Correlation Between Structural Parameters and the Charge of Ln-heteroatom Nuclei in Isostructural Salts $Na_9[Ln(W_5O_{18})_2]\cdot 35H_2O$ (Ln = Nd, Eu, Gd, Tb, Dy, Ho, Er)

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Abstract - Comparison of structural parameters in the isostructural sodium heteropoly decatungstolanthanidates(III) with Peacock–Weakley type anion $Na_9[Ln(W_5O_{18})_2]\cdot 35H_2O$ (Ln = Nd, Eu, Gd, Tb, Dy, Ho, Er) showed the linear dependences for decreasing of Ln—O_b(W) bond lengths and O…O interatomic distances in the $[Ln(W_5O_{18})_2]^{9-}$ anion vs. the charge of Ln–heteroatom nuclei.

Keywords - heteropoly decatungstolanthanidate, peacock–weakley anion, FT-IR spectroscopy, X-ray single crystal analysis, lanthanide.

Introduction

The precis presents the results of investigation of synthesized neutral salts $Na_9[Ln(W_5O_{18})_2]\cdot 35H_2O$ with lanthanides as a heteroatom by elemental analysis, X-ray Single Crystal analysis, FT-IR spectroscopy. It also confirms the linear dependence between bond lengths and interatomic distances, and the charge of Ln-heteroatom nuclei.

Experimental

The synthesis of $Na_9[Gd(W_5O_{18})_2]\cdot 35H_2O$ was carried out as follows. Sodium tungstate solution (V = 19.27 mL, C = 0.5190 mol/L) was added to 56.19 mL of distilled water, and then HNO_3 solution (V = 23.07 mL, C = 0.3467 mol/L) was added dropwise with vigorous stirring. After that $Gd(NO_3)_3$ solution (V = 1.47 mL, C = 0.5749 mol/L) was added dropwise very slowly with vigorous stirring. For synthesis of $Na_9[Er(W_5O_{18})_2]\cdot 35H_2O$ instead of gadolinium nitrate, the solution of $Er(NO_3)_3$ (1.03 mL, C=0.9751 mol/L) was used, and the initial volume of distilled water was 56.63 ml. Isolated salts investigated by elemental analysis, X-Ray Single Crystal, and FT-IR spectroscopy.

Results and Discussion

The results of X-ray Single Crystal analysis and the analysis of literature showed that among the compounds with Peacock–Weakley type anion, one can distinguish a number of isostructural salts $Na_9[Ln(W_5O_{18})_2]\cdot 35H_2O$ (Ln = Eu [1], Gd [this study], Tb [2], Dy [2–3], Ho [2], Er [this study, 2, 4]), mainly with lanthanides of the yttrium subgroup. It worth mentioning that only $Na_9[Nd(W_5O_{18})_2]\cdot 32H_2O$ has similar crystallographic characteristics, and differs in crystallohydrate H_2O molecules content [5].

It was interesting to compare some of the structural parameters of these salts. For this purpose, we selected and analyzed the following parameters: bond lengths Ln—O_b(W); interatomic distances between Ln and five-coordinate oxygen atoms O_C; interatomic distances O...O in the planar fragments of lacunar isopoly anions $[W_5O_{18}]^{6-}$, by which they are coordinated to Ln heteroatom; values of the bond lengths W=O_t, which are on the same axis with Ln heteroatom.

Comparison of structural parameters of isostructural neutral salts $Na_9[Ln(W_5O_{18})_2]\cdot 35H_2O$ (Ln = Eu, Gd, Tb, Dy, Ho, Er) allowed us to establish linear dependences between decreasing

lengths of Ln—O_b(W) bonds and interatomic distances O…O in Peacock–Weakley type heteropoly anions, and the charge of Ln–heteroatom nuclei (Fig. 1).

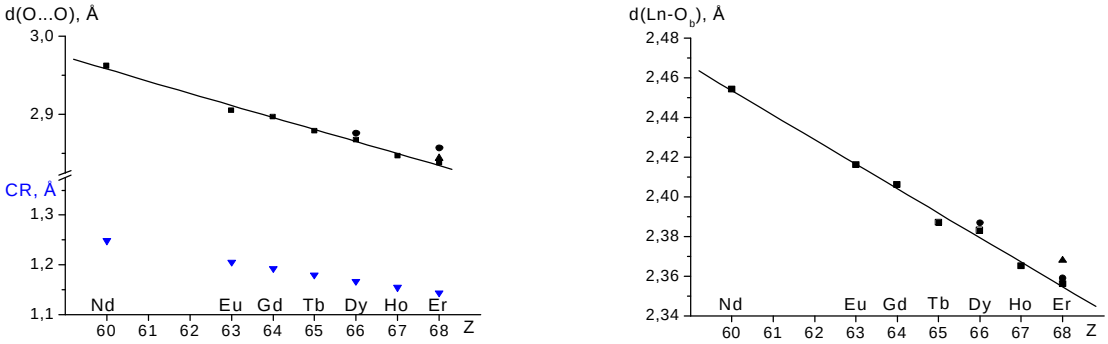

Fig.1. Left — Dependence of the mean values of interatomic distances O...O in the planar fragments of lacunar isopolyanions $[W_5O_{18}]^{6-}$ vs. the charge of Ln–heteroatom nuclei. The blue color indicates the dependence of crystalline radii (CR) in the row of ions Ln^{3+} (Ln = Nd, Eu–Er) for coordination number 8 vs. the charge of the lanthanide atom nuclei (coefficient of determination R^2 = 0.9916); Right — Dependence of the mean values of bond lengths Ln—O_b(W) vs. the charge of Ln-heteroatom nuclei (coefficient of determination R^2 = 0.9932).

Conclusion

In present research the linear dependences between decreasing of Ln—O_b(W) bond length and interatomic distances O…O vs. charge of Ln–heteroatom nuclei in the row of isostructural heteropoly salts $Na_9[Ln(W_5O_{18})_2]\cdot 35H_2O$ (Ln = Nd, Eu, Gd, Tb, Dy, Ho, Er) were established.

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