

## Inorganic Six-membered Ring Inversion. The Inversion Barrier in the Tris(pentasilphane-1,5-diyl)platinate(IV) Anion

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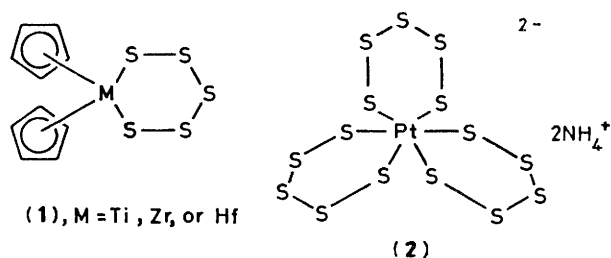
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<sup>195</sup>Pt N.m.r. studies of the ring inversion in the tris(pentasilphane-1,5-diyl)platinate(IV) anion reveal two conformations separated by a barrier ( $\Delta G^\ddagger$  at 273 K) of  $50.5 \pm 1.3$  kJ mol<sup>-1</sup>.

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Practically all examples of measured barriers to inversion of six-membered rings are found in organic compounds.<sup>1</sup> The few examples in the literature of inversion in rings not containing a carbon atom relate to the MS<sub>5</sub> rings in organo-

metallic derivatives of the group 4b elements (1).<sup>2,3</sup> In these cases inversion of the MS<sub>5</sub> ring was followed by <sup>1</sup>H n.m.r. spectroscopy of the cyclopentadienyl groups. We now report our observations of the PtS<sub>5</sub> ring inversion process in the



$\text{PtS}_5^{2-}$  (2) anion by means of  $^{195}\text{Pt}$  n.m.r. spectroscopy. This is the first example of ring inversion in a purely inorganic compound.

Diammonium tris(pentathio-1,5-diyl)platinate(IV) (2) first discovered by Hofmann and Höchtlen,<sup>4</sup> has been investigated recently by two of us<sup>5,6</sup> and gives stable enantiomers. The all-chair  $C_3$  conformation of the anion in the racemic solid has been confirmed by X-ray crystallography.<sup>6,7</sup> One can also envisage other conformations of the anion where the  $C_3$  axis has been lost, for example those with one  $\text{PtS}_5$  ring inverted, or with one or more rings in a non-chair conformation.

The interconversion between these conformations must occur by inversion of one or more of the  $\text{PtS}_5$  rings and should be amenable to study by  $^{195}\text{Pt}$  n.m.r. spectroscopy. Such a process is in fact observed.

The 17.2 MHz  $^{195}\text{Pt}$  n.m.r. spectrum of (2) at ambient temperature in  $[\text{D}_4]\text{methanol}$  shows a single broadened line. The line sharpens on warming and broadens followed by sharpening on cooling. The maximum line width is observed at  $273 \pm 5$  K. At this temperature there is also a point of inflection in the variation of chemical shift with temperature. This is consistent with the separation of a minor peak to a position at lower frequency.

The position of this minor peak was initially found in spectra run at 77.2 MHz and later confirmed at 17.2 MHz. The shifts of the two resonances (at 195 K relative to  $\bar{\nu}^{195}\text{Pt} = 22.4$  MHz) are + 2067 (major) and + 1970 p.p.m. (minor). Integration of the 77.2 MHz spectrum gives an equilibrium constant of 30, from which  $\Delta G = 5.4$  kJ mol<sup>-1</sup>.

Extrapolation of the chemical shift variation at low temperature back to the coalescence point in the 17.2 MHz spectrum gives  $\Delta\nu = 2020 \pm 120$  Hz (at 17.2 MHz) from which the Anet equations<sup>8</sup> give  $\Delta G^\ddagger$  in the direction minor  $\rightarrow$  major = 45.1 kJ mol<sup>-1</sup>. The free energy of activation in the forward direction (major  $\rightarrow$  minor) is thus 50.5 kJ mol<sup>-1</sup>. We estimate errors of  $\pm 1.3$  kJ mol<sup>-1</sup> based on our experimental uncertainties.

We presume that the observed resonances are from the  $C_3$  all-chair conformation, and from a conformation with one

**Table 1.** Barriers to inversion of  $\text{MS}_5$  rings (kJ mol<sup>-1</sup>) from references 2, 3, and this work.

Row	M in (1)	Barrier	M in (2)	Barrier
3	Ti	76	Ni	—
4	Zr	49	Pd	—
5	Hf	58	Pt	51

$\text{PtS}_5$  ring inverted, although at present we cannot assign which is the major conformation. The optical stability of the anion rules out any dissociation-association mechanisms for the ligands on platinum as a cause of the effects observed in the n.m.r. spectra, and other explanations such as ion pairing or solvation can also be dismissed. Only for ions which have a small volume and consequently a high charge density (*e.g.* some complexes of Be) has this sort of mechanism been observed to give dynamic changes in n.m.r. spectra. Our first experiments on the current compound were performed in  $\text{Me}_2\text{SO}$  (in anticipation of a higher barrier) and give entirely similar results to those in methanol.

The observed barriers reported for  $\text{MS}_5$  rings are recorded in Table 1. The factors upon which ring inversion barriers in organic six-membered rings are based include torsional strains and bond angle deformation. Whilst it seems certain that the barriers observed in these  $\text{MS}_5$  rings derive in large part from the S-S torsion potential,<sup>1</sup> the effects of M-S bond length and rotation barrier, S-M-S bond angle size and deformation, the formal oxidation state of the metal, and the nature of the M-S bonding remain to be quantified.

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## References

- See for example: F. G. Riddell, 'The Conformational Analysis of Heterocyclic Compounds,' Academic Press, London, 1980.
- E. W. Abel, M. Booth, and K. G. Orrell, *J. Organomet. Chem.*, 1978, **160**, 75.
- J. M. McCall and A. Shaver, *J. Organomet. Chem.*, 1980, **193**, C37.
- K. A. Hofmann and F. Höchtlen, *Ber.*, 1903, **36**, 3090.
- R. D. Gillard and F. L. Wimmer, *J. Chem. Soc., Chem. Commun.*, 1978, 936.
- E. H. M. Evans, R. D. Gillard, J. P. G. Richards, and F. L. Wimmer, in preparation.
- M. Spangenberg and W. Bronger, *Z. Naturforsch., Teil B*, 1978, **33**, 482.
- F. A. L. Anet, I. Yavari, I. J. Ferguson, A. R. Katritzky, M. Moreno-Manas, and M. J. T. Robinson, *J. Chem. Soc., Chem. Commun.*, 1976, 399.