

## POSSIBLE ORGANOMETALLIC STRUCTURES IN THE COAL SUBSTANCE OF CZECH COALS

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*(Received July 2003, accepted October 2003)*

### ABSTRACT

Modes of occurrence of metal elements in coal substance of coals from Ostrava-Karviná District and North Bohemia Basin and the element affinities to organic and mineral part of coal are evaluated. On this basis and by means of described reactions of metals with organic structures the possible organometallic complexes are presented. As other types carbon-metal and metal carboxyl compounds are considered. In the case of metal phenol structures with oxygen-metal bond a model compound is considered and bonding energies are calculated and discussed. On this basis the metal phenol structures in coal substance are suggested.

**KEYWORDS:** coal, organometallic compounds, complexes

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### INTRODUCTION

The bonding of metals in the organic structure of coal, the course of coalification process and the formation of organic structures with metals was influenced by the mineral components of coal. The mineral substances contained in coal represent an inhomogeneous mixture of chemical compounds. The prevailing part of mineral substances represents an independent, both physically and chemically distinct phase and forms particles of various sizes, ranging from microscopic ones to those with the size of several centimeters or even larger ones. Therefore, from the point of view of quantity, only a smaller part of inorganic elements is chemically bound in organic structures. Because the content in metals bound in the organic substance of coal is relatively low, up to now, organic structures containing metals were presented very rarely and ideas about the organic structures containing metals are very vague only.

Environmentally important part of the coal matter is represented by the trace elements – heavy metals and halogens. The trace elements are distributed between the organic and the mineral part of coal according to the degree of their association with the respective part, expressed numerically by their affinity. Many of the metal elements are considered to be toxic for the environment. During combustion and carbonization mainly total concentration and distribution of metal trace elements between mineral and organic part of coal influence their mobilization into the environment (Spears and Martinez-Taragona, 1993; Swaine and Goodarzi, 1995). Therefore, the detection of their bonds in coal is important from both the structural and the technological point of view. It is also important for

mineral processing of coal. The bonds of metal elements in coal are investigated at present especially in connection with the emissions of toxic elements during coal combustion.

The aim of this work is to estimate forms of organometallic compounds in the Czech coals from Ostrava-Karviná District (OKD) and North Bohemia Basin (NBB), hard coal and brown coal, resp.

### ORIGIN OF INORGANIC ELEMENTS IN COAL SUBSTANCE

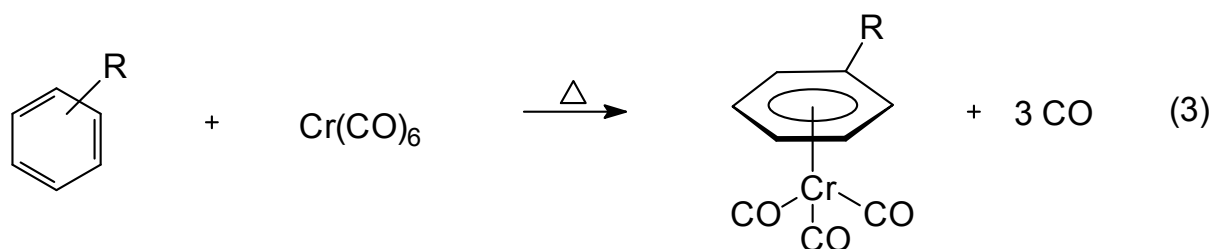
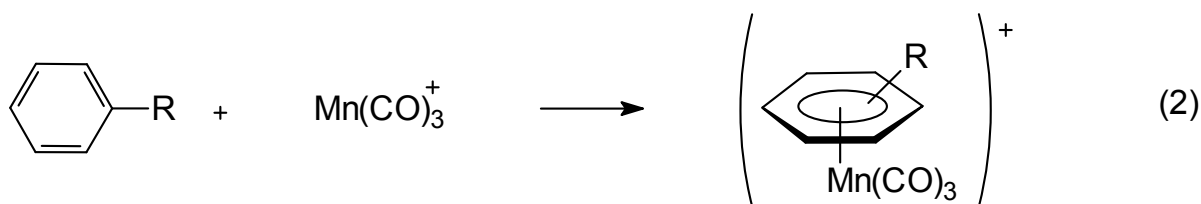
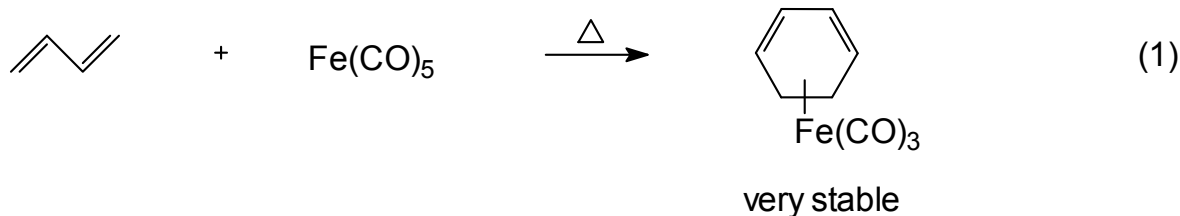
The mineral substances contained in coal originate from the mineral components of the original coal-forming plants and from the mineral substances accumulated in the coal during all stages of the coalification process. For this reason, two types of inorganic compounds may be discerned in the coal: those integrally linked with organic structures by chemical bonds and those of external origin which may be rather easily separated from coal. The existence of inorganic substances and inorganic elements bound by chemical bonds to the organic structures is – apart from other evidence – indicated by the fact that strong mineral acids do not dissolve completely the mineral matter even during high-temperature extraction. Thus the inorganic compounds/elements are linked with the coal substance only by rather strong bonds (Jasienko, 1995).

Inorganic elements chemically bound to the coal substance originate partly from the original coal-forming plants. The accumulation of the mineral components takes place already during the vegetation stage of the plants. An important role in the life of the plants is played by iron as the lack of it leads to the

prevention of chlorophyll formation. The leaves exhibit a considerable content in calcium, magnesium and sulfur, the blossoms contain potassium and phosphorus, the seeds contain phosphorus and an amount of inorganic elements (Jasienko, 1995). In comparison with the major elements, calcium, magnesium, iron and potassium, a very important role in the life of plants is played by trace elements which are present in very low quantities, namely boron, arsenic, germanium, cobalt, beryllium and iodine. Bulbs, seeds and fruits contain a considerable amount of inorganic substances, up to 4 wt.-%. Woods contain 0.2 – 0.4 wt.-% of mineral substances. In the decomposition of plant material, chlorophyll and amino acids having nitrogen as the donor element were complex-forming agents for metal nitrogen complexes with e.g. Be, Co, Cu, Ga, Ge, Ni, Sb, V and Zn (Zubowicz et al., 1966).

During coalification process the vegetable matter was transformed to coal matter. In this process, the deposits of inorganic materials in the peat bogs were submitted to the influence of humic acids and decomposition products of the vegetable matter: carbon dioxide, sulfane, ammonia and hydrogen. Clay minerals (e.g. of the kaolinite group) were transformed into amorphous materials (allophanes), which mixed with colloid solutions and organic gels. At elevated temperatures (150 – 200 °C) in the presence of potassium illite was formed from the colloid solutions. Pyroxenes

(e.g.  $\text{MgSiO}_3\text{-FeSiO}_3$ ,  $\text{Ca}_2\text{Si}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6\text{-Fe}_2\text{Si}_2\text{O}_6$ ) amphiboles (e.g.  $\text{Ca}_2(\text{Mg,Fe})_5[\text{Si}_4\text{O}_{11}](\text{OH})_2$ ) and serpentines ( $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$ ) also became components of colloid solutions and organic gels. By the effect of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , formed from the organic materials, these gels gave origin to carbonates of calcium, magnesium and iron as well as to sulfides of iron. The amorphous carbonates were transformed into crystalline forms as calcite, dolomite, ankerite and siderite. In case that  $\text{CO}_2$  or  $\text{H}_2\text{S}$  were not present in a sufficient quantity, the ions of Ca, Mg and Fe reacted with the organic structures of coal and structures with metals – humates and oxalates of calcium, magnesium, iron, manganese and zinc – were formed (Jasienko, 1995). But also carbonyls of Fe ( $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$ ) and Mn ( $\text{Mn}(\text{CO})_3$ ) could be formed in these gels (by the effect of CO formed from the organic materials) and subsequently, by reactions of them with unsaturated unstable hydrocarbons formed during coalification process and simple aromatics of coal, metal complexes as diene iron tricarbonyl complex (eq. 1) and arene manganese tricarbonyl complex (eq. 2). Also chromium can form  $\text{Cr}(\text{CO})_6$  and arene chromium tricarbonyl complex (eq. 3). (Reactions (1), (2) and (3) were described in connection with methods of synthesis of organometallic compounds by means of transition metals (Hegedus, 1999; Gibson et al., 1997)). Further, metal phenol structures were formed (Swaine, 1990).



**AFFINITY OF INORGANIC ELEMENTS TO COAL SUBSTANCE**

Besides the major inorganic elements (Si, Ti, Al, Fe, Ca, K and S) coal contains also trace elements distributed between the mineral and organic part of coal. Zubowicz et al. give for the various trace elements different affinities to the organic matter of coal. According to the authors there exist a constant order of elements with regard to the decreasing affinity to organic substances: Ge > Be > Ga > Ti > B > Y > Ni > Cr > Co > Mo > Cu > Sn > La > Zn (Zubowicz, Stadnichenko and Sheffey, 1960). Simultaneously, the content in trace elements in coal decreases with increasing coal range. Xiaohua et al. consider Ge and Be as elements with a considerable affinity to the coal organic matter (Xiaohua Lu, Hancai Zeng, Tao Xu and Rong Yan, 1995).

By means of a new model for the calculation of the affinities of trace elements to the organic substance (OEA) and to the mineral part (IEA) of coal (Klika, Mrozek and Kolomazník, 1999) the affinities of both major and trace elements contained in Ostrava-Karviná District and North Bohemia Basin coals were calculated (Klika and Kolomazník, 2000). On

this basis, regarding work (Bouška, Pešek and Sýkorová, 2000), the metal elements can be divided into three groups:

- metals with prevailing affinity to the mineral part: Major elements: K, Na and Ti, elements: As, Cd, Cs and Rb, further Ag, Hg, Li, Se, Th;
- trace metals with prevailing affinity to the organic part: major elements: -, trace elements: Cr, Ga, La, Ni, Pb, Sb, Sn, V and W, further Be, Ge, Mo;
- metals with variable affinity: major elements: Al, Ca, Fe, Mg, trace elements: Ba, Ce, Co, Cu, Mn, Nb, Sr, Tl, Y, Zn, Zr, further Hf.

From the calculation of the affinities of metals to the organic and mineral part of Czech coals (5 samples of hard coal and 6 samples of brown coal) it follows that from 24 determined metal trace elements 17 exhibit a significantly high affinity to the organic substance (OEA more than 70 %) (Tab. 1). As metals as e.g. Ba, Ce, La, Mn, Sr, W, Y and Zn have a high

**Table 1** The affinities of trace elements of NBB coal (brown coal) and OKD coal (hard coal) to the organic substance (OEA – organic element affinity) and to the mineral part (IEA – inorganic element affinity) (Klika and Kolomazník, 2000, adapted)

Element	OEA (%)	IEA (%)	Element	OEA (%)	IEA (%)
brown coal NBB			hard coal OKD		
As	9.6	90.4	<b>Ag</b>	50.4	-
<b>Ba</b>	<b>90.9</b>	9.1	Ba	45.6	54.4
Cd	21.0	79.0	Cd	30.1	69.9
<b>Ce</b>	<b>81.0</b>	-	Ce	26.0	74.0
Co	53.7	46.3	<b>Co</b>	<b>92.6</b>	7.4
<b>Cr</b>	<b>71.5</b>	28.5	<b>Cr</b>	<b>86.9</b>	13.1
Cs	2.3	97.7	Cs	-	-
Cu	19.0	81.0	<b>Cu</b>	<b>72.2</b>	27.8
<b>Ga</b>	<b>73.5</b>	-	<b>Ga</b>	<b>94.8</b>	5.2
<b>La</b>	<b>80.5</b>	19.5	La	57.2	42.8
<b>Mn</b>	<b>80.5</b>	19.5	Mn	4.6	95.4
Nb	23.0	77.0	<b>Nb</b>	<b>88.9</b>	11.1
Ni	55.1	44.9	<b>Ni</b>	<b>94.4</b>	5.6
Pb	62.3	-	<b>Pb</b>	<b>74.1</b>	25.9
Rb	36.3	63.7	Rb	41.5	58.5
<b>Sb</b>	<b>84.4</b>	-	<b>Sb</b>	<b>90.5</b>	9.5
<b>W</b>	<b>85.3</b>	14.7	<b>Sn</b>	<b>88.2</b>	11.8
<b>Sr</b>	<b>90.4</b>	-	Sr	41.0	59.0
Tl	26.0	74.0	Tl	68.5	31.5
<b>V</b>	<b>77.5</b>	22.5	<b>V</b>	<b>92.5</b>	7.5
<b>Y</b>	<b>76.7</b>	-	Y	35.9	64.1
<b>Zn</b>	<b>72.0</b>	-	Zn	48.3	51.7
Zr	52.6	47.4	<b>Zr</b>	<b>61.9</b>	38.1

OEA to brown coal substance an association with COOH and phenolic OH groups can be considered, namely with Ba, Mn, Sr and Zn. Moreover, with Mn above-mentioned arene manganese tricarbonyl complex and with Zn the Zn-porphyrine complex can be expected. Also with W organometallic complexes were suggested (Eskenazi, 1977). Because of a high OEA to hard coal substance in the case of Co, Cu, Nb, Ni, Pb and Sn was observed, the metal porphyrins can be expected, namely at Co, Cu and Ni. Moreover, the Cu-phenols can be considered with Cu. High OEA values to both brown and hard coal substance at Cr, Ga, Sb, and V mean that arene chromium tricarbonyl complex, Ga- and V- porphyrins or vanadyl porphyrins and Ga-phenols can be formed.

Bouška, Pešek and Sýkorová, 2000, declare for a number of elements their presence in the form of metal-phenols and metal-carboxyls. For Ge an etheric form Ge-O-Ge and for Be, Cu, Ge, U and W the formation of organic complex compounds are suggested. A strong ability to form a complex is stated especially in case of Cu. In connection with the existence of complex compounds it is important that complexes of porphyrine with central atoms of Mn, Ni and V are mentioned. Also the importance of water in the constitution of the organic substance must be considered – a frequent occurrence of water molecules as ligands.

Beside that in coal also the presence of compounds in which the metal is directly bound to carbon must be taken into account. With the metals of the main subgroups of the periodic system (Li, Na, Al, Ga, Ge, Sn, Pb, Sb) the metal carbon compounds are formed easily and they are very stable. The same is valid for the metal carbon compounds of Zn, Cd and Hg. A number of metal carbon compounds with transition d-elements exists, however, they are less stable. Besides that stable iron complexes of the ferrocene type are known. Formation of ferrocenes in coal can be as follows. Non-conjugated dienes (formed during coalification process) often rearrange to give conjugate diene complexes in the presence of  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}_2(\text{CO})_9$  (Hegedus, 1999). These iron tricarbonyl complexes of dienes (see reaction (1)) are stable and can undergo reactions with C-C bond formations contained in coal substance. As result, ferrocene can form in coal substance.

From this outline of the formation of organic structures with metals, the evaluation of elements from the point of view of their affinity and the basic structural considerations it follows that in coal five types can exist:

- porphyrine complexes with metal-nitrogen bonds,
- arene metal tricarbonyl complexes,
- metal carbon compounds (R-Me) and ferrocene complexes,
- oxalates and humates with metal carboxyl formations ( $\text{R}_m(\text{COO})_n\text{Me}$ ),
- metal phenols with metal-oxygen bonds.

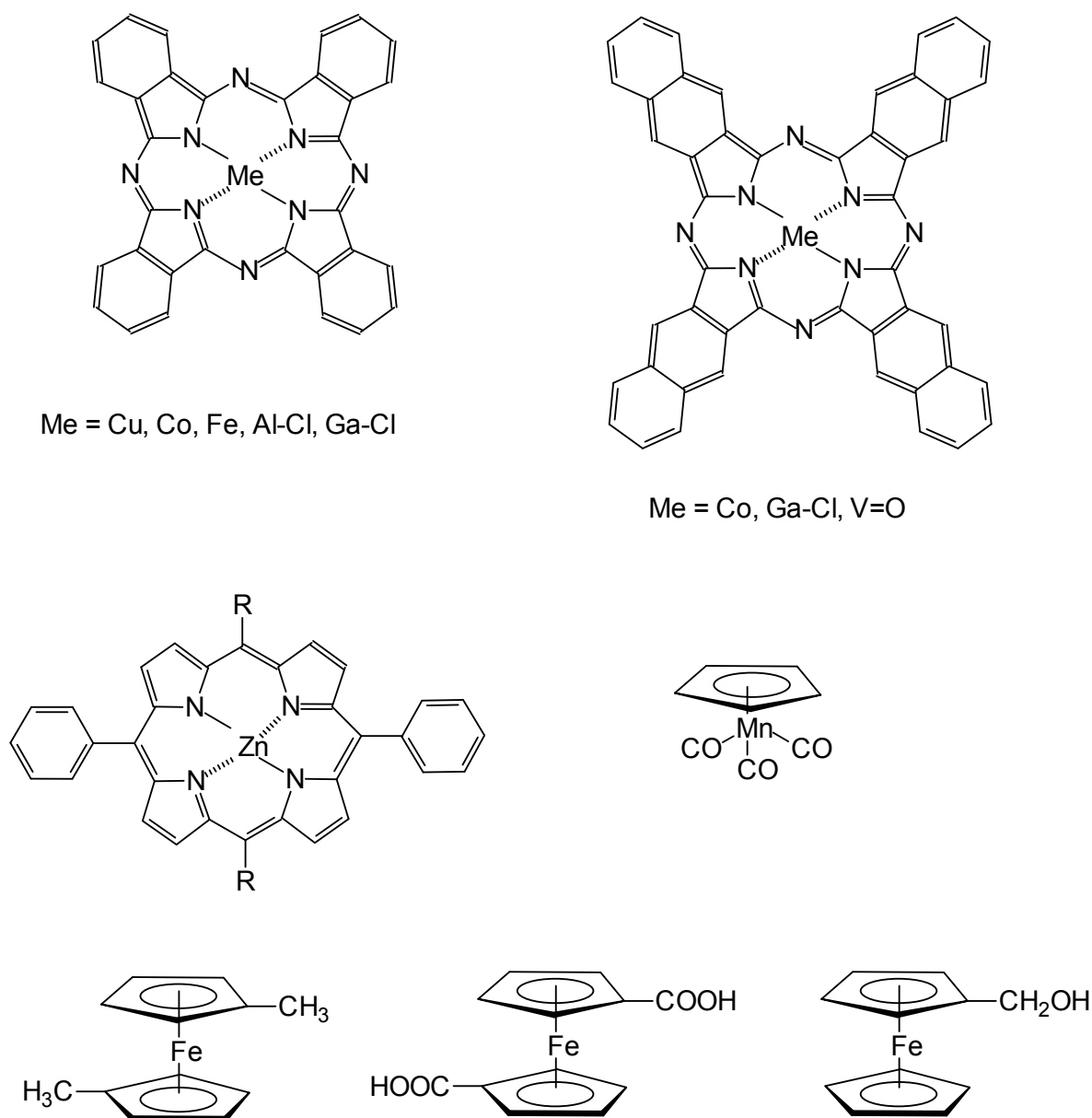
Beside complexes in equations (1), (2) and (3), examples of organometallic complex structures are given in Fig. 1. Model of metal phenol structure will be discussed later.

#### MODEL OF METAL PHENOL STRUCTURE

Metal-containing phenolic structures in coal can be quite different from phenolic compounds known up to now as they have been formed during long-time periods, under variable, higher temperatures and high pressures.

As it has been already mentioned, organic structures of coal containing metals have been described up to now only to a negligible extent. The only model which takes into account the metal-oxygen bond in phenolic like structure and which represent a basis of the calculations of bonding energies is the model suggested by Spiro and Kosky (Spiro and Kosky, 1982). As preliminary calculations have shown excessive energies of the suggested molecule, the model was reduced and variants of this reduced model were tested. Energetically acceptable values were obtained with the model presented in Fig. 2. In this model atoms of metals (Me) were altered and the bonding energies were calculated. For this calculation the software SPARTAN was used which was outlined for the calculations of the energies of organometallic molecules. This software was used for calculations by the method of molecular mechanics SYBYL. The results are summed up in Table 2. For easier comparison the bonding energies are given in hartree units ( $2623 \text{ kJ.mole}^{-1}$ ). The calculation was performed in such a way the larger is the hartree number, the more stable is the bond. On the basis of the above given affinity data (Table 1) and considerations, from the trace metal elements Hg, As, Co, Cu and Mn were chosen for structural considerations and calculations of the bonding energy. From the elements with a very low affinity to the organic substance Hg was chosen (OEA of which is generally very low). According to the data in Table 1 As as well as Mn were further selected. Arsenic was considered as an element with a low OEA both to the brown and hard coal substance. Mn was considered as an element with a high OEA to brown coal substance and low OEA to hard coal substance. On contrary Cu was chosen as an element with a high OEA to hard coal substance and rather low OEA to brown coal substance. From the elements with a higher or high OEA to both brown and hard coal substance Co were chosen.

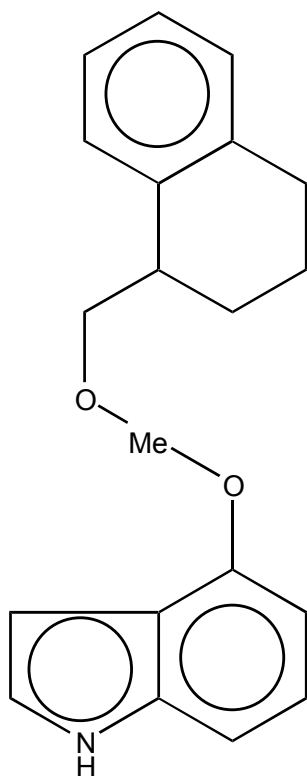
From Table 2 it is evident that Hg as an element with low OEA exhibits the lowest value of bonding energy. Due to this and due to very low OEA both to brown and hard coal substance the considered structure cannot be taken into account with Hg. Further element, As, exhibits a higher bonding energy in comparison with Hg. It means that As can exist in the phenolic structure, but due to low OEA with both brown and hard coal it is not probable. Therefore another structure must be considered. An important



**Fig. 1** Possible complex structures in coal substance

**Table 2** OEA of metals and their bonding energies ( $E_{\text{bond}}$ )

Element	OEA (brown coal) (%)	OEA (hard coal) (%)	$E_{\text{bond}}$ (hartree)
Hg	very low <sup>a</sup>	very low <sup>a</sup>	12.7
As	9.6	low <sup>a</sup>	18
Mn	80.5	4.6	26.2
Cu	19.0	72.2	19.0
Co	53.7	92.6	19.2



**Fig. 2** Model for the calculation of the bonding energy of metals in the phenolic like structure of coal substance

work dealing with the structural expression of the organic bond of arsenic in bituminous coal is the paper of Chinese authors (Zhao F., Ren Deyi, Zheng B., Hu T., Liu T., 1998) which on the basis of the analysis of coal substance containing up to 3.2 wt.-% of arsenic (determined by neutron activation analysis with the XAFS and XANES methods) presents arsenite ( $\text{AsO}_3^{3-}$ ) or arsenate ( $\text{AsO}_4^{3-}$ ) anions as the form of As occurrence in the organic substance of the investigated anthracitic coal (from the province Guishou, China). Another Chinese work (Ding Z., Zheng B., Zhang J., 1999) prefers arsenate ions and considers them to be the dominant form.

Further chosen elements, Cu and Co, exhibit a higher bonding energy in comparison with As. It means that they can exist in the considered phenolic structure, moreover, due to high OEA with hard coal substance and higher OEA with brown coal substance (in the case of Co) or not very low one (in the case of Cu) it is probable.

In the case of Mn the highest bonding energy among the investigated elements was found (for brown coal). Because of very low OEA to hard coal substance the structure in question with Mn can exist only in brown coal. From the value of the bonding energy of Mn and its affinity to the organic substance of brown coal it is evident that Mn is able to form a very stable bond in phenolic structures.

We may say that the model considered is realistic. However, it seems that metal elements form in the structure of coal or of coal fractions autonomous organometallic units with a MW similar to that of compounds of the coal low-molecular mobile phase which is non-covalently bound to the coal polymers or macromolecules. Units consisting of two polymers bound covalently by a metal atom had incalculable energies and molecules consisting only of two three-rings clusters connected by a metal atom had a markedly high energetic content which indicates their instability.

#### CONCLUSION REMARKS

Many inorganic elements of Czech coals are organically bound in organometallic compounds. As OEA values proved, with Ba, Ce, La, Mn, Sr, Y and Zn organometallic bonds formed in brown coal were gradually broken down during coalification. Due to this, OEA 80.5 – 90.9 % for brown coal substance decreased up to 4.6 – 57.2 % for hard coal substance. But in the case of Co, Cr, Cu, Ga Nb, Ni, Pb, Sb and V the OEA values for hard coal substance were higher or significantly higher in comparison with them for brown coal substance. It means that our images about formation and behaviour of organometallics during coalification are rather schematic. As it is quite clear that the fundamental process of the element concentration in coal was sorption and the decisive factors of this process are known, it is not clear which reaction conditions of complexes formation ruled and which reaction mechanisms led to organometallic compounds in coal. In the next research as a first step isolation and description of them will be carried out. In the first place, mineral substances have to be separated from coal. The present wet procedures using strong acids are unsuitable as the organic and organometallic structures can be damaged in this way. It seems that physical separation and extraction with organic liquids are a better procedures.

#### ACKNOWLEDGEMENT

The Grant Agency of the Czech Republic supported this work as the grant project No. 105/02/0163.

#### REFERENCES

- Bouška, V., Pešek, J. and Sýkorová, I.: 2000, *Acta Montana, Series B*, No.10(117), 53.
- Ding, Z., Zheng, B. and Zhang, J.: 1999, *Science in China, Series D*, 42/6, 655.
- Eskenazi, G.: 1977, *Chem. Geol.*, 19, 153-159.
- Gibson, E.S., 1997: *Transition Metals in Organic Synthesis*, Oxford University Press, New York.
- Hegedus, L.S.: 1999, *Transition Metals in the Synthesis of Complex Organic Molecules*, 2<sup>nd</sup> Edition, University Science Books, Sausalito, California.

- Klika, Z., Mrozek, S. and Kolomazník, I.: 1999, *Uhlí-Rudy-Geologický průzkum* 6, 9.
- Klika, Z. and Kolomazník, I.: 2000, *Fuel* 79, 659.
- Spartan Plus PC Wawefunction, Inc.: 1999, CA/USA, Irvine.
- Spears, D.A. and Martinez-Taragona, M.R.: 1993, *Int. J. Coal Geol.* 22, 1.
- Spiro, C.L. and Kosky, P.G.: 1982, *Fuel* 61, 1080.
- Swaine D.J.: 1990, *Trace elements in coal*, Butterworths, London.
- Swaine, D.J. and Goodarzi, F.: 1995, *Environmental aspects of trace elements in coal*, Kluwer Academic, London.
- Xiaohua, L., Hancai, Z., Tao, X. and Rong, Y.: 1995, *Fuel* 74, 1382.
- Zhao, F., Ren, Deyi, Zheng, B., Hu, T. and Liu, T.: 1998, *Chinese Science Bulletin* 43/19, 1660.
- Zubowicz, P., Stadnichenko, T.M. and Sheffey, N.B.: 1960, *Comparative abundance of the minor elements in coals from different parts of the United States*, U.S. Geol. Survey Prof. Paper 400 B, pp.84-87.