2480	2.0020	2.0020	2.2480	2.0590	1.5350	1.5350	1.5410	1.7960

Table 2

Bond angles for central Co²⁺ ion and attached vinylphosphonate atoms

Model/ Angle	O _{1P11} -Co ₁ - O _{w1}	O _{1P11} -Co ₁ - O _{2P11}	O _{2P11} -Co ₁ - O _{1P12}	O _{1P12} -Co ₁ - O _{2P14}	O _{2P14} -Co ₁ - O _{1P11}	O _{3P14} -Co ₁ - O _{w1}	O _{1P11} -P ₁₁ - O _{3P11}	O _{2P11} -P ₁₁ - O _{3P11}	O _{3P11} -P ₁₁ - O _{1P11}	O _{1P11} -P ₁₁ - C _{1P11}	Co ₁ -O _{2P11} - Co ₃
TriVP-Co	-	83.3283	89.7990	97.3462	89.8233	174.1890	104.3710	104.5270	120.0220	104.5270	-
TetraVP-Co	89.8380	79.6550	93.2930	93.3780	87.8530	167.1820	89.6840	112.1970	114.7820	112.9190	-
VP-2Co	90.4810	82.0640	79.8100	96.4800	97.0500	160.7530	95.9770	99.0720	131.2550	97.4850	-
VP-7Co	92.1122	90.7880	85.3510	95.8420	87.8643	176.4930	107.2880	106.9400	107.2880	112.4900	129.3280
VP-9Co	93.5210	91.9532	86.0154	94.3015	87.7117	178.0210	92.3173	100.3810	100.4800	99.5901	129.5360
RX	93.8000	86.9000	90.6000	93.8000	87.4000	173.1000	108.1000	108.1000	109.9000	109.5000	123.3000

Table 3

Torsion angles for central Co²⁺ ion and attached vinylphosphonate atoms

Model/ Torsion angle	P ₁₃ - O _{3P13} - Co ₁ -O _{w1}	O _{w1} -Co ₁ - O _{2P11} -P ₁₁	O _{1P12} - Co ₁ - O _{3P11} - P ₁₃	O _{3P13} - Co ₁ - O _{2P11} -P ₁₁	O _{w1} - Co ₁ - O _{2P14} - Co ₇	O _{3P13} - Co ₁ - O _{2P14} - Co ₇	Co ₇ - O _{2P14} - Co ₁ - O _{1P11}	O _{1P11} - Co ₁ - O _{2P11} -P ₁₁	O _{1P12} - Co ₁ - O _{2P11} -P ₁₁	O _{2P14} -Co ₁ - O _{1P11} -P ₁₁	P ₁₁ - O _{1P11} - Co ₁ - O _{2P11}	P ₁₁ - O _{2P11} - O _{2P14}	C _{1P11} - P ₁₁ - O _{2P11} - Co ₁	C _{2P11} - C _{1P11} - P ₁₁ -Co ₁	C _{2P11} - C _{1P11} - P ₁₁ -O _{2P11}
TetraVP-Co	161.435	-78.172	107.78	109.807	-	-	-	-10.521	150.634	-153.867	10.521	-46.850	-127.593	120.204	-139.924
VP-2Co	169.059	-73.280	61.591	105.542	-	-	-	-17.019	160.141	-145.563	55.975	-45.563	-129.926	128.988	-127.482
VP-7Co	175.110	-107.195	45.767	75.542	160.775	-19.111	62.620	-13.377	170.099	-169.388	13.022	-55.283	-112.518	88.413	-152.167
VP-9Co	142.745	-115.613	47.087	64.031	156.725	-22.909	62.947	-21.924	158.823	-161.359	19.969	-97.969	-144.907	90.981	-126.172
RX	180.000	-92.100	52.600	84.100	161.900	-12.600	74.300	-3.900	174.400	-174.400	49.600	-49.600	-110.200	120.800	-120.800

Table 4

Net charges for central Co²⁺ ion and attached atoms

Model/Atom	Co ₁	O _{w1}	O _{1P11}	O _{2P11}	O _{1P12}	O _{3P13}	O _{2P14}	P ₁₁	O _{3P11}	C _{1P11}
TriVP-Co	0.1310	-	-0.6930	-0.6800	-0.5990	-0.6050	-0.6610	1.7990	-1.0250	-0.5410
TetraVP-Co	0.1710	-0.6790	-0.6080	-0.2230	-0.7310	-0.7740	-0.6440	1.7390	-1.0220	-0.7140
VP-2Co	0.1300	-0.2030	-0.6560	-0.5770	-0.7060	-0.7290	-0.6370	1.8420	-0.6860	-0.4070
VP-7Co	0.0590	-0.2870	-0.4420	-0.5430	-0.5560	-0.6720	-0.5390	1.4570	-0.6270	-0.3590
VP-9Co	-0.0700	-0.1480	-0.4810	-0.4600	-0.4580	-0.5250	-0.6440	1.2230	-0.6130	-0.4410

Table 5

Electronic properties

Model/Electronic properties	ΔH _{form}	v _{min}	v _{max}	ZPE	HOMO	LUMO	LUMO-HOMO
TriVP-Co	-732.3130	67.4600	3238.2600	95.2415	1.8548	12.3769	10.5221
TetraVP-Co	-2.1758	20.7900	3838.3200	1.4859	9.2486	14.7805	5.5319
VP-2Co	-1227.5290	12.3600	3785.0800	275.6630	5.8568	12.9034	7.0466
VP-7Co	-1578.0320	14.5600	3849.8700	608.1840	19.6643	22.8339	3.1696
VP-9Co	-2866.8920	17.3800	3873.0700	718.0381	19.6340	21.0990	1.4650

The LUMO-HOMO energetic difference decreases from the TriVP-Co to the VP-9Co reaching to a value of 1.465 eV. This very small difference can explain the semiconductive proprieties of VP-9Co metal organic network. The small difference allows one electron transition from the superior level into a conduction band (Fig. 3).

From the preliminary electrical conductivity studies of Co^{2+} vinylphosphonate, the compound was pressed between two 2 mm thickness, 2 cm diameter brass electrodes. After applying 10 minutes a 22 atm constant pressure, the final

compound thickness was 1.6 mm. The electrodes have been stimulated in 0-20V DC voltage range using a 1V step, at a constant temperature of 25°C. Current measurements for each voltage value indicate linear I-V dependence with a 4 k Ω slope, typical for semiconductors.²⁴

From the orbital analysis it can be observed that the highest occupied levels are positive and the lowest occupied levels are negative. For each model the first negative level is 36 for TriVP-Co, 29 for TetraVP-Co, 73 for VP-2Co, 63 for VP-7Co and 73 for VP-9Co.

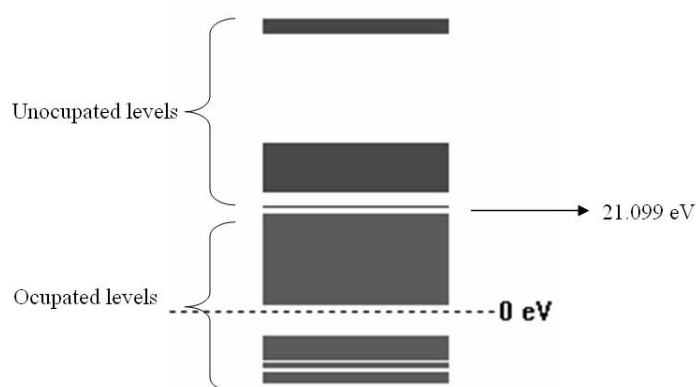
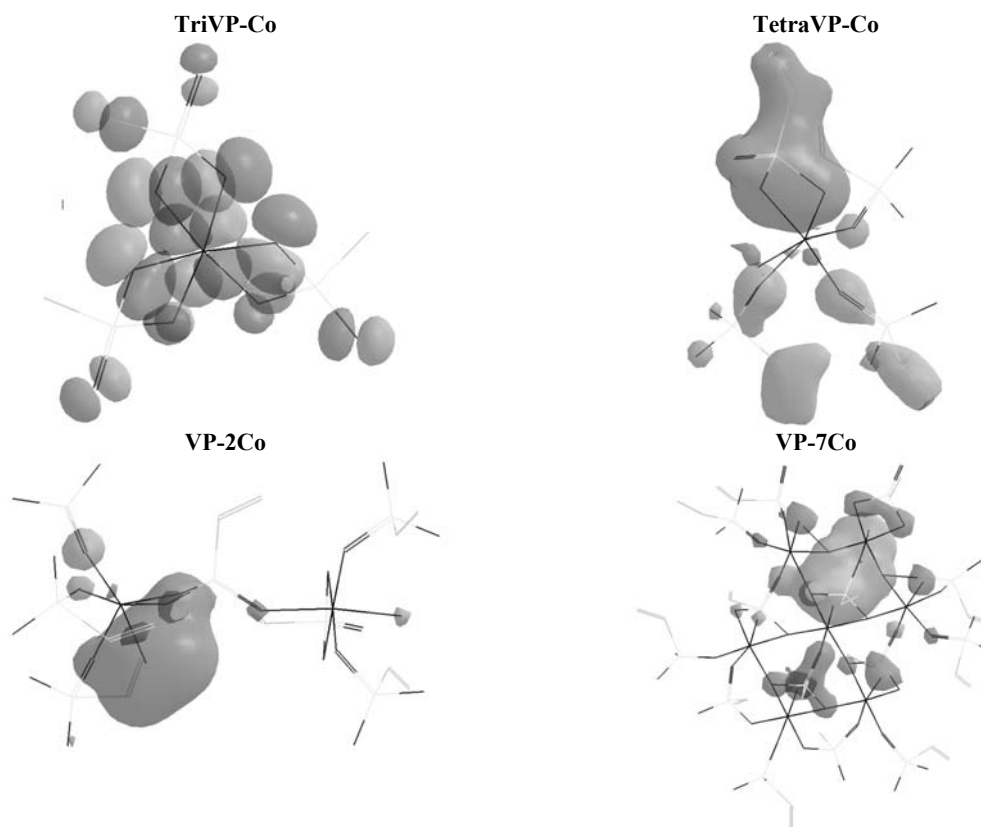


Fig. 3 – The VP-9Co orbital distribution.



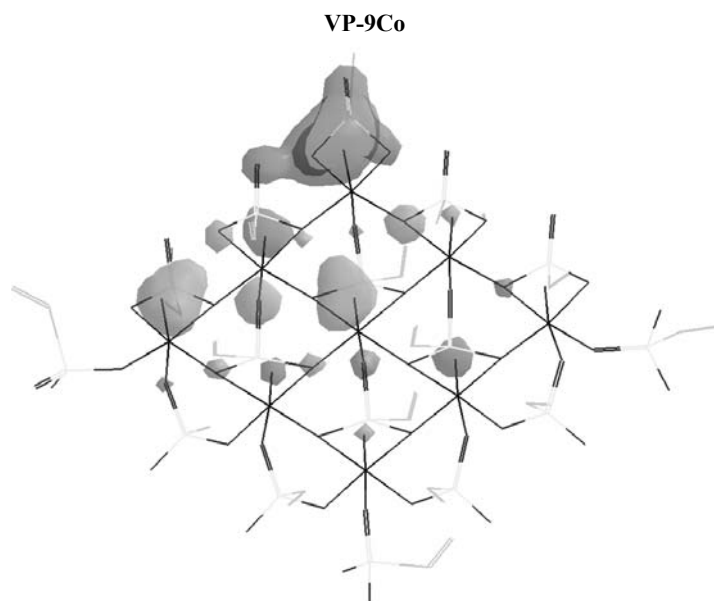


Fig. 4 – The HOMO orbital components.

From the orbital components analysis (Fig. 4) it can be observed that from VP-2Co and TetraVP-Co models in HOMO level are involved σ bonds of the organic functionalities. The d orbitals are implied in HOMO level only in case of TriVP-Co model.

From orbital analysis can be observed that d orbitals of Co^{2+} ions are involved in chemical bonds at different levels (Fig. 5). For the TetraVP-Co compound the first energetic level in which involves the d orbital appears at 72 level. For the VP-2Co compound the first energetic level in which involves the d orbital appears at 89 level. For the VP-7Co compound the first energetic level in which involves the d orbital of all cobalt ions appears at 161 level. For the VP-9Co compound the first energetic level in which involves the d orbital of all cobalt ions appears at 314 level, the central cobalt ion participate with the d_{z^2} orbital.

CONCLUSION

The analysis of the geometrical data by PM3 semi-empirical method gives shorter bond lengths than the experimental data. The bond angles are similar with the experimental values and torsion angles are smaller or comparable with those experimental.

From charge densities values the negative value of the central Co^{2+} ion from VP-Co7 and VP-Co9 network can be noticed due to the charge transfer from oxygen atom to central ion. This negative value can explain the gas storage, heterogeneous catalysis, separation, ion exchange, magnetism, sensors properties of the Co^{2+} vinylphosphonate.

The calculated thermodynamic data explain the metal organic network formation tendency.

From the orbital analysis it can be observed that the highest occupied levels are positive and the lowest occupied levels are negative. The d orbitals are implied in HOMO level only in case of TriVP-Co model. For all the other models in HOMO level are involved σ bonds of the organic functionalities (see supplementary materials).

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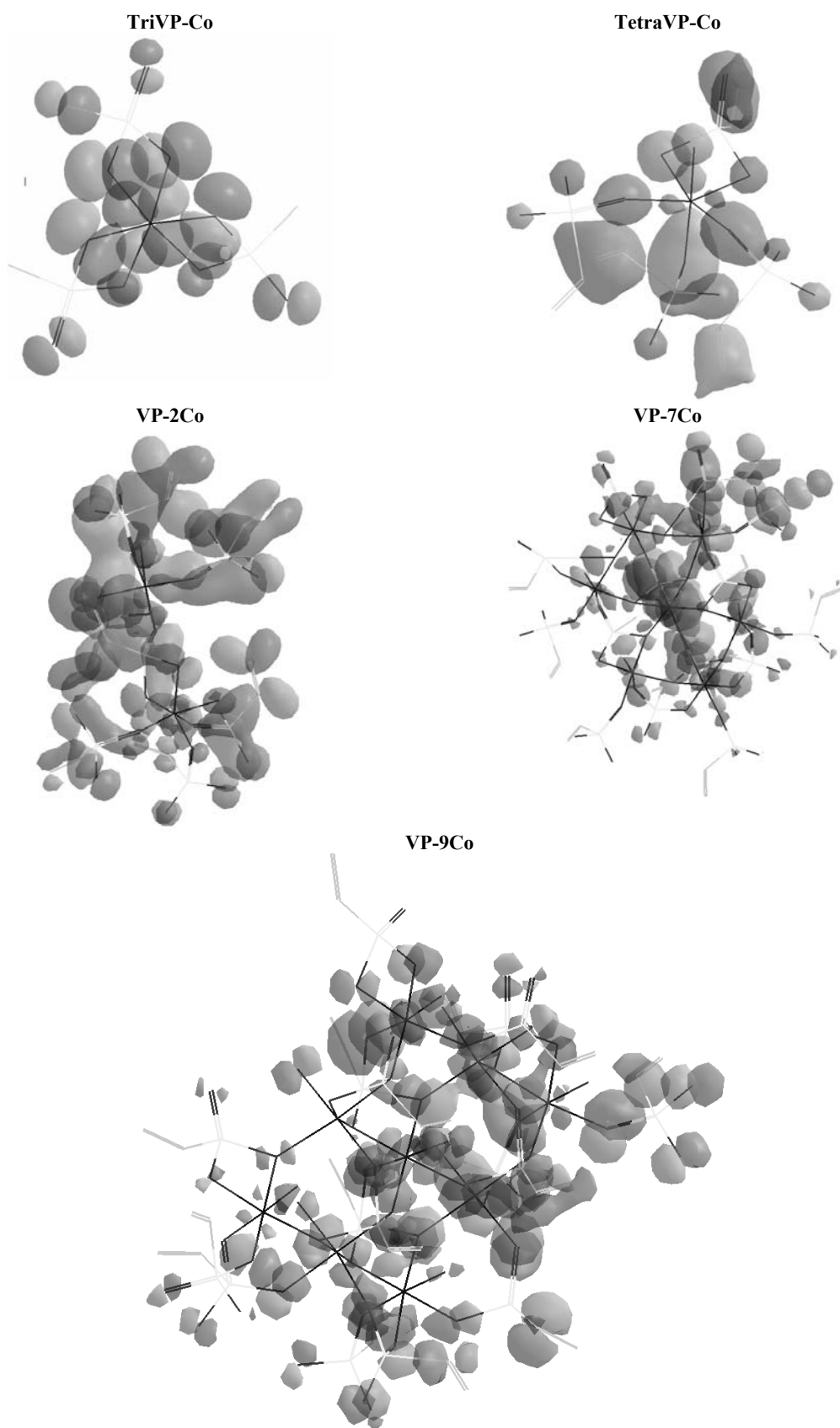


Fig. 5 – First energetic level in which the Co²⁺ central ion have implied a d orbital.

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