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FORMATION AND THERMAL DECOMPOSITION OF ALUMINIUM NITROXY COMPOUNDS

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During the reactions of lithium oxide with aluminium nitride, and of lithium nitride with aluminium oxide, the formation has been observed of a previously unknown compound, of composition Li_2AlNO. The course of its thermal decomposition has also been determined.

In earlier work concerning the preparation and reactivity of boron nitride, the existence of the BNO^{2-} anion in H_2BNO [1, 2] and its lithium and sodium salts [3] was found. Since compounds with a mixed nitroxy coordination shell round the central element are known in the chemistry of carbon, silicon and germanium [4–8], it seemed reasonable that aluminium, lying in the direct proximity of the above elements in the periodic system, may also form such salts. The reactions of aluminium nitride with lithium oxide, and of aluminium oxide with lithium nitride, have been studied by means of thermal analysis. When the reactions were carried out on a large scale in a tube furnace under a protective atmosphere, a previously unknown crystalline phase with the stoichiometry Li_2AlNO was obtained. The course of the thermal decomposition of this compound has also been investigated. The discussion of the results is based on the morphological classification of simple species modified for heteroligand bonding [4, 9–12]. The transformations of the anions taking part in the reactions and of neutral species are presented in a classification table within the $e_zO^{2-} - e_zN^{3-}$ coordinate system, where e_zO^{2-} denotes the number of elementary negative charges formally introduced into the coordination shell by oxide ligands, and e_zN^{3-} is the number of elementary negative charges formally introduced into the coordination shell by nitride ligands [4]. Purely nitride anions of aluminium lie on the $e_zO^{2-} = 0$ line, and species with purely oxide coordination shells lie on the $e_zN^{3-} = 0$ line. For example:

$$\begin{aligned} &AlN && e_zO^{2-} = 0;\ e_zN^{3-} = 3;\\ &Al_2O_3 && e_zO^{2-} = 3;\ e_zN^{3-} = 0;\\ &AlNO^{2-} && e_zO^{2-} = 2;\ e_zN^{3-} = 3. \end{aligned}$$

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The addition of an oxide ligand causes an increase in the e_zO^{2-} number, and that of a nitride anion causes a corresponding increase in the e_zN^{3-} number. Besides the classification of the structures, this table also permits a presentation of the elementary transformations connecting the particular species.

Experimental

In this work the following reagents were used: AlN and Li_3N prepared by us, Li_2O from Research Organic and Inorganic Laboratories (USA) and Al_2O_3 from POCh, Gliwice (Poland).

The courses of the reactions and the thermal decompositions were studied by thermal analysis on a MOM (Budapest) derivatograph. The syntheses and thermal decompositions at characteristic temperatures were carried out in tube furnaces under the required atmosphere. The reaction products were studied after freezing, by means of X-ray phase analysis and quantitative analysis.

Results and discussion

Figure 1 presents thermal curves for the AlN + Li_2O mixture at a molar ratio of 1 : 1, recorded under nitrogen atmosphere. At 850° a weak exothermic effect is observed, and X-ray studies show the presence of a previously unknown crystalline phase. X-ray identification data are presented in Table 1; they differ from the X-ray data for all known compounds in the Li–Al–N–O system. The phase obtained is stable up to 1100°, when its thermal decomposition begins, accompanied by an exothermic effect and a loss of mass; lithium meta-aluminate, aluminium nitride and lithium nitride, vaporizing at these temperatures, are the decomposition products.

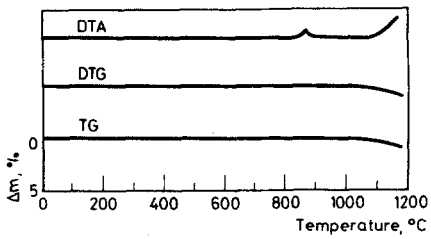

Fig. 1 TG, DTG and DTA curves of Li_2O = AlN; m = 0.162 g, N_2

Figure 2 presents thermal curves for the $Al_2O_3 + 2Li_3N$ mixture, recorded under nitrogen atmosphere. In the temperature range 550–750°, three consecutive exothermic effects are observed; of these, that at 600° is probably connected with the double exchange reaction

$$2\,Li_3N + Al_2O_3 \rightarrow 2\,AlN + 3\,Li_2O$$

for at 700° X-ray studies show the presence in the reaction products of AlN, Li_2O and a small quantity of $LiAlO_2$. The exothermic effect at 750° is connected with the synthesis of a new crystalline phase, identical to that formed in the AlN and Li_2O reaction studied earlier (X-ray identification data in Table 1).

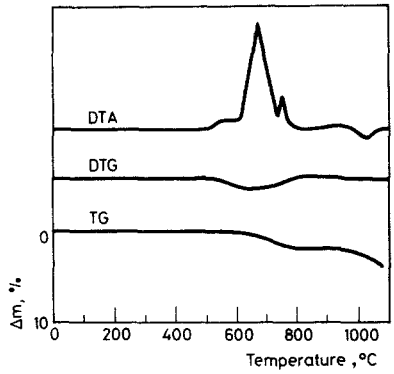

Fig. 2 TG, DTG and DTA curves of $2Li_3 + Al_2O_3$; m = 0.225 g, N_2

Table 1 X-ray diffraction data for identification of Li_2AlNO

d, Å	4.484	3.708	2.614	1.926	1.833	1.608
I/I	15	40	100	15	15	45

The thermal decomposition course of the new phase accords with that described earlier. The decomposition products are aluminium nitride, lithium aluminate and also lithium nitride (which leaves the reaction medium). Elemental analysis of the new phase and of its thermal decomposition products indicates that exactly half of the bonded nitrogen passes into the gas phase in this reaction, as Li_3N.

The elemental analysis reveals that the new phase has the stoichiometry Li_2AlNO. Since the boron salts Li_2BNO and Na_2BNO were obtained earlier in our laboratory [3], it can be assumed that such types of compounds also exist in the chemistry of aluminium.

Figure 3 shows the known oxygen and nitrogen species of aluminium and the postulated $AlNO^{2-}$ anion within the $e_zO^{2-} - e_zN^{3-}$ coordinate system. The e_zO^{2-}

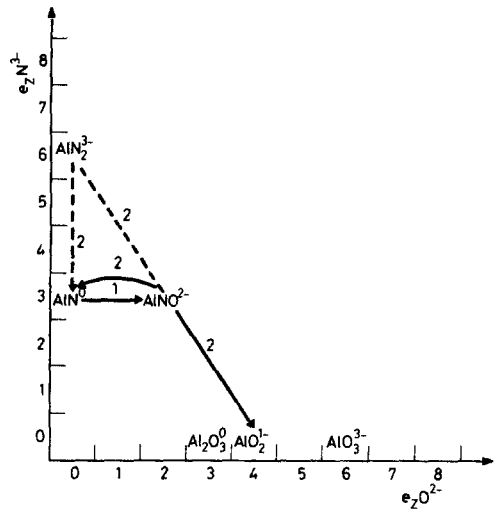

Fig. 3 Classification stable of oxynitride compounds of aluminium

and e_zN^{3-} numbers correspond to the numbers of elementary negative charges formally introduced into the coordination shell by the respective ligands. Thus, purely oxygen compounds are placed in the $e_zN^{3-} = 0$ field, and purely nitrogen ones in the $e_zO^{2-} = 0$ field.

Analogously to the postulated compound, the boron compounds Li_2BNO and Na_2BNO are formed in the reactions [3]:

$$Li_2O + BN \rightarrow Li_2BNO$$

$$Na_2O + BN \rightarrow Na_2BNO$$

and their thermal decompositions proceed as follows [3]:

$$2\,Li_2BNO \rightarrow LiBO_2 + Li_3BN_2$$

$$3\,Na_2BNO \rightarrow Na_3BO_3 + 2\,BN + Na_3N$$

If the thermal decomposition of the hypothetical compound Li_2AlNO proceeds in a similar way, as is known in carbon chemistry (cyanide decomposition), when two products with a uniform coordination shell are formed from compounds with a mixed nitroxy coordination shell, this could be considered as additional proof of the existence of Li_2AlNO. It is formed from the reaction

$$Li_2O + AlN \rightarrow Li_2AlNO \qquad (1)$$

The results obtained suggest that the reaction of Li_2AlNO decomposition should be expressed as follows:

$$2\,Li_2AlNO \xrightarrow{1100^\circ} LiAlO_2 + AlN + Li_3N \qquad (2)$$

The number of the reactions correspond to those of the transformations in the classification table (Fig. 3).

The fact that the decomposition does not proceed identically, but only similarly as in the chemistry of boron, probably results from the differences in the thermal stabilities of Li_3BN_2, Na_3BN_2 and Li_3AlN_2.

Conclusions

Aluminium nitride reacts with lithium oxide at 850° to form a previously unknown crystalline phase with the stoichiometry Li_2AlNO. The thermal decomposition of this compound is analogous with the decompositions of similar salts of other elements, and proceeds in the direction of products with a homogeneous coordination sphere.

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Zusammenfassung — Es wurde das Auftreten einer bisher unbekannten Verbindung der Zusammensetzung LiAlNO bei den Reaktionen von Lithiumoxid mit Aluminiumnitrid und Lithiumnitrid mit Aluminiumoxid beobachtet. Der Verlauf der thermischen Zersetzung dieser Verbindung wurde bestimmt.

Резюме — При изучении реакций окиси лития с нитридом алюминия и нитрида лития с окисью алюминия наблюдали образование ранее неизвестного соединения состава Li_2AlNO. Определен также процесс его термического разложения.