

TEMPERATURE CONDITIONS OF COAL FORMATION

Pavel STRAKA * and Jana NÁHUNKOVÁ

*Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, v.v.i.,
V Holešovičkách 41, 182 09 Prague, Czech Republic*

**Corresponding author's e-mail: straka@irms.cas.cz*

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ABSTRACT

In the frame of advanced studies of coal structure the temperature conditions of coal origin were investigated through thermal stability of aluminum complexes in coal substance. These compounds were discovered by solid-state nuclear magnetic resonance measurements of ^{27}Al as a part of coal substance closely bonded to organic mass of coal. In obtained spectra, Al-hexaphenoxide and Al-tetrahydroxy-diphenoxide complexes were identified. These complexes were further prepared and their thermal stability tested by thermal analysis method. It was found that a) they can originate under room temperature and atmospheric pressure and b) they are thermally stable only up to approximately 85 or 95 °C. As both Al-hexaphenoxide and Al-tetrahydroxy-diphenoxide complexes are the integrated constituents of coal substance it can be deduced that, in the beginning, coal was formed under very mild thermal conditions. As investigated materials, coals and clays from the Czech basins and gagatite from Poland were measured.

KEYWORDS: aluminum complexes, coal, NMR, thermal analysis

1. INTRODUCTION

Thermal conditions of coal origination are still yet intricate and our knowledge in this area lacks clarity. As thermal gradient in the beginning of coal formation is not known a suitable indicator was searched. After preliminary studies (Straka and Klika, 2004) the aluminum complexes appear as the suitable thermal indicator for several reasons. Firstly, aluminum is strongly capable of forming complexes with different and characteristic physical and thermal properties (CRC Handbook of Chemistry and Physics, Section 4, 1993-1994), further, formation of Al-hydroxy-humate complexes was described (Violante et al., 1999); secondly, concentrations of Al in bituminous coals and lignites are often quite high, 0.5–1 %, moreover, aluminum is one of the elements with a high affinity to coal substance (Klika and Kolomazník, 2000); thirdly, the magnetic properties of Al-atom (CRC Handbook of Chemistry and Physics, Section 9, 1993-1994) make possible the measurements of characteristic chemical shifts in dependence on the chemical environment of the central Al-atom in complexes, which is crucial for the identification of Al-complexes by the solid-state NMR method. Therefore, if the presence of the aluminum complexes/organo-complexes in coal substance and thermal conditions for their formation/decomposition are ascertained and described, it may clarify the temperature conditions of coal formation at the beginning of its history, in other word, understanding of thermal stability namely of organo-aluminum

complexes may contribute to a new perception of the coal formation in early phases.

The aim of this work is to describe the aluminum complexes discovered in the organic substance of bituminous coals and lignites and quantify their thermal properties. On this basis the temperature conditions of coal origination express.

2. EXPERIMENTAL

Low-ash samples of bituminous coals from the Czech part of the Upper Silesian Basin, (Ostrava-Karviná District), lignites from the Czech Republic (Sokolov, North Bohemian and South-Moravian Lignite Basins) and gagatite from Poland as Cetraceous Period coal were examined.

Aluminum complexes in coal samples were identified by solid-state nuclear magnetic resonance of ^{27}Al (^{27}Al MAS NMR method) on Bruker Avance 500 spectrometer (Bruker, Rheinstetten). In all the cases, aluminum hexa-coordinated with oxygen was identified in the ^{27}Al MAS NMR spectra, as signals at 13.5–15 ppm or 3.5–5 ppm, also at both 13.5–15 and 3.5–5 ppm were found. In one case, with the Lazy coal, also signal at 71.9 ppm was found. Standards for identification of Al-complexes were as follows:

- aluminum phenoxide (Sigma Aldrich);
- $\alpha\text{-Al}_2\text{O}_3$ (Sigma Aldrich);
- Al-hexaphenoxide complex, prepared by extraction with ethanol from the Al-phenoxide

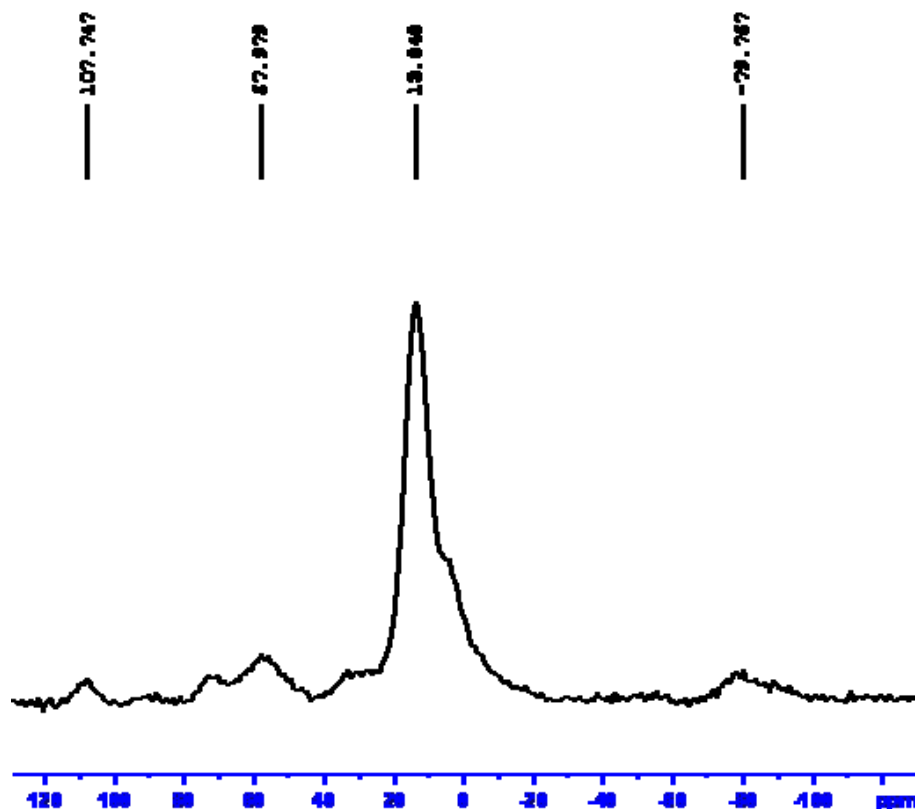


Fig. 1 ^{27}Al MAS NMR spectrum of the Staříč coal.

phtalocyanine commercial mixture (Sigma Aldrich) as $\text{H}_3[\text{Al}(\text{C}_6\text{H}_5\text{O})_6]$;

- $\gamma\text{-Al}(\text{OH})_3$, gibbsite, proven by XRD method (Lachema Brno);
- Kaolin Sedlec IA Standard (Sedlecký kaolin AS, Czech Rep.);
- Al-tetrahydroxy-diphenoxide, prepared as $\text{H}_3[\text{Al}(\text{OH})_4(\text{C}_6\text{H}_5\text{O})_2]$ by long-term reaction (20 months) of AlCl_3 with phenol in water solution;
- blackterry (black-colored clay) from the Nová Ves locality, Cheb basin;
- argil (white-colored clay) from the same locality.

For organic elemental analyses of complexes in question the Flash 1112 EA analyzer (Thermo Finnigan, Rodano) was used; for analyses of aluminum the XRF spectrometer EDS Spectro X-Lab (SPECTRO Analytical Instruments, Kleve) was used.

Thermal stability of identified and prepared complexes was tested by thermogravimetric methods (TG and DTG) on SETARAM Setsys Evolution 18 analyzer (SETARAM, Caluire).

3. RESULTS AND DISCUSSION

In obtained ^{27}Al MAS NMR spectra of coal samples the chemical shifts at 13.5–15 and 3.5–5 ppm (Figs. 1 and 2, respectively), also at both 13.5–15 and 3.5–5 ppm (Figs. 3 and 4), were found. These shifts are typical for hexa-coordination of aluminum to oxygen (Duxson et al., 2007). Moreover, the found chemical shifts corresponded with those obtained for the aluminum-hexaphenoxide and the aluminum-tetrahydroxy-diphenoxide standards (Table 1). From Table 1 it follows that by comparison with a scale of standards two types of complexes can be established: a) with the chemical shift at 13.5–15 ppm belonging to an Al-hexaphenoxide complex $\text{H}_3[\text{Al}(\text{C}_6\text{H}_5\text{O})_6]$ while b) at 3.5–5 ppm to an Al-tetrahydroxy-diphenoxide complex $\text{H}_3[\text{Al}(\text{OH})_4(\text{C}_6\text{H}_5\text{O})_2]$. An overview of the chemical shifts ascertained with the coals investigated is summarized in Table 2.

It arises from an overview of the standards, their signals in the spectrum and their description (Table 1) that the first type complex, with the signal in the spectrum at 13.5–15 ppm, has 6 phenoxide ligands arranged into deformed octahedron in molecule, like in $\alpha\text{-Al}_2\text{O}_3$ as described in monograph (Gažo, 1981), whereas the second type, with signal at 3.5–5 ppm,

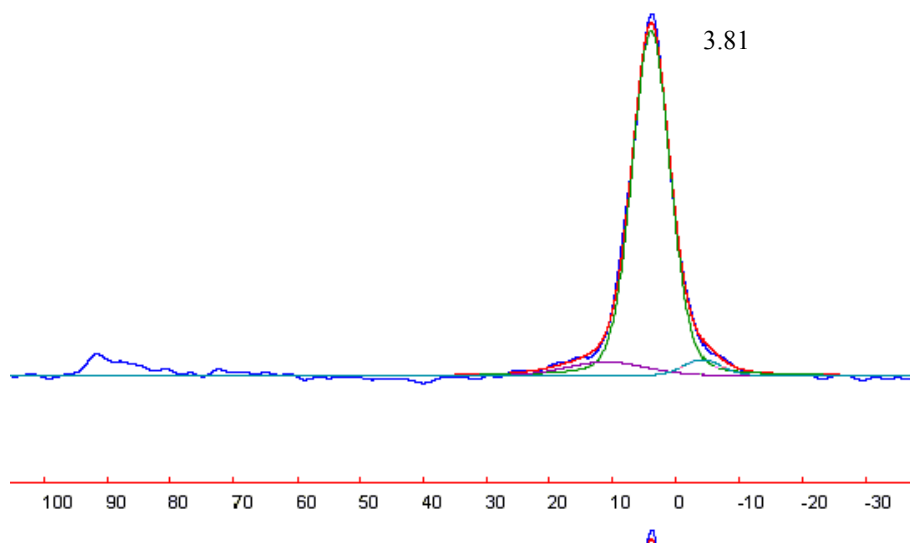


Fig. 2 ^{27}Al MAS NMR spectrum of the Jiří lignite.

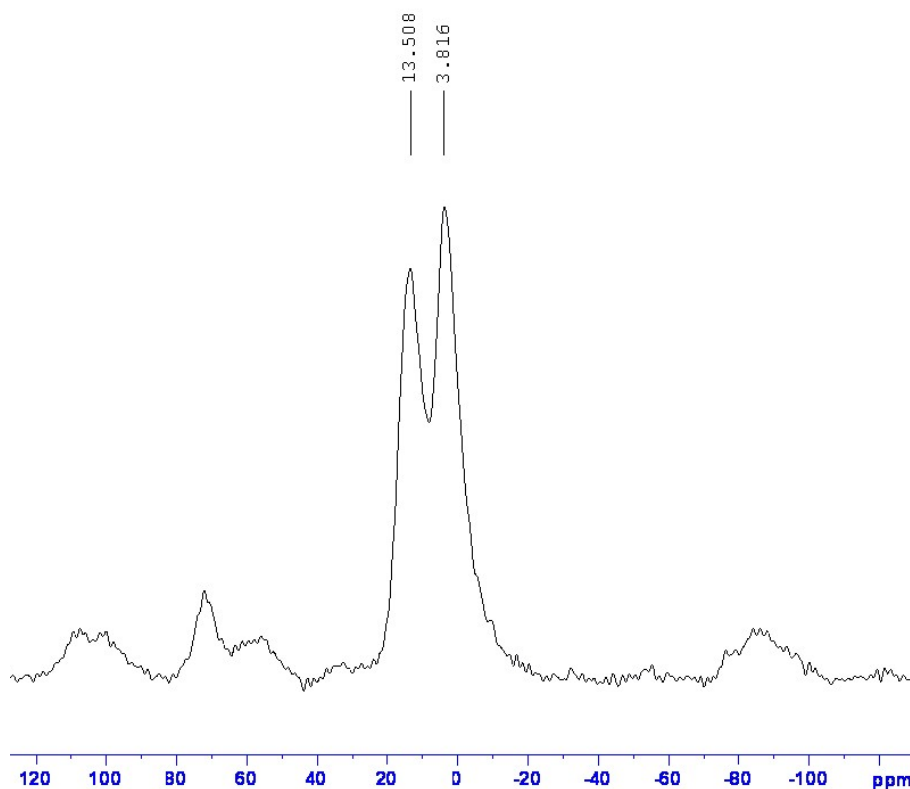


Fig. 3 ^{27}Al MAS NMR spectrum of the Paskov coal.

contains 4 hydroxyl groups and 2 phenoxide ligands arranged into regular octahedron, like in kaolinite (Weiss and Kužvart, 2005).

In coal, the Al-tetrahydroxy-diphenoxide complex seems to be an intermediate product in the transient time of the formation of the Al-hexaphenoxide complex. Laboratory experiments proved that both complexes can be prepared by long-

term reaction of AlCl_3 with phenol in water solution at room temperature, it means under very mild thermal conditions. Based on organic elemental analyses, XRF and thermogravimetric analyses of the mixture obtained, the yields of Al-hexaphenoxide complex $\text{H}_3[\text{Al}(\text{C}_6\text{H}_5\text{O})_6]$ and Al-tetrahydroxy-diphenoxide complex $\text{H}_3[\text{Al}(\text{OH})_4(\text{C}_6\text{H}_5\text{O})_2]$ were about 10 % and 40 %, respectively. As both these considered

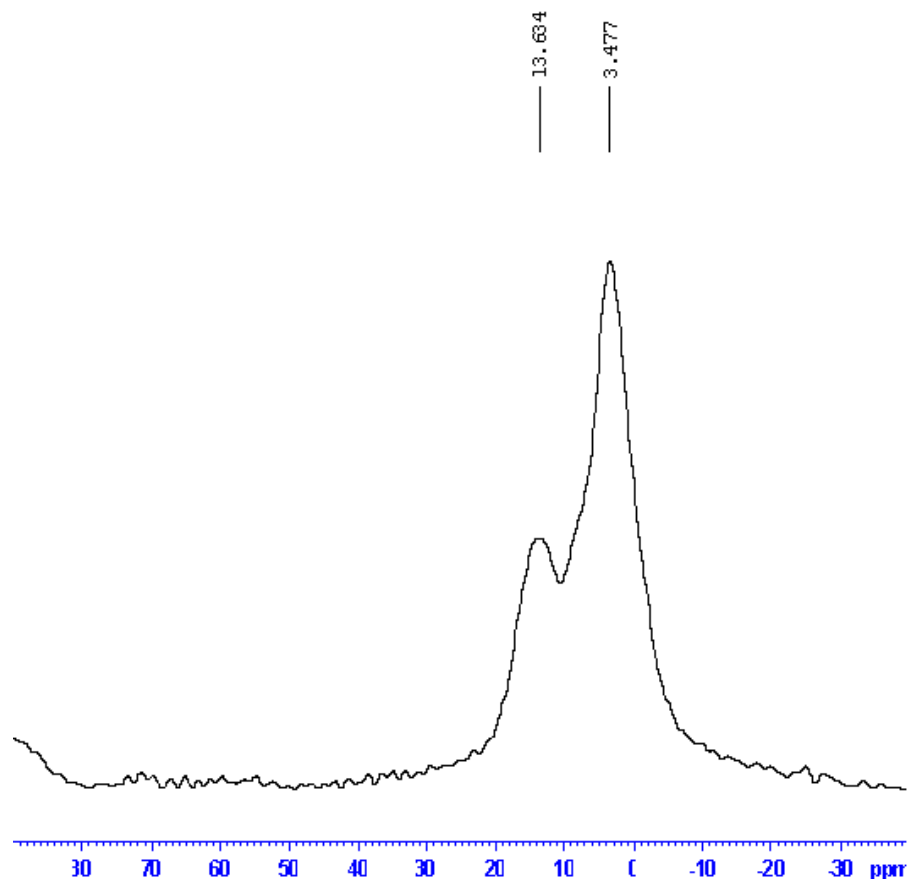


Fig. 4 ^{27}Al MAS NMR spectrum of the ČSA lignite.

Table 1 Standards and clays for identification of aluminum complexes in coal substance, and their positions in the ^{27}Al MAS NMR spectrum.

Standard	Position (ppm)	Description
aluminum phenoxide	20.90 and 23.29	dark crystalline mass
$\alpha\text{-Al}_2\text{O}_3$	14.16	deformed octahedra
Al-hexaphenoxide complex $\text{H}_3[\text{Al}(\text{C}_6\text{H}_5\text{O})_6]$	13.85	Al hexa-coordinated with 6 phenoxide oxygens
$\gamma\text{-Al}(\text{OH})_3$	8.86	gibbsite
Kaolin Sedlec IA Standard	4.82	kaolinite regular octahedra
Al-tetrahydroxy-diphenoxide complex $\text{H}_3[\text{Al}(\text{OH})_4(\text{C}_6\text{H}_5\text{O})_2]$	4.15	Al hexa-coordinated with 4 hydroxy- and 2 phenoxide oxygens
blackterry (black-colored clay from the Nová Ves locality)	3.64	kaolinite with coal organics
argil (white-colored clay) from the Nová Ves locality	2.86	natural kaolinite

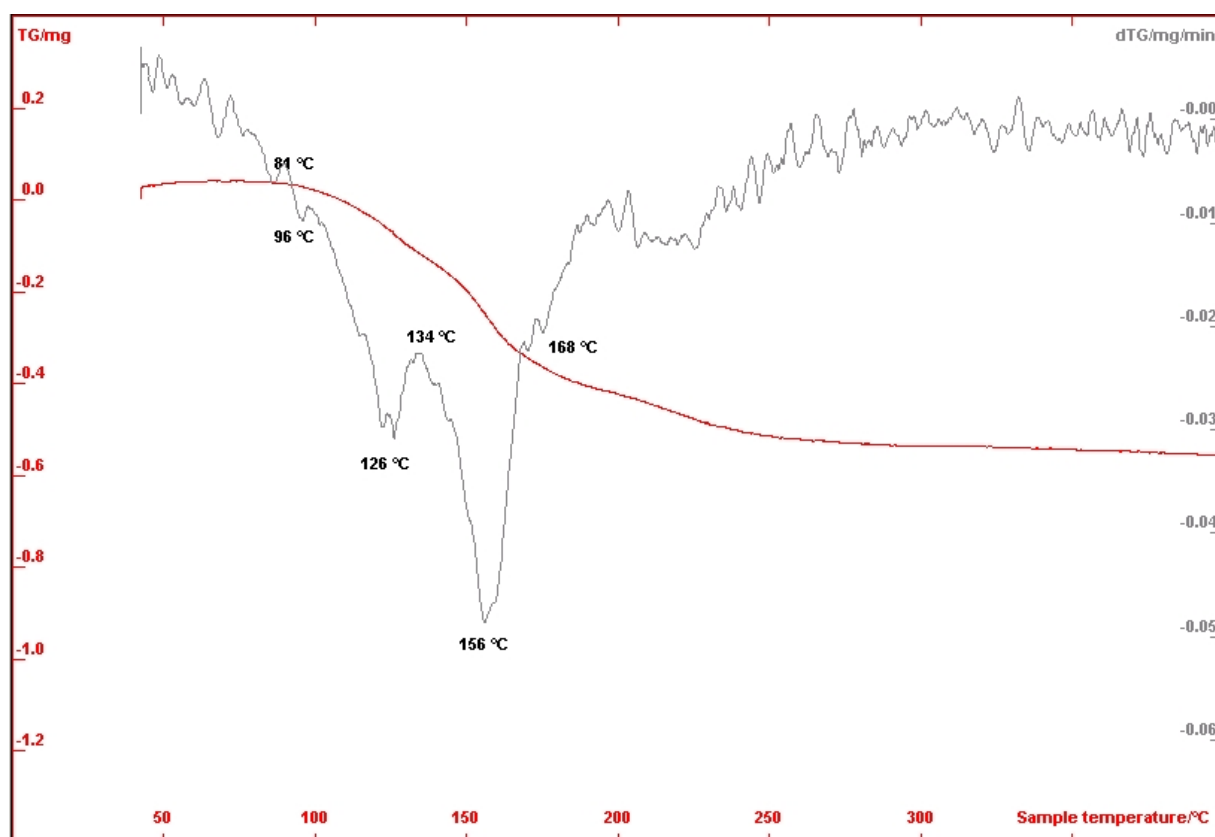
complexes are closely bonded to coal substance it can be suggested that coal was formed at mild temperatures.

The thermal properties of these complexes were further studied by thermogravimetric methods (TG and DTG) and, subsequently, compared with the thermal properties of Al-phalocyanine complex. This complex is well defined and not very thermally stable – up to 135 °C. From results a thermal stability was

evaluated. Thermogravimetric curves are presented in Figs. 5 and 6. It was found that a) the complexes in question are thermally stable up to 85 or 95 °C, b) they decompose in the range of approximately 90–135 or 100–160 °C with the maximum decomposition occurring at about 125 or 145 °C. It means that complexes in question are not thermally very stable.

Table 2 ^{27}Al MAS NMR signals of low-ash bituminous coals and lignites.

Coal/lignite	Basin/locality/state	Position (ppm)
Paskov		13.5 and 3.8
Darkov	Czech part of the Upper	14.0
Dukla	Silesian Basin	14.8 and 3.6
Lazy		5.2 and 71.9
ČSA	North Bohemian Basin	3.5
Jiří	Sokolov Basin	3.8
South-Moravia	South Moravian Lignite Basin	4.0
Gagatite	Poland, Cetraceous Period	3.5

**Fig. 5** TG/DTG curves of Al-hexaphenoxide (maximum at 126 °C) and Al-phtalocyanine (maximum at 156 °C) complexes in the mixture.

From all the mentioned findings following two interpretations can be propose. The first is based on reactions of aluminum from kaolinite with phenol molecules. Aluminum in Al-complexes in question can originate from kaolinite, as this clay mineral is very frequent in coal (Thomas, 2002). If considered Al-complexes were formed in coal through the reaction of kaolinitic Al with phenol molecules, the primary octahedral structure of the hexa-coordinated aluminum was retained, but the ligands, coordinated around the central Al atom, have changed – first through substituting two oxygen atoms of the

Al-kaolinite octahedron with two phenoxide groups while preserving four hydroxyl groups in this octahedron and, subsequently, through substituting also these hydroxyl groups with phenoxide groups, thus yielding in successive steps two complexes: tetrahydroxy-diphenoxide and hexaphenoxide. The formation of these complexes was preceded by exfoliation (delamination) of the kaolinitic structure through the effect of organic compounds, especially phenols, accompanying coal formation. This has resulted in the separation of the gibbsite octahedral and silicon tetrahedral layers. Through the effect of

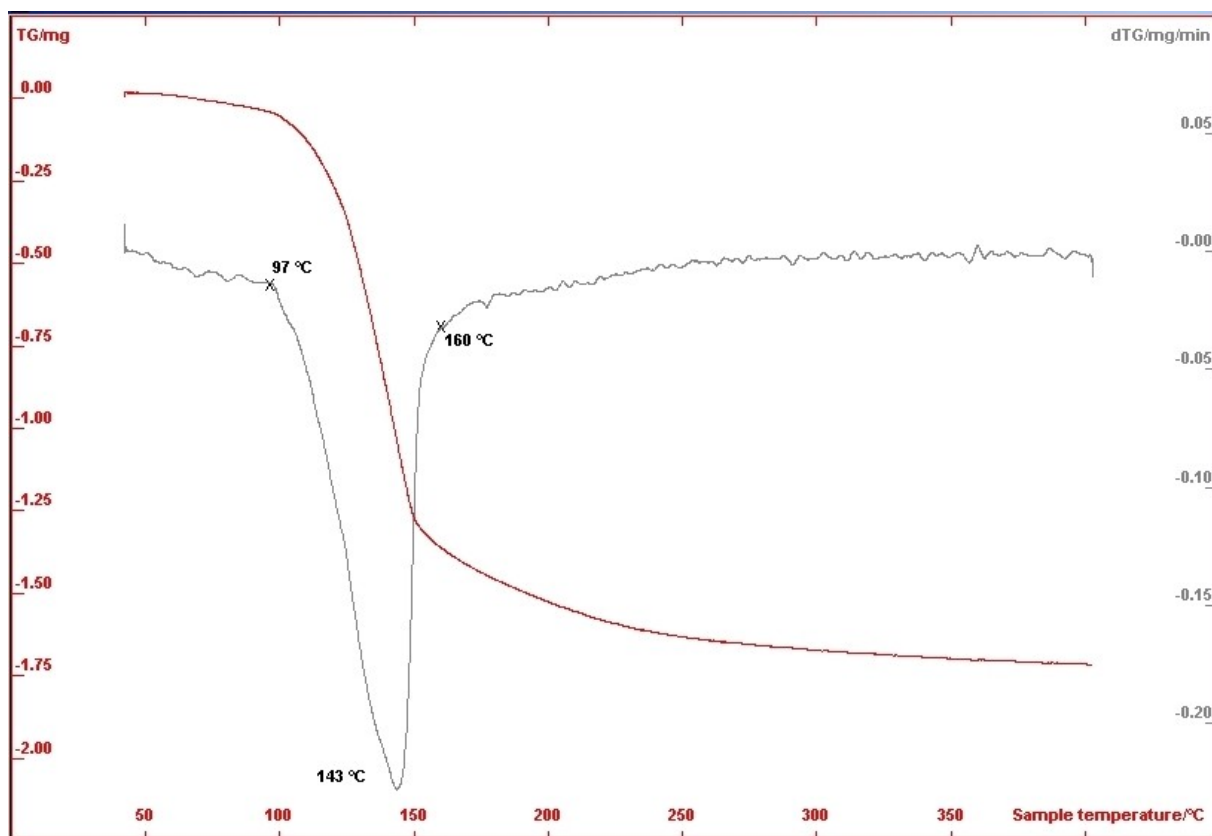


Fig. 6 TG/DTG curves of the Al-tetrahydroxy-diphenoxide complex.

the phenols, the Al-complexes with ligands in octahedral arrangement have thus formed from the gibbsite-layer aluminum octahedrons, which is in the ^{27}Al MAS NMR spectrum manifested via signals at 13.5–15 and 3.5–5 ppm.

Other interpretation is based on findings that some plants important for coal formation contain higher amounts of Al (Bouška, 1981). E.g. *Lycopodium* and the wood and bark of some deciduous trees concentrate Al in larger amounts; the cryptogams tolerate the relatively highest Al-concentrations. Aluminum concentration in swamp waters may be as high as 1 mg/l. The presence of Al in humates suggests that the fossilized plants remains in coal may contain considerable amounts of Al. As sugars, polyphenols and phenols are the main precursors of humic matters and coal substance (Liu and Huang, 2002), Al contained in original plants created the Al-O bonds predominantly with phenol.

Aluminum tetra-coordinated with oxygen exhibits a signal in the spectrum at 60–80 ppm (Duxson et al., 2007), therefore the above-mentioned signal found in the case of the Lazy coal at 71.9 ppm undoubtedly belonged to Al tetra-coordinated with organic oxygen ligands. Probably, this bituminous coal was thermally altered as it originates from the vicinity of red beds bodies of the Upper Silesian Basin. Chemical structure of altered coals is atypical

as compared with current bituminous ones (Taraba, 2003) and chemical changes can be expected also with complex compounds. Thermal action caused change of coordination number of Al from 6 to 4 in this case, analogously as it is in the case of creation of metakaolinite from kaolinite at the temperatures higher than 400 °C. However, in the case of altered coal the temperature of Al coordination change is markedly lower.

As has already been stated, the Al-complexes with hexa-coordinated Al found are thermally stable up to 85 or 95 °C. Since they were identified in coal substance, it implies that the coal was being formed at mild, in fact even common temperatures, because otherwise these complexes would not have been preserved and would have decomposed. Under laboratory conditions, i.e. at room temperature and atmospheric pressure, both were formed only after a long-term reaction – after 20 months. This indicates that under natural conditions the formation of both complexes was a long-term process, namely through a reaction with phenolic substances at relatively low temperatures, not exceeding 85 °C.

Other question is a stability of these complexes under pressure. This stability was tested in a steel reactor at pressure of inert gas of 2.1 MPa and temperature of 68 °C. Under these conditions both complexes were kept during one month. No changes

in chemical constitution were observed. So, the considerable pressure stability of complexes in question was found.

4. CONCLUSIONS

Coal substance contains at least two aluminum complexes with phenoxide ligands. The significant chemical shifts in ^{27}Al MAS NMR spectra proved that Al-hexaphenoxide and Al-tetrahydroxy-diphenoxide complexes are presented in coal organic mass as a) the ^{27}Al MAS NMR signals both at 13.5–15 and 3.5–5 ppm belong to aluminum hexa-coordinated to oxygen, b) complexes were identified by scale of standards. Thermal stability tests of Al-hexaphenoxide and Al-tetrahydroxy-diphenoxide complexes showed that they are stable only up to approximately 85 or 95 °C. As investigated Al-complexes are the integrated parts of coal substance it can be concluded that coal was formed at very mild thermal conditions.

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