

Poster Presentation

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

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6,8,15,17-tetramethyldibenzo-5,9,14,18-tetraazacyclotetradecinato-nickel (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-4Cl)] shown in Figure (X = Cl), exhibited pseudo-polymorphism 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-polymorphism. 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.



Structure of the [Ni(tmtaa-4X)]
X = Cl, Br



Distorted Saddle-shaped Structure of 1

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