Coordination Polymers by Primary Diamines and Co(II): Studies with [3-(Aminomethyl)phenyl]methanamine and 1,4-Cyclohexanediamine.

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Introduction

Primary diamines are perhaps the most obvious monomers candidates for metal-organic frameworks and coordination polymers described in the literature. Even though many metal complexes of those molecules are widely known, there are relatively only few MOFs or coordination polymers reported with those molecules. The most probably reason for this is the high basicity of the diamines, which prevents the synthesis by hydro-thermal method due to concurrent precipitation of the metal ion. In this work we report the preparation of coordination polymers by using Co(II) with [3-(aminomethyl)phenyl]methanamine (1,3-XDA) and 1,4-Cyclohexanediamine (1,4-CHDA). The synthesis were made by slow diffusion of $CoCl_2.6H_2O$ solution into individual solutions of diamines in molar ratio of 1:2. Both solutions dissolved in DMSO and let standing from 3 weeks.

Results and Discussion

Initially, attempts were made to obtain crystalline compounds of Co(II) with benzene-1,4-diamine, hexane-1,6-diamine, 1,3-XDA and 1,4-CHDA by hydrothermal method, all of which failed. Attempts of synthesis using ethanol, DMF and acetonitrile were also unsuccessful. Futher attempts in DMSO resulted in crystalline solids, initially blue, after a few hours of contact between the solutions when using 1,4-CHDA and 1,3-XDA. Searches in the CCDC database showed few known structures formed by these molecules (either MOFs or coordination polymers) such as compounds with 1,4-CHDA and Ag(I)[1], and 1,3-XDA and Cu(II)[2], Zn(II)[2,3] and Ni(II)[4]. The blue solids are very unstable and they decompose when exposed to air. It was possible to determine only the crystal structure of the formed compound with 1,4-CHDA. To accomplish that, the crystals were kept sheltered from contact with air by immersing them in solution of the reaction medium, and when collected they were immersed in highly viscous perfluoropolyether vacuum oil. After a few weeks, the reactional medium (solution and precipitate) with Co(II) and 1,3-XDA changed from blue to a reddish solid of crystalline appearance. The same applies to the compound formed by Co(II) and 1,4-CHDA, but only after heating for 4 hours at 80°C. The crystalline structure of those compounds was determined since both are stable in contact with dry air, but they decompose in moisture. The results indicated that the blue compound corresponds to a one-dimensional coordination polymer with formula $[C_6H_8Cl_2CoN_2.2(CH_3)_2SO]_n$, where Co(II) is in tetrahedral field forming a monoclinic structure that belongs to space group $P2_1/m$ (a = 6.0361(6); b = 16.9610(15); c = 9.2455(9), α = 90; β = 101.925(4) and γ = 90). On the other hand, in the reddish compounds the Co(II) is in octahedral field, resulting in two-dimensional coordination polymers with chloride ions linked to the metal in *trans* position above and below to the two-dimensional plane formed by the respective diamine molecules. Both structures are monoclinic. However, while the one formed with 1,4-CHDA, $[C_{12}H_{16}Cl_2CoN_4.(CH_3)_2SO]_n$, belongs to the space group Cc (a = 13.3454(7); b = 13.18266; c = 11.6982(6), α = 90; β = 103.458(4) and γ = 90), the compound with 1,3-XDA, $[C_{16}H_{16}Cl_2CoN_4.2(CH_3)_2SO]_n$ belongs to the space group $P2_1/m$ (a = 5.9468(3); b = 14.0369(7); c = 15.4017(9), α = 90; β = 91.599(2) and γ = 90).

Due to the reasonable instability of those compounds, they may be used as starting materials to obtain further self-organized structures.

Conclusion

Although it was not possible to determine the structure of the blue compound formed by Co(II) and 1,3-XDA, based on the observed to the mixture Co (II) and 1,4-CHDA, there are indications that the one-dimensional tetrahedral coordination polymers, with 1:1 metal:diamine molar ratio, evolves two-dimensional coordination polymers with metal:diamine molar ratio 1:2, where the metal is in octahedral field.

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