Supramolecular Chemistry-I

Prof. Parimal Kanti Bharadwaj

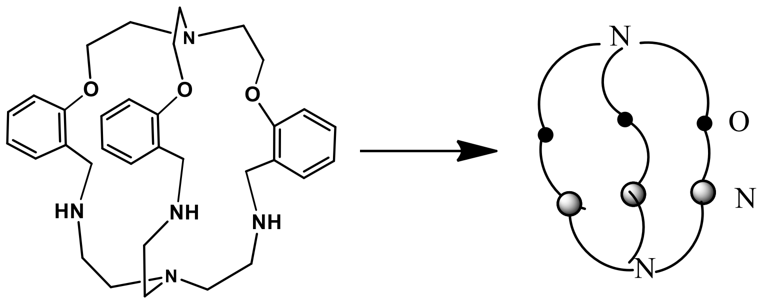
Department of Chemistry

IIT Kanpur

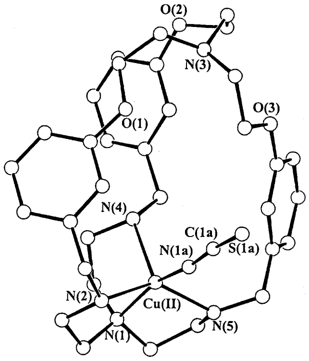
Week - 03

Lecture - 11

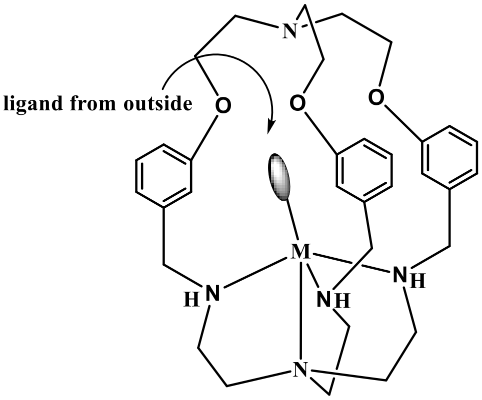
Let me continue from the last class. We talked about synthesis of cryptands and just started discussion on metal complexes. As I told you when the metal is transition metal like Co^{2+} or Cu^{2+} they bind to the N donors present in the cryptand. First let me write the cryptand structure and its cartoon form so that you will understand how to represent in the cartoon form.



Now what is the characteristics of these compounds? If I put a transition metal ion I told you that it will be bonded to 4 nitrogen: three N in the bridges and the bridgehead N. This way the space above the metal is empty and anything can coordinate. You know that Cu^{2+} likes 5 coordination, 6 coordination; similarly, Co^{2+} also likes higher coordination. That means, there is a provision for some ligand to come inside the cavity to bind the metal. In case of meta-substituted cryptand there is even more room and we have isolated with meta-substituted cryptand, Cu^{2+} cryptate where thiocyanate is bonded to Cu^{2+} if you use say potassium thiocyanate KSCN, ok ?

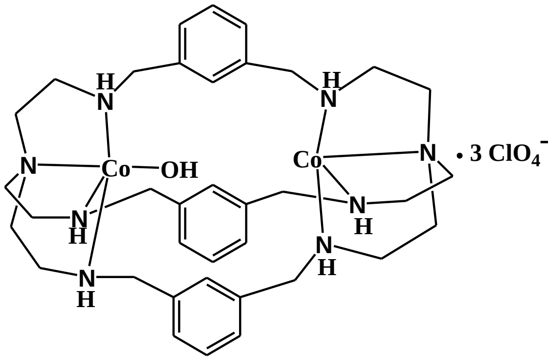


The extra stability of the Cu^{2+} complex with the cryptand is called the cryptate effect meaning it is a very stable system both thermodynamically and kinetically. So, the metal ion is very happy here and is bound it cannot be moved very easily. When I say very easily you have to understand that anything can be moved with proper reagents, but this is I am saying that difficult to move alright. Now if I put Cu^{2+}-perchlorate, the metal goes in but perchlorate remains outside because it has poor coordinating ability and is quite bulky. The geometry will be like this: the metal is bound to the four N. Three of the N forms a plane and the fourth N i.e. the bridgehead N pushes the metal above this plane away from the bridgehead N as shown in the following figure. Now if I put potassium thiocyanate, thiocyanate goes in. If I put sodium cyanide, the cyanide ion goes in and binds the copper ion.



The extra ligand binds the metal such a way that the other end of it is outside the cavity or pointing away from the cavity, why? Because it likes to avoid hydrophobic aromatic spacers. Since the metal is tightly held inside the cavity, the system can be used for a large number of organic transformations like room temperature oxidation of olefinic and benzylic substrates. I have given you a table on this in the Transcript No. 10.

Let us discuss dinuclear cryptate and its catalytic activity. First, I draw the systems:



This cryptate exhibits high selectivity and efficiency for the photocatalytic reduction of CO_2 to CO. The reaction is carried out in CH_3CN/H_2O (v/v, 4:1) under a 450 nm LED light irradiation, with a light intensity of 100 mWcm^{-2}. The selectivity reaches as high as 98 %, and the turnover numbers and turnover frequencies reach as high as 16896 and 0.47 s^{-1} both of which are remarkable. This is attributable to the synergistic catalytic effect between the two Co^{2+} ions where one Co^{2+} serves as a catalytic center, and the other Co^{2+} acts as an assistant catalytic site to facilitate the cleavage of C–OH bond of O=C–OH intermediate. You know the problem of carbon dioxide in global warming and all that. So, people are trying to do trying to reduce carbon dioxide by reacting carbon dioxide to other useful substances like carbon monoxide and then carbon monoxide is more reactive than carbon dioxide. So, carbon monoxide can react with suitable reagents and that way carbon dioxide can be removed. Thank you.