Uses of (−)-Propylene-1,2-diaminetetra-acetic Acid in Spectropolarimetric Titrimetry

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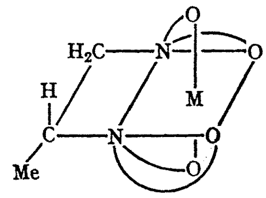
Spectropolarimetric acid–base titrimetry[1,2] and three spectropolarimetric metal ion–ligand titrations[1,3] have been described. This technique appears to offer many advantages.

(−)-Propylene-1,2-diaminetetra-acetic acid [(−)-PDTA] was prepared from (−)-propylenediamine by a modification of the method of Dwyer and Garvan.[4] This compound is a powerful chelating agent, similar in structure to EDTA; however, it is optically active and is stereospecific in its reaction with metal ions.[4,5] The free energy difference due to a methyl–acetate interaction in the D*-isomer compared to the L*-isomer approaches 3 kcal./mole;[5] this gives a minimum of 99·99% stereospecificity in reactions. The stability constants for PDTA are greater than those for EDTA for most metals in solution. The observed rotations of metal chelates and ligands are a simple linear function of their concentrations over a very wide range. The concentrations of buffers commonly used have a negligible effect on the rotations, and the effect of all ions investigated is not appreciable. A pH-rotational dependence study of (−)-PDTA showed that the molecular rotation exhibited small changes up to pH 8; however for pH > 8, it changed as much as 200° with a change of one pH unit. The effect of change in pH on certain metal chelates was even greater. A temperature–rotational study showed no appreciable change in molecular rotation over a range of 30°.



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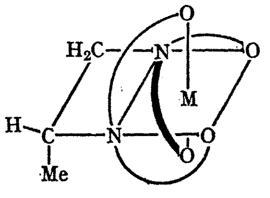

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Direct titrations of 0·01M-aluminium, strontium, and barium have been performed with (−)-PDTA, monitored with a Perkin-Elmer 141 spectropolarimeter. Lead was determined by this method over the range of 10^{-1} to 10^{-5} M. By altering the conditional equilibrium constants, it was possible to determine equimolar concentrations of zinc and cadmium, sequentially, by this method. The results compared well with those obtained by classical wet chemical methods and were accurate to within 0·5 %.

Thus it appears possible to titrate most other metals, and to determine mixtures of metals that have very similar chemical properties without the need for indicators, separations, or special conditions.

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