Chapter 2
Experimental Techniques

2.1 Introduction

Analysis techniques are essential for quantifying the properties and characteristics of materials. In this study, different coloured materials were formed with various host molecules. Thus in order to understand the formation as well as the physical and chemical properties associated with each structure, various analytical techniques were utilised. Techniques such as X-ray diffraction, thermal and spectroscopic techniques as well as theoretical calculations were all employed.

2.2 X-Ray Diffraction

X-rays were first discovered over a century ago by a German professor, Wilhelm Conrad Roentgen. The discovery that X-rays could be diffracted by crystals lead to an increase in research, as scientists were able to make use of the short wavelength to delve deeper into the atomic level of a structure. Thereby making it possible to determine precise bond angles and inter-atomic distances within molecules and structures (Atkins, 1998, Cheetham *et al*., 1994, West, 1999).

The two most popular X-ray diffraction techniques currently being employed are powder X-ray diffraction (PXRD) and single crystal X-ray diffraction (SCXRD). Each method works on the same principles of diffraction, and requires X-rays to be directed onto a powder or crystalline material. Atoms within the material then scatter these X-rays, either in phase or out of phase, thus resulting in a diffraction pattern of various peak strengths (Atkins, 1998, Cheetham *et al*., 1994, West, 1999).

2.2.1 Powder X-ray Diffraction (PXRD)

PXRD relies on the diffraction of an infinite number of randomly orientated crystallites that are in a powder form. Particle size of the powder has proved to be of

immense importance, as a too small size will result in peak broadening with decreased peak resolution. This technique has established itself to be one of the most useful ways in determining formation of new materials, as each material has its own unique pattern. Unfortunately the main weakness of this technique is determining of the exact structure of a material from powder, as this is not a trivial matter (Atkins, 1998, Cheetham *et al*., 1994, West, 1999).

All samples were ground up using a mortar and pestle in air until the correct particle size was acquired. The powder was then placed on a zero-background sample holder, levelled out and inserted into a Bruker D2 Phaser powder diffractometer. The diffractometer employed a copper (1.54Å) incident beam, with a single fixed sample stage and a Lynxeye position sensitive detector. All samples were scanned through a range 5°-50°, 2θ, with a step size of 0.01° and the total run time of 13 minutes.

2.2.2 Single Crystal X-ray Diffraction (SCXRD)

SCXRD utilises a monochromatic X-ray beam to determine the precise position of atoms within a structure. It is able to achieve this by obtaining various reflections from the crystal (at different angles) when the beam passes through it. Once all the reflections with their relevant intensities are obtained, all structural data (bond lengths, angles, molecular conformations, packing, unit cell dimension and space groups) can be acquired (Atkins, 1998, Cheetham *et al*., 1994, West, 1999).

Currently the only problem plaguing this technique is that relatively large single crystals are required that are free from defects. Obtaining large single crystals of a material is not always easy, especially when the chemistry becomes more complex.

All SCXRD determinations were carried out at -100°C, and intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K_α radiation (50kV, 30mA) using the APEX 2 (Bruker, 2005a) data collection software. The collection method involved ω-scans of width 0.5° and

512x512 bit data frames. Data reduction was carried out using the program *SAINT+* (Bruker, 2005b).

Crystal structures were solved by direct methods using *SHELXTL* (Bruker, 1999). Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using *SHELXTL*. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using WinGX (Farrugia, 1999), SHELX 97 (Sheldrick, 1997), PLATON (Spek, 2003), Mercury (Macrae *et al.*, 2006) and ORTEP-3 (Farrugia, 1997).

2.3 Lattice Energy Calculations.

Lattice energies associated with crystals can be obtained by theoretical means. It utilises force fields which contain many adjustable parameters to provide information with regard to molecular and intermolecular properties (Dunitz *et al.*, 2005, Gavezzotti, 2003).

There are many problems associated with lattice energy calculations. A major problem currently being faced is the definition of atomic charges, as there is no default method (Mulliken, Hirshfield and Bader charges). These differences in charge definition coupled with changes in other parameters will inevitably lead to differences in the overall stabilization energy obtained.

In this study the Oprop module associated with the OPiX program suite was utilised which was designed for organic molecules (Gavezzotti, 2003). The module provides insight into molecule-molecule or fragment-fragment interaction energy (Omondi *et al.*, 2005, Gavezzotti, 2003) as well as the corresponding distances and angles between the molecules. This is achieved by looking at atom-atom interactions of a reference molecule group (*i*) with its surrounding molecular groups (*j*) within a

specific distance (Gavezzotti, 2003). The module utilises the UNI force field with Mulliken point charges generated by the program itself (removing the need to determine charges elsewhere) and the following equation in the energy calculations (Gavezzotti, 2003).

$$E(pot,tot) = \Sigma_i \Sigma_j E(i,j) \qquad E(i,j) = A \exp(-BR_{ij}) - CR_{ij}^{(-6)} + q_i q_j / R_{ij}$$

where A, B, C are parameters associated with the atom types involved, q_i and q_j are charges assigned to the atoms, and R_{ij} is the distance between any two atoms i and j in different molecules (Gavezzotti, 2003).

2.4 Thermal Methods

2.4.1 Thermogravimetric Analysis (TGA)

TGA is a method that records a change in weight of the material as a function of either heat or time. It does this by using a specified weight of sample and then applying a constant rate of heat to it. The sample then escapes/decomposes at a specific temperature, which leads to a step like decomposition of the material within the plotted graph. The step size is dependant on the weight lost by the sample, and this trend continues until the material is either decomposed or reaches a specified temperature (West, 1999).

TGA analysis was done on 8-20 grams of sample, which was added to ceramic pans, and placed into a TGA Perkin Elmer STA 6000 at 25^{o}C under nitrogen. A constant heating rate of 10^{o}C/min was then applied under atmospheric condition up to 650^{o}C/750^{o}C.

2.4.2 Differential Scanning Calorimetry (DSC)

DSC allows us to quantitatively measure enthalpy changes as a function of temperature or time. It makes use of two sample pans, one of which contains the relevant sample whilst the other is empty and is referred to as the reference. Both these pans are placed on the heating stage next to one other, and both undergo the same

heating rate. The only difference is that the sample pan will undergo enthalpy changes upon heating and/or cooling, whereas the reference pan will not. This enthalpy change is plotted on to a graph in terms of peaks pointing upwards and downwards. The peaks pointing upwards relates to exothermic changes whereas peaks pointing downwards refer to endothermic change. The quantitative measure of these changes is found by the integration of the peak area (West, 1999).

A Mettler Toledo DSC 822 instrument was used for this project, in which 40µl aluminum sample pans were used. Holes were punched on both the reference and sample pans before sealing. All samples underwent a cooling phase from 25^{o}C - -40^{o}C and then a heating phase at 10°C per minute to just above its melting point as determined by TGA. The Star$_e$ software computer package was used to analyse all DSC curves obtained.

2.5 Spectroscopic Techniques

2.5.1 Ultraviolet-visible spectroscopy (UV-Vis)

UV-Vis is a spectroscopic technique that works by passing a light that is in the visible to ultra-violet range through a sample, thus resulting in the excitation of the bonding electrons. The adsorption peaks obtained can be linked with the type of bonding interactions occurring within the species. Samples can range from solids to gases and is dependant on the instrument used. A useful feature of this technique with respect to this work is in the determination of the electronic transition in CT complexes (Skoog *et al*., 1998).

Solid state UV-Vis was carried out using a Cary 500 Varian UV-VIS-NIR spectrophotometer. Crystals were placed into the pathway of the beam and scanned from 800nm-300nm at 0.5nm per second.

CT complexes were formed in solution, upon addition of the donor species. Five drops of this solution was placed in a 1cm cuvette and filled with the appropriate solvent.

The cuvette was then placed in an Analytikjena SPECORD 50, and samples were ran from 200-900nm.

2.5.2 Infrared Spectroscopy

Infrared spectroscopy makes uses of the infrared region, to identify functional groups found within molecules (Skoog *et al*., 1998, http://orgchem.colorado.edu). It is able to achieve this by supplying enough energy to the molecule to induce vibrations or rotations (http://orgchem.colorado.edu). Absorption only occurs once the specific molecular vibration matches the radiant energy.

All CT ATR-IR determination was done in the near IR range, on a Bruker Vertex 70 at 32 scans per minute with a resolution of 4. Samples were ground up to a powder and placed on the sample area.

2.6 References

Atkins, P.W. (1998). Physical Chemistry, 6th edition, Oxford University Press, chapter 21.

Bruker (1999). SAINT+. Version 6.02. (includes XPREP and SADABS) Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2005a). APEX2. Version 2.0-1. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2005b). SAINT-NT. Version 6.0. (includes XPREP and SADABS) Bruker AXS Inc., Madison, Wisconsin, USA.

Cheetham, A. K. & Day, P. (1994). Solid State Chemistry: techniques, 4th edition, Oxford University Press.

Farrugia, L. J. (1997). J. Appl. Cryst. 30, 565.

Farrugia, L. J. (1999). J. Appl. Cryst. 32, 837.

Gavezzotti, A. (2003). OPiX, A computer program package for the calculation of intermolecular interactions and crystal energies, University of Milano, 2003.

Macrae, C.F., Edgington, P.R., McCabe, P., Pidcock, E., Shields, G.P., Taylor, R., Towler, M., van de Streek, J. (2006). J. Appl. Cryst., 39, 453.

Omondi, B., Fernandes, M. A., Layh, M., Levendis, D. C., Look, J. L., Mkwizu, T. S. P. (2005). CrystEngComm, 690.

Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Gottingen, Germany.

Skoog, D. A., Holler, F. J., Nieman, T. A. (1998). Principles of Instrumental Analysis, 5th edition, Thomson Learning, chapter 14, 16, 17.

Spek, A. L. (2003). J. Appl. Cryst. 36, 7.

West, A.R. (1999). Basic Solid State Chemistry, 2nd edition, John Wiley & Sons, chapter 3, 4.

http://orgchem.colorado.edu/hndbksupport/irtutor/IRtheory.pdf.