

Aluminium Complexes in Coal and their Thermal Stability

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ABSTRACT: On the basis of solid-state nuclear magnetic resonance measurements of ^{27}Al in coal samples (^{27}Al MAS NMR) the new organo-aluminum complex compounds in coal substance were discovered. For measurements, the original coals, the solid phases of leaches, and the solid residues after leaching were used. As original coals, those from Ostrava-Karviná District (Czech part of the Upper Silesian Basin), North Bohemian Basin and Sokolov Basin (Czech Republic), the An Tai Bao open-pit coal mine (Shanxi, China), Peak Downs Mine (Queensland, Australia) and Kukovo locality (Russia) were tested. The solid phases of leaches and the solid residues after leaching were obtained by long-term leaching of the Ostrava-Karviná bituminous coal from the Dukla mine and its fractions (separates). For leaching 2-methoxyethanol was used.

It was found that the significant chemical shifts in ^{27}Al MAS NMR spectra correspond with those obtained for the aluminum-hexaphenoxide and the aluminum-tetrahydroxy-diphenoxide complexes as the ^{27}Al MAS NMR signals found at 14–15 and 4–5 ppm are typical for hexa-coordination of aluminum to oxygen. Other signal found with the Lazy coal at 72 ppm is typical for tetra-coordination of aluminum to oxygen. Therefore, the phenoxide- and hydroxy-aluminum complexes with hexa/tetra-coordination of Al to oxygen are present in coal substance. ^{27}Al MAS NMR measurements of coal fractions proved that these complexes are concentrated mainly in the coal parts with a medium density.

Thermal stability of identified complexes was tested by thermogravimetric methods. For this purpose, Al-hexaphenoxide complex was isolated from a commercial mixture of Al-complexes by ethanol; Al-tetrahydroxy-diphenoxide complex was prepared by long-term reaction of AlCl_3 with phenol at room temperature and atmospheric pressure. Also Al-hexaphenoxide complex can be prepared in this way, but the yield was only about 10 %. It was found that these complexes are stable only up to approximately 85 or 95 °C. As both Al-hexaphenoxide- and Al-tetrahydroxy-diphenoxide complexes are a part of coal substance it can be concluded that coal was formed under very mild thermal conditions.

KEY WORDS: aluminum complexes, coal, NMR, thermogravimetric methods.

Introduction

Complexes in coal are among the least investigated compounds. However, their research may lead to the discovery of entirely new, thus far unknown, complex compounds and to the increase of the knowledge on the chemical composition of coal. Learning about the properties of these compounds, mainly their thermal stability, may further contribute to a new perception of the coal formation. For several reasons, we have focused on the complex compounds of aluminum with organic ligands. Firstly, aluminum is strongly capable of forming complexes; secondly, organo-aluminum compounds and complexes have very different and characteristic physical and chemical properties, with the conditions of their formations also being quite different. Therefore, if the presence of the aluminum complexes in coal substance and the conditions for their formation are ascertained, it may clarify the conditions of coal formation. Thirdly, concentration of Al in bituminous coals and lignites is often quite high (0.5–1 %). Moreover, the new complexes can be discovered during investigation of organo-aluminum compounds in coal substance.

Materials and methods

Aluminum complexes in coal samples were identified by means of the solid-state nuclear magnetic resonance measurements of

^{27}Al (^{27}Al MAS NMR method) on the Bruker Avance 500 spectrometer (Bruker, Rheinstetten). The thermal stability of identified complexes was tested by thermogravimetric methods (TG and DTG) on the SETARAM Setsys Evolution 18 analyzer (SETARAM, Caluire). Samples of different coals and coal fractions were measured.

Samples of bituminous coals from the Czech Republic (Czech part of the Upper Silesian Basin, Ostrava-Karviná District), China (Shanxi Province, the An Tai Bao open-pit mine), and Australia (Queensland, Peak Downs), and anthracite from Russia (the Kukovo locality) were examined, along with two lignites from the Czech Republic (Sokolov Basin and North Bohemian Basin) and humic acid from South-Moravian lignite coal field.

The coal fractions were obtained by applying a sink-float method on the bituminous Dukla coal in the organic liquids (xylene-carbon tetrachloride mixtures) of varying densities (Zubková 2003). As result, the fractions with apparent densities of $<1.27 \text{ g.cm}^{-3}$, in the range of $1.27\text{--}1.50 \text{ g.cm}^{-3}$ and $>1.50 \text{ g.cm}^{-3}$ were separated.

The obtained fractions were further leached. In each case 60–70 g of coal fraction was mixed with 140–150 ml 2-methoxyethanol and then it was leached in sealed flasks at a room temperature for a period of 20 months. Then, liquid phase was separated; subsequently, 2-methoxyethanol having evaporated; the

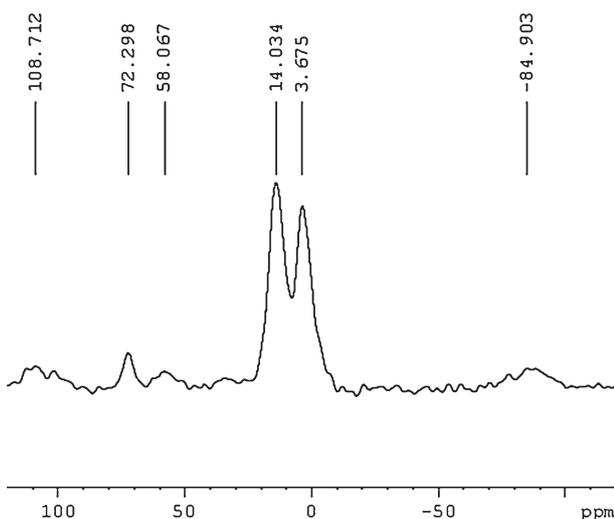
obtained solid phase of leach and solid residue after leaching were analyzed by the solid-state ^{27}Al MAS NMR method.

For thermal stability measurements, two complexes identified in coal substance were prepared. Al-tetrahydroxy-diphenoxide complex was prepared synthetically, by long-term reaction of AlCl_3 with phenol in water solution at room temperature and atmospheric pressure. Al-hexaphenoxide complex was isolated from a commercial mixture of Al-complexes (Sigma Aldrich) by extraction by means of ethanol at room temperature. For the organic elemental analyses of these complexes the Flash 1112 EA analyzer (Thermo Finnigan, Rodano) was used; for the analyses of aluminum the XRF spectrometer EDS Spectro X-Lab (SPECTRO Analytical Instruments, Kleve) was used.

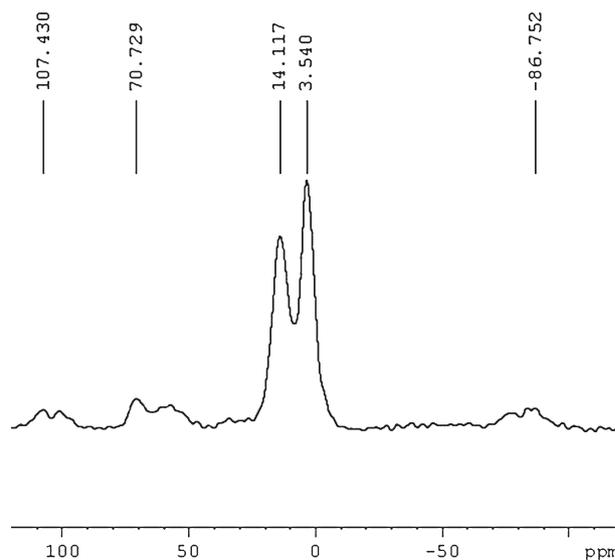
Results and discussion

In all the cases, aluminum hexa-coordinated with oxygen was identified in the ^{27}Al MAS NMR spectra. Signals at 14–15 ppm, frequently at 4–5 ppm, also at both 14–15 and 4–5 ppm were found (Figs. 1 and 2, Table 1). An important finding was made in the case of Lazy bituminous coal (the Lazy mine, Czech part of the Upper Silesian Basin, Ostrava-Karviná District), where also aluminum tetra-coordinated with oxygen was repeatedly detected at 72 ppm. It was established by a comparison with a number of standards (see below) that the hexa-coordinated aluminum identified in the spectra at 14–15 ppm belongs to an Al-hexaphenoxide ion while at 4–5 ppm to an Al-tetrahydroxy-diphenoxide ion. The aluminum tetra-coordinated with oxygen belongs likely to an Al-tetraphenoxide ion. An overview of the values ascertained can be found in the Table 1. These findings correspond with those of formation of Al-hydroxy-humate complexes (Violante et al. 1999).

The ^{27}Al MAS NMR measurements of fractions separated from Dukla bituminous coal (by the sink-float method) have shown that both the Al-hexaphenoxide complex and Al-tetrahydroxy-diphenoxide complex are very probably concentrated chiefly in the coal substance of medium density. In fractions



■ **Fig. 1.** A characteristic ^{27}Al MAS NMR spectrum of the Ostrava-Karviná coals.



■ **Fig. 2.** ^{27}Al MAS NMR spectrum of the Peak Downs coal.

coal	basin/locality/state	signal (ppm)	Al-coordination
<i>bituminous:</i>			
Paskov		3.8	6
		13.5	6
Staříč	Czech part of the Upper	13.9	6
Lazy	Silesian Basin	5.2	6
		71.9	4
Dukla		3.6	6
		14.8	6
An Tai Bao	Shanxi (China)	3.6	6
Peak Downs	Queensland (Australia)	3.5	6
		14.1	6
<i>anthracite:</i>			
Kukovo	Russia	15.2	6
<i>lignites:</i>			
ČSA	North Bohemian Basin	3.5	6
Jiří	Sokolov Basin	3.8	6
<i>humic acid:</i>			
South-Moravia	South-Moravian lignite coal field	4.0	6

■ **Tab. 1.** ^{27}Al MAS NMR signals of the bituminous coals, anthracite, lignites and humic acid.

with low or conversely high apparent density, the complexes in question have not been found (Table 2). In the case of lignites this finding is vague in this time (Straka 2007).

It arises from an overview of the standards, their signals in the spectrum and their structure (Table 3) that the first type, with the signal in the spectrum at 14–15 ppm, has 6 phenoxide ligands, arranged into deformed octahedrons (like in $\alpha\text{-Al}_2\text{O}_3$, as described in monograph of Gažo (1981)), whereas the second type, with signal at 4–5 ppm, contains 4 hydroxyl groups and

the Dukla coal fractions (g.cm ⁻³)	analyzed sample	ppm	Al-coordination
-1.27	solid phase of leach	no signals	
	solid residue after leaching		
1.27-1.33	solid phase of leach	14.5	6
1.27-1.33	solid residue after leaching	3.6	6
1.33-1.40	solid phase of leach	no signals	
	solid residue after leaching		
1.40-1.50	solid phase of leach	no signals	
	solid residue after leaching		
+1.50	solid phase of leach	no signals	
	solid residue after leaching		

■ **Tab. 2.** Hexa-coordinated aluminum identification in bituminous coal fractions (leaching by means of 2-methoxyethanol).

standard	ppm	structure
Al-hexaphenoxide complex (extracted by ethanol from the <i>Sigma Aldrich</i> mixture as H ₃ [Al(C ₆ H ₅ O) ₆])	13.85	Al hexa-coordinated with 6 phenoxide oxygens
α-Al ₂ O ₃ (thermal analysis standard)	14.16	deformed octahedra (Gažo 1981)
Al-tetrahydroxy-diphenoxide complex (prepared as H ₃ [Al(OH) ₄ (C ₆ H ₅ O) ₂])	4.15	Al hexa-coordinated with 4 hydroxy- and 2 phenoxide oxygens
Kaolin Sedlec IA standard	4.82	kaolinite regular octahedra
Aluminum phenoxide (<i>Sigma Aldrich</i>)	20.90/ 23.29	dark crystalline mass
γ-Al(OH) ₃	8.86	gibbsite
H ₃ Al(OH) ₆	-1.10	Al complex with symmetrically arranged OH-ligands

■ **Tab. 3.** Standard substances and mixtures for identification of aluminum complexes in coal, and their signals in the ²⁷Al MAS NMR spectrum.

2 phenoxide ligands, arranged into regular octahedrons, like in kaolinite.

In coal, the Al-tetrahydroxy-diphenoxide complex seems to represent an intermediate product in the intermediate stage in the formation of the Al-hexaphenoxide complex, which is entirely new compound with organic ligands, present in bituminous coals, lignite as well as anthracite. Since no data on the physical and chemical properties of mentioned Al-complex compounds exist, the focus of further study was their thermal stability, namely by means of the thermogravimetric (TG/DTG) methods, which was subsequently compared with the thermal stability of other aluminum compounds. The results are summarized in the Table 4.

It was found that the complexes in question are thermally stable up to 85 or 95 °C, in the range of approximately 100–160 °C they decompose, with maximum decomposition occurring at about 125 or 145 °C. From all the mentioned findings following interpretation can be propose. Very probably, hexa-coordinated aluminum of these compounds originates from kaolinite, as this mineral is very frequent in coal (Thomas 2002, Bouška 1981). Since the complexes in question are likely to have formed in coal through the reaction of kaolinitic Al with

Al complex	stable up to	range of decomposition	max. of decomposition
Al-hexaphenoxide	85	85–135	125
Al-tetrahydroxy-diphenoxide	95	95–160	145
Al-phtalocyanine	135	135–175	155
Al-naphtalocyanine	605	605–900	695

■ **Tab. 4.** The thermal stability of Al complexes evaluated by the thermogravimetric.(TG/DTG) methods (°C).

phenolic compounds, the octahedral structure of the hexa-coordinated aluminum was retained, but the ligands, coordinated around the central aluminum atom, have changed – first through substituting two oxygen atoms of the 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 two complexes, namely 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- and silicon tetrahedral layers. Through the effect of the phenols, the Al complex compounds with ligands in octahedral arrangement have thus formed from the gibbsite-layer aluminum octahedrons, which is in the ²⁷Al NMR spectrum manifested via signals at 14–15 and 4–5 ppm, because in both cases Al hexa-coordinated with oxygen is concerned, which in general manifests itself via a signal in the interval between -20 and 20 ppm. On the other hand, Al tetra-coordinated with oxygen exhibits a signal in the spectrum at 60–100 ppm, therefore the above-mentioned signal found in the case of the Lazy coal at 72 ppm undoubtedly belonged to the aluminum tetra-coordinated with organic oxygen ligands.

As has already been stated, the Al-complexes 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 moderate, 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. Based on organic elemental analyses, the yield of Al-hexaphenoxide complex H₃[Al(C₆H₅O)₆] was about 10 %, the yield of Al-tetrahydroxy-diphenoxide complex H₃[Al(OH)₄(C₆H₅O)₂] about 40 %. This means that even 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.

Conclusions

The significant chemical shifts in ²⁷Al MAS NMR spectra proved that aluminum- hexaphenoxide and aluminum-tetraphenoxide complexes are present in the coal substance as the ²⁷Al MAS NMR signals at 14–15 or 4–5 ppm are typical for hexa-

coordination of aluminum to oxygen. Further, signal at 72 ppm which is typical for tetra-coordination of aluminum to oxygen was found in the case of the Lazy coal. ^{27}Al MAS NMR measurements of coal fractions proved that mentioned complexes are concentrated mainly in the coal parts with a medium density.

Both Al-tetrahydroxy-diphenoxide- and Al-hexaphenoxide complexes were prepared synthetically, by long-term reaction of AlCl_3 with phenol under very mild laboratory conditions (room temperature, atmospheric pressure). Thermal stability of obtained complexes was tested by thermogravimetric methods. It was found that these complexes are stable only up to approximately 85 or 95 °C. As investigated Al-complexes are the parts of coal substance it can be concluded that coal was formed at very mild thermal conditions.

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