Synthetic and Structural Studies on Photoactivated Complexes

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Photocrystallography[1] is the technique for determining the structure of molecules in their excited state. Single crystal X-ray diffraction studies have been carried out on a number of complexes that have metastable or microsecond lifetimes[2]. These are very challenging experiments and it is difficult to maximise the level of excitation without destroying the crystal. In order to overcome these difficulties we are investigating several new strategies.

We are developing methods of studying metastable and excited state structures using X-ray **powder diffraction**. This relies on significant structural changes in the molecules such as isomerism, and in the initial investigations we are studying the linkage isomerism of $[Ru(SO_2)(NH_3)_4L][X_n]$ (L=Cl, X=Cl, n=1; $L=H_2O$, $X=MeC_6H_4SO_2$, n=2) where the coordination mode of the SO_2 changes from μ_1-$\underline{S}$ to μ_2-$\underline{S}$-$\underline{O}$ under illumination by a bright white light source. The μ_2-$\underline{S}$-$\underline{O}$ isomer is metastable at temperatures below 120K.

In a related series of synthetic studies, we are co-crystallizing the ruthenium complexes with cyclodextrin molecules, so that the cations may be held in the cyclodextrin pocket. Then if photocrystallographic studies are carried out on these systems, higher levels of excitation may be observed because the SO_2 group will be free to isomerise shielded from the rest of the crystal structure by the cyclodextrin cage.

[1] Coppens P., Ma B. , Gerlits O., Zhang Y., Kulshrestha P., *Cryst. Eng. Comm.,* 2002, **4**, 1. [2] Novozhilova I.V., Volkov A.V., Coppens P., *J. Am. Chem. Soc.,* 2003, **125(4)**, 1079-1087.

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