

Highly selective separation of Pd²⁺ and Pt⁴⁺ using novel oxathia-crown ethers: Experimental and DFT complexation studies

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Novel oxathia-crown ethers (CE) derivatives were successfully synthesized via cyclization of bis-epoxides with 1,2-benzenedithiol using trimethylamine catalyst and metal template in water. Liquid-liquid extraction (LLE) was performed to evaluate the CE complexations with Pd²⁺ and Pt⁴⁺. Among the CEs, 2HDBS214C4 (2i) exhibited the highest Pd²⁺ selectivity even in the presence of other platinum- or precious group metals (Pt⁴⁺, Ru³⁺, Rh³⁺, Au³⁺). DFT studies reveal that 2i has the most compatible cavity dimension ($\text{ØCE}=1.58 \text{ \AA}$) with Pd²⁺ ($\text{ØPd}^{2+} = 1.56 \text{ \AA}$) and the most stable complex based on binding energy calculations. NMR analysis demonstrates that S heteroatoms of 2i participated in 1:1 CE-Pd²⁺ coordination. The results demonstrate its applicability as selective extractant for the separation of Pd²⁺ and Pt⁴⁺ in secondary automobile catalyst waste. This work was supported by NRF funded by the Korea government funded by the Ministry of Science and ICT (2017R1D1A1B03028102 and 2017R1A2B2002109) and Ministry of Education(2009-0093816 and 22A20130012051(BK21Plus)).