Poster Presentation

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The crystallochemical role of malonate ions in coordination polymers

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All compounds that contain malonate dianions $C_3H_2O_4^{2-}$ (mal^{2-}) and atoms of d- or f-metals were analyzed. Dianions mal^{2-} in structures of examined compounds reveal 17 topological types of coordination against metal atoms. Available data shows that mal^{2-} more often form six-membered metal cycles which is the most abundant case for all 570 crystallographic sorts of analyzed mal^{2-} (80%). For those mal^{2-} which form six-membered metal cycles the average observed valence angle CCC is equal to 120°. Results of regression analysis of all mal^{2-} showed linear dependence of ∠CCC on dihedral angel (ϕ) between planes which go through oxygen and carbon atoms of different carboxyl groups of one anion. For the equation ∠CCC = 124.9 – 0.207ϕ, correlation coefficient is -0.90. Discovered that in structures of crystals when ϕ < 60° mal^{2-} necessarily form six-membered metal cycles. Structural slackness of mal^{2-} influence on characteristics of six-membered metal cycles formed by them. Those metal cycles usually have bath conformation. Coordination polymers with fixed type of metal atom and identical type of coordination of mal^{2-} can have different dimension even in the absence of other linkers. This effect is evident on the example of $[UO_2(mal)(L)]\bullet nH_2O$ compounds. Reportedly [1], change of composition and structure of ligand L lead to changes in the system of intramolecular hydrogen bonds which influence on conformation of six-membered metal cycles. The change of conformation of this cycles lead to different relative spatial distribution of the three uranium atoms, connected with one mal^{2-}. Although of the same stoichiometric composition and crystallochemical role of uranium atoms and coordinated ligand resulting polymeric groups $[UO_2(mal)(L)]$ in crystals have different dimension: 3D, 2D or 1D respectively for L – carbamide, water or dimethylacetamide. This work was supported by the base part of the government mandate of the Ministry of Education and Science of the Russian Federation.

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