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Introduction

The bidentate N-donor ligands 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) have attracted considerable attention in the field of coordination chemistry over the last decades because of their remarkable stability towards a wide variety of transition metals.¹ The coordination chemistry of uranium (U) has been explored with these N-donor ligands as well with a primary focus on its hexavalent state (U(VI) as UO_2^{2+}). To the contrary, much less attention has been paid for the lower oxidation states, such as a tetravalent state (U(IV)). Here we present a systematic study on the coordination chemistry of U(IV) and -^{VI} with bipy and phen under different chemical conditions, such as different solvents and changing the metal / ligand ratio.

Results and Discussion

In this study we succeeded to obtain a series of U(IV) complexes with U:ligand ratios of 1:1 and 1:2, all of which show an eight-fold coordinated uranium centre. In addition to the ligand, chloro and methanolato ligands are coordinating to the metal centre for charge compensation. Interestingly, the complexation between U(IV) and the ligand does occur even in protic solvents, in which the ligand is expected to be protonated. We also obtained another series of U(VI) complexes with both bipy and phen, underlining the versatile coordination chemistry of uranyl (UO_2^{2+}). That is, the coordination between uranyl and the ligand depends strongly on the pH of the solvent used. For instance, in media with lower pH mononuclear complexes are formed, showing the uranyl unit in an unusually bent geometry.³ On the other hand, dinuclear uranyl arrangements with hydroxo-bridging are dominated in the media with higher pH.

References

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