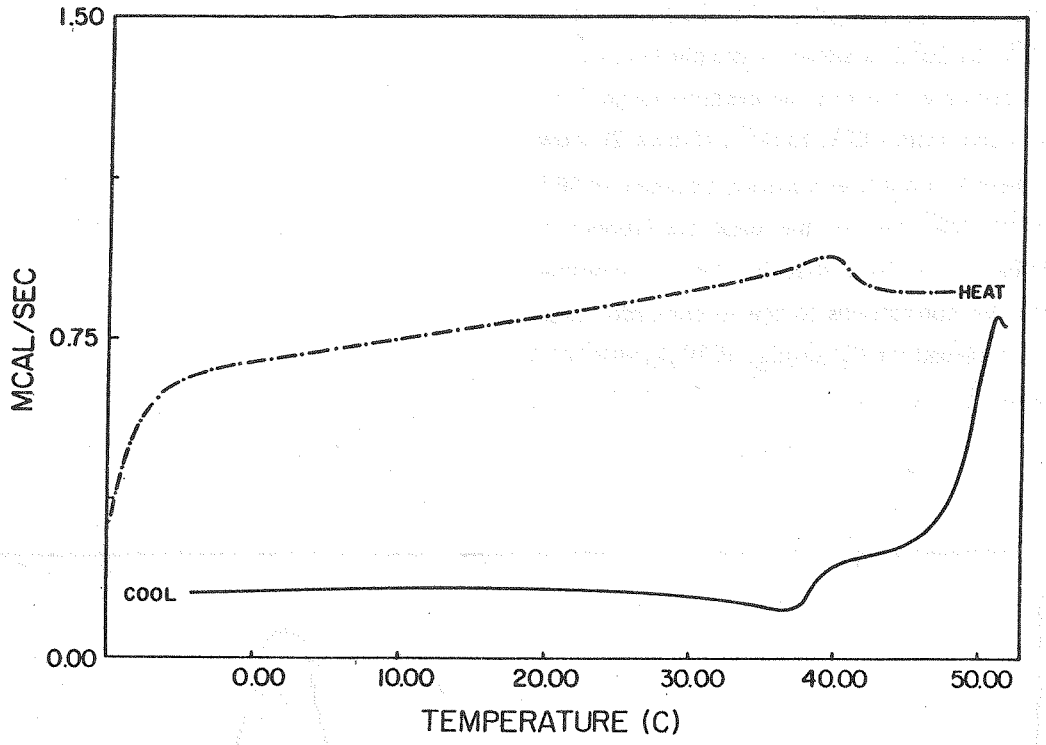

Figure 2 . Differential scanning calorimetry of $[Mn(urea)_6](ClO_4)_3$.

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Jahn-Teller-distorted geometry. The DSC curve taken from -60°C to 20°C is simply a straight line, i.e., no transition occurs within this temperature range. However, the curve from - 10°C to 50°C (Figure 2) shows an endothermic transition occuring between 16.86°c to 43.77°C. The area of the peak corresponds to 1.31 kJ/mole. It is likely that the observed endothermic transition corresponds to the second-order phase transition observed for $[Cr(urea)_6]$ $(C10_4)_3$ near room temperature.[8]

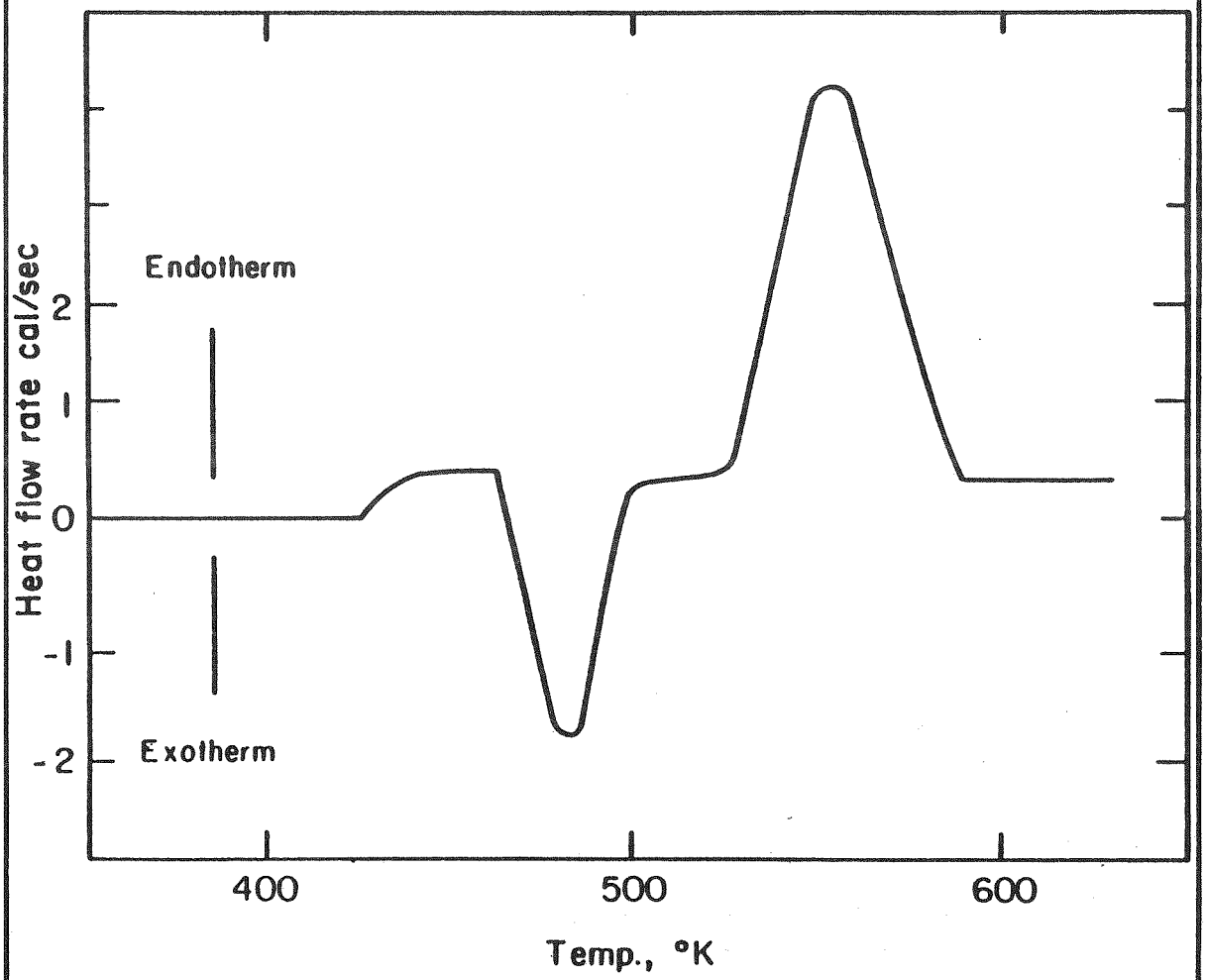

Figure 1. A typical Differential Scanning Calorimetry curve.

Differential Scanning Calorimetry of Hexaurea manganese (III) perchlorate

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Thermal analysis can be defined as techniques in which a few physical parameters of the system are determined as a function of temperature. Thermal methods of analysis are based on the fact that thermal energy is absorbed. or .evolved during a physical or chemical change of a samply.[1. 2] Differential Scanning Calorimetry (DSC) is the only technique which measures these changes directly in energy units. DSC was first used by Watson et al. to explain the instrumental technique developed by the Perkin-Elmer Corp. in 1963[3]. The theory of the Perkin-Elmer Caloritere has been presented by O'Neill, [4] Gray,[5] and Flynn.[6] Figure I shows a typical DSC curve.[2] An increase in enthalpy (or endothermic transformation) is represented by a peak in upward direction; an exothermic transformation is represented by a peak in the opposite direction.[2]

The basic differences between differential thermal analysis (DTA) and DSC lie in the design of the heating system and the mode of operation of the instrument.[7]

The DSC technique can determine, directly, the total heat transferred to/from the sample and the rate of a reaction, as a function of time or of temperature. DSC can be used for the measurement of specific heat, temperature and heat of fusion, phase transitions, dehydrations, decompositions; identification and analysis of solid state reactions and transformations; stability, decomposition thermodynamics and kinetics of metal comlexes; temperature and heat of crystallization. Heats of transition and specific heat can be determined with a precision of about +2%[7]

The area of the DSC curve peak is directly proportional to the enthalpy change, area = $K\Delta Hm$, where ΔH is the heat of transition (or reaction), K is the calibration coefficient, and m is the mass of reactive sample.[2]

Single crystals of $[Al(urea)_6]$ $(c10_4)_3$ doped with maganese (III) were gown from a hot solution of 60% perchloric acid nearly saturated with urea at room temperature. The urea complexes are nearly insoluble in this solution at room temperature; however, a significant amount dissolves at 75-80°C. Slow cooling of the solution in a dewar over a period of 24 hours gave single crystals. Some difficulties were experienced in growing large single crystals (≤2x2xl mm). However, suitable crystals were obtained by selective and repetitive seeding. A weighed amount of the sample was placed in the DSC-2C (Perkin-Elmer) and equilibrated at -70°C for several hours -- in one case, overnight.

Microcrystalline $[Mn(urea)_6]$ $(C10_4)_3$ was studied by differential scanning calorimetry in an attempt to identify a temperature at which the complex would cease to pseudorotate and, instead, assume a static