Application of Strain Energy Minimisation to Geometric Isomers of Metal Complexes

By MARK DWYER* and G. H. SEARLE

(*Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, South Australia* 5001)

Summary The comparisons of the experimental and calculated equilibrium ratios of the three geometric isomers of the bis(diethylenetriamine)cobalt(III) cation suggest that the 'core field' terms neglected in strain energy summations are insignificant.

THE accuracy of the prediction of molecular structures of cobalt(III) complexes based upon minimum strain energy is now established.[1] This energy, constructed from summation of bond-length deformations, angle deformations, and non-bonded contact and torsional energies has a somewhat artificial zero level, being that of a molecule strainless with respect to the above four modes.

To date, comparative calculations have been confined to the comparison of conformational isomers and internal diastereoisomers.[1] This choice was logical, since in these systems the core field terms (the interaction of the metal ion field with ligand atoms), not specifically considered in the summation, should be approximately constant. This exclusion effectively adds the 'core field' energy to the zero level, but these contributions should be essentially equal for each isomer in the above instances. However, for geometric isomers, where the contributions might differ significantly, there exists the possibility of zero level imbalances, resulting in possible poor correlation of calculated and experimental equilibrium data. The magnitude of such zero level imbalances is not known.

For the $[Co(dien)_2]^{3+}$ (dien = diethylenetriamine) geometric isomers a moderately good correlation of experimental and calculated data has been obtained. Strain energies[2] of 17·2, 17·2, and 17·6 kcal mol^{-1} were obtained for the *s–cis-*, *u–cis-*, and *trans-isomers*,[3] respectively. These values are exact within the force field utilised[1] and have significance only as their differences, which may be equated to the ΔH between isomers. Their magnitudes would imply approximately equal concentrations of the *s–cis-*, *u–cis-*, and *trans*-isomers under equilibrium conditions. Experimentally the *trans*-isomer is present in highest proportion (for the chlorides and bromides *s–cis*:*u–cis*:*trans* = 7:28:65), but these proportions show a dramatic dependence upon the counter ion (for example, phosphate ion modifies the above equilibrium proportions considerably).[4]

The apparent failure of the minimisation technique can be partially ascribed to the comparison of calculated ΔH with experimental ΔG values. The sensitivity[4] of the isomer proportions to the counter ion suggests in these instances significant zero level imbalances believed to be a consequence of specific ion-pairing. The magnitude of these imbalances precludes any estimate of the variation of the core field terms. However, for counter ions, upon which the isomer ratio shows no dependence (chloride, bromide), calculated and experimental data correlate within acceptable limits. Under these conditions variation of the core field term appears to be insignificant compared with other assumptions in the minimisation method normally taken as valid.

Theoretical and experimental work is proceeding to obtain the ion-pair stereochemistries and the magnitude of imbalances ascribed to such specific ion pairs.

(*Received, 24th March* 1972; *Com.* 491.)

---

[1] (a) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 2617; (b) D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 2663; (c) M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 2610; (d) R. J. Geue and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 2981.

[2] Force field ref. 1a. Computer program MOL adapted from R. Boyd (1966), modified by M. R. Snow (1968), I. E. Maxwell (1969), an d M. Dwyer (1970), M. Dwyer and R. J. Geue (1970, 1971).

[3] Nomenclature as in F. R. Keene and G. H. Searle, *Inorg. Chem.*, 1972, **11**, 148.

[4] F. R. Keene and G. H. Searle, unpublished results.