Poster Presentation

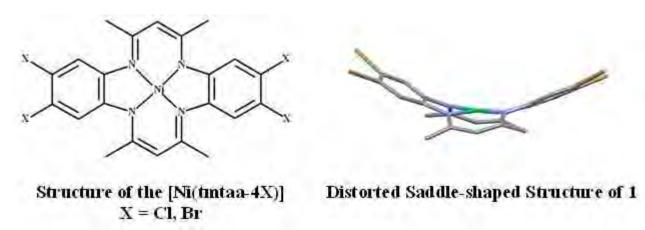
MS67.P17

Pseudo-polymorphism of Halogen Substituted Tetraaza[14]annulene Complexes

S. Ichimura¹, M. Saeki¹, Y. Tamaki¹, K. Miyamura¹

Tokyo University of Science, Department of Chemistry, Tokyo, Japan

6,8,15,17-tetramethyldibenzo-5,9,14,18-tetraazacyclotetradecinatonickel (II) (tmtaa) bears strain within its 14-membered ring and is known to adopt saddle-shaped structure. As a consequence, tmtaa has an asymmetric apical coordination sites at both sides of the saddle. Our previous study revealed that the chlorine substituted complex, [Ni(tmtaa-4CI)] shown in Figure (X = CI), exhibited pseudopolymorphism with dichloromethane and chloroform. This behaviour is due to the good affinity between halogen substituents and halomethane solvent. In this study, we grew single crystals of [Ni(tmtaa-4Br)] using various halomethane solvent as crystallization solvents and elucidated the role of the solvents related to the generation of pseudo-polymorprhism. We have succeeded in obtaining two kinds of single crystals 1 and 2 from the same vial container using bromoform. From X-ray structural analysis, 1 and 2 formed twist dimer as with previous report, and are found to include bromoform in their crystal structure. Note that these complexes adopted more distorted saddle-shaped structure than normal tmtaa complexes. The Ni-N4 planes were not planar. The difference of 1 and 2 was the degree of distortion around Ni-N4 plane, and 1 was more distorted than 2. The space group of these complexes were Aba2 and C2/c respectively. The interactions that led to the difference in packing of dimers were CH... π interaction in 1 and π ... π interaction in 2.



Keywords: Ni complex, pseudo-polymorphism