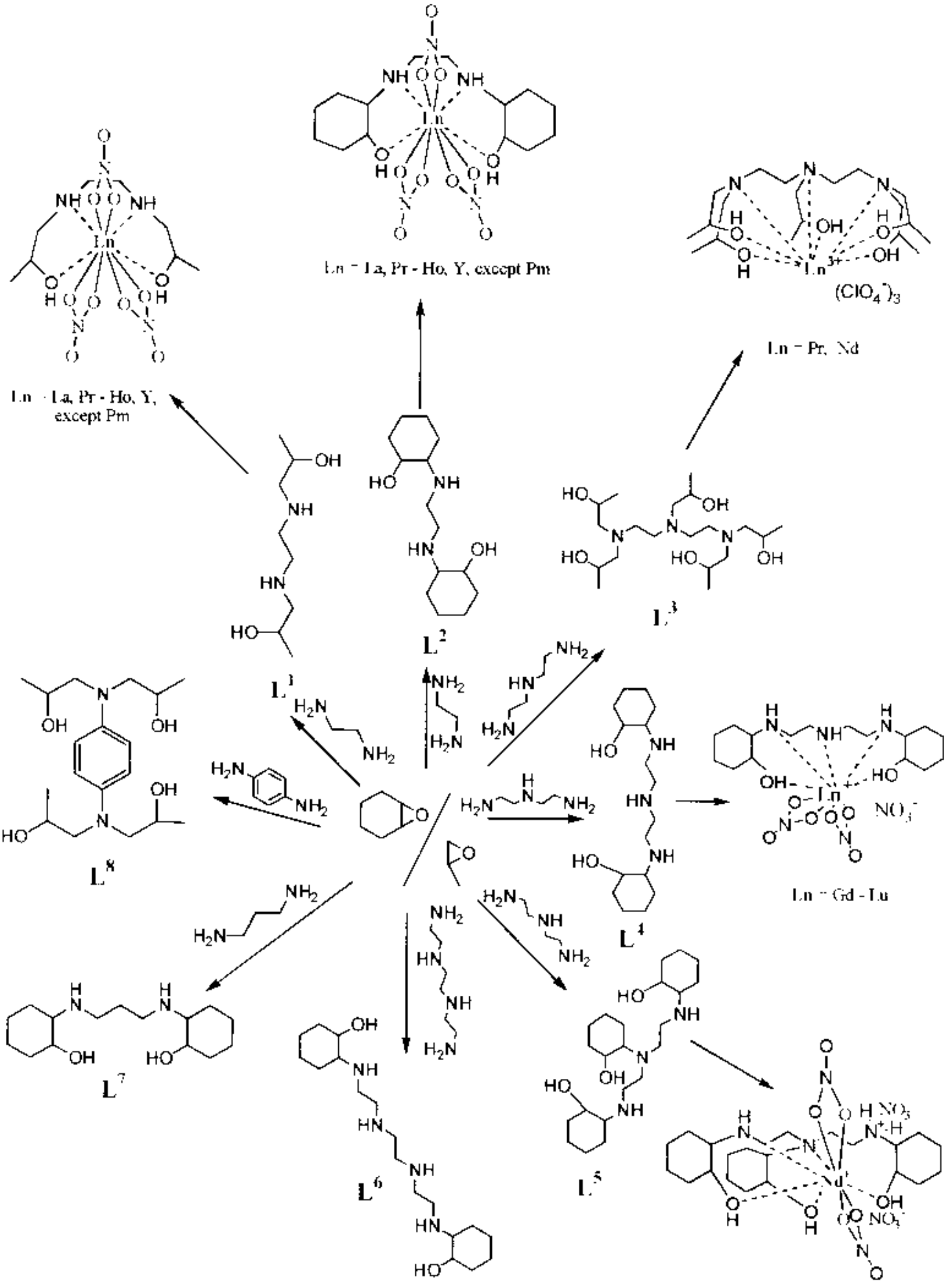
ABSTRACT

The increasing concentrations of carbon dioxide in the atmosphere and its contributions to global warming have spurred much research interest in its activation and industrial utilisation. However, CO_2 is thermodynamically and kinetically stable and thus its utilization to form industrially useful carbonaceous materials has been a great challenge. Thus the recent preliminary report by Barrett Adams et al of an unusual water tolerant formation of polymeric lanthanide(III) oxalates from atmospheric CO_2 was of great interest. Metal salts are known to activate CO_2, which may result in the formation of oxalate bridging complexes, but invariably this requires total exclusion of water. To determine the role of the lanthanide metal ions, novel mononuclear lanthanide(III) complexes were synthesized and their interactions with CO_2 studied.

The acyclic lanthanide(III) complexes were synthesised from alkoxyalkylamines utilizing epoxides. Of the 8 novel alkoxyalkylamines synthesized and characterized 5 formed mononuclear Ln(III) complexes that were isolated and characterised, ***Scheme 1***.



Scheme 1 Summary of the alkoxyalkylamines formed from epoxides and their metal complexes.

A synthetic study on the ease of formation of Ln(III) oxalates from two (2) environmental pollutants, CO_2 and nitrogen dioxide (NO_2), was done. This study investigated the role of NO_2 and the reaction conditions under which these oxalates could be formed. The role of solvents, and the effects of the variation of temperature were also examined.

Labelled CO_2 ($^{13}CO_2$) studies established the conversion of CO_2 to $C_2O_4^{2-}$ anions when Fast Atom Bombardment – Mass Spectroscopy (FAB-MS) studies confirmed the formation of $\{[Pr_2(^{13}C_2O_4)_3(H_2O)_6].4H_2O\}_n$.

Oxalate deposition occurred under a variety of conditions from temperatures ranging from -17^0C to 60^0C and from a variety of solvents such as methanol, ethanol, acetonitrile, nitromethane, ether, tetrahydrofuran, and most importantly from water. By varying the temperature and the solvent of the reaction the NO_x species present was also varied. At low temperatures, of *ca.* 5^0C, the major NO_x species are N_2O_4 and N_2O_3 (in dry solvents), but at higher temperatures, of *ca.* 100^0C, the major NO_x species is NO_2.

Benzene derivatives; phenol, paracresol, nitrobenzene, salicylaldehyde, benzaldehyde, 4-chloroaniline, 4-nitrobenzene and benzoquinone were added to the reaction mixtures to trap the NO_x^- cation species that were being formed. The NO_x^- cation species formed after the reduction of CO_2 to $C_2O_4^{2-}$ could act as electrophiles and the subsequent aromatic electrophilic substitution products would be isolated and characterised. These revealed formation of only nitration products in average yields of *ca.* 55%. This confirms the presence of the nitronium ion, NO_2^+. We therefore propose that NO_2 is the NO_x species responsible for the reduction of CO_2, but no $CO_2^{\cdot-}$ radical anions are involved in the mechanism in which oxalate anions are formed.

Lanthanides are hard- Lewis acids and thus preferentially bind with hard- Lewis bases. The alkoxyalkylamines, $\mathbf{L^1}$ – $\mathbf{L^8}$, possess both nitrogens and oxygens and thus are good groups for binding with lanthanides. The direct reaction between methyl oxirane (propylene oxide) or 1,2-epoxy-cyclohexane (cyclohexane oxide) with ethylenediamine, diethylenetriamine, triethylenetetramine, 1,3-diaminopropane and 1,4-phenylenediamine resulted in the alkoxyalkylamines $\mathbf{L^1}$- $\mathbf{L^8}$. Direct reaction of the alkoxyalkylamines,

L^1- L^5, with lanthanide(III) salts in a ratio of *ca.* 0.7:1 respectively yielded the acyclic mononuclear lanthanide(III) complexes. X-ray crystallography studies on the complexes of **$NdL^1(NO_3)_3$**, **$LnL^2(NO_3)_3$, Ln** = La, Sm and **$LnL^4(NO_3)_3$, Ln** = Tb, Er revealed the low symmetry of the coordination polyhedron, extensive hydrogen bonding and anhydrous nature of these complexes.

Luminescent studies on the Ln(III) complexes, from the tetradentate (**L^1**, **L^2**) and pentadentate (**L^4**) ligands, **$LnL^1(NO_3)_3$, Ln** = Eu, Tb; **$TbL^2(NO_3)_3$** and **$TbL^4(NO_3)_3$** showed that the luminescence decay behaviour is temperature independent, single exponential and as expected that there was no sensitisation from the ligands.

The mixed Eu^{3+}/Dy^{3+} complex system **$Dy_{1-x}Eu_xL^1(NO_3)_3$** was studied in more detail. The dipolar coupling constant was calculated from the bimolecular $Eu^{3+}(^5D_0)$-to-Dy^{3+} energy transfer rate 2.7×10^3 m^6s^{-1} derived from a corresponding Stern- Völmer plot and found to be 2×10^{-51} m^6s^{-1}. This relatively strong Eu^{3+}/Dy^{3+} coupling interaction is about 10 times that (7×10^{-52} m^6s^{-1}) calculated for europium-to-dysprosium dipole-dipole energy transfer in dinuclear systems across phenolate Eu^{3+}-O-Dy^{3+} bridges. The energy transport regime in **$EuL^1(NO_3)_3$** was found to be typical of the dynamic regime whereby energy migration over the Eu^{3+} sub-lattice occurs at a much faster rate than Eu^{3+}-to-Dy^{3+} energy transfer. Therefore both processes, energy transfer and energy migration, are very efficient.

Overall, two important accomplishments are reported: i) an extraordinary water tolerant process by which the net reaction is activation, reduction and coupling of atmospheric CO_2 to $C_2O_4^{2-}$. This will provide significantly new insight into the activation of CO_2 and might contribute to its increased use as a carbonaceous starting material. ii) The synthesis of novel acyclic alkoxyalkylamines and subsequently mononuclear lanthanide(III) complexes. The alkoxyalkylamines are attractive for the formation of stable anhydrous Ln(III) complexes with the potential as starting materials for the preparation of robust polyanionic chelates. These chelates are required for metal ion transport in luminescent devices and in magnetic resonance imaging (MRI) contrast enhancement and radiological agents. The Ln^{3+} coordination sites are not satisfied by the ligands and therefore the complexes could also be used for catalysis and aggregation.