wavelengths suggests that in dibenzenechromium the rings retain considerable benzenoid character.[8]

Acknowledgment.—The authors wish to thank Dr. S. Valcher, who kindly provided a sample of Cr(bz)$_2$I.

[8] Regarding the symmetry of dibenzenechromium compounds, two alternative molecular point groups have been proposed: D$_{3d}$[9a] or D$_{6h}$.[9b] Our finding that the π–π^* transition is not far from being benzenoid is in accordance with the D$_{6h}$ symmetry.

[9] (a) H. P. Fritz and W. Lüttke, Proceedings of the 5th International Conference on Coordination Chemistry, London, Special Publication No. 13, The Chemical Society, London, 1959, p 123; F. Jellinek, *Nature*, **187**, 871 (1960); F. Jellinek, *J. Organometal. Chem.*, **1**, 43 (1963); (b) H. P. Fritz, W. Lüttke, H. Stammreich, and R. Forneris, *Chem. Ber.*, **92**, 3246 (1959); F. A. Cotton, W. A. Dollase, and J. S. Wood, *J. Am. Chem. Soc.*, **85**, 1543 (1963); A. Haaland, *Acta Chem. Scand.*, **19**, 41 (1965).

[10] Centro Nazionale di Chimica dei Composti di Coordinazione ed Elemento-organici del C.N.R., Sezione IV, Ferrara, Italy.

[11] Centro Nazionale di Chimica delle Radiazioni e dei Radioelementi del C.N.R., Sezione III, Bologna, Italy.

ISTITUTO CHIMICO DELL'UNIVERSITÀ
FERRARA, ITALY
ISTITUTO CHIMICO DELL'UNIVERSITÀ
BOLOGNA, ITALY

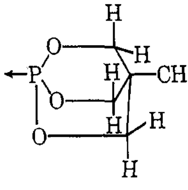
FRANCO SCANDOLA[10]
VINCENZO BALZANI[11]
VITTORIO CARASSITI[10]

RECEIVED NOVEMBER 10, 1965

Nuclear Magnetic Resonance Spectra of Symmetrical Spin Systems Containing Phosphorus

Sir:

During the past 2 years, several papers[1-6] have appeared describing briefly the proton magnetic resonance spectra of symmetrical spin systems for inorganic compounds containing two or more phosphorus nuclei. These spectra seem to have caused some mystification, the features which could not be explained on a "first-order" basis being attributed to "phosphorus–phosphorus or long-range coupling." In certain cases attempts have been made to treat the spectrum using a simplified nuclear spin system. Verkade, *et al.*,[6] for instance, studied the spectra of metal carbonyl complexes of the type M(CO)$_m$L$_2$, where M = Ni, Fe, Cr, Mo, and W, and L is the 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ligand (I). For each compound the spectrum of the methylene protons of the two ligand groups was examined and treated as the X part of an AA'X$_2$ subsystem, where A and A' are the two phosphorus nuclei (one in each ligand L), and the long-range coupling J'_{AX} is assumed to be zero. These authors gave no proof of the validity of their approach, but such a proof is desirable in view of the fact that, in general, it is *not* possible to use a nonsymmetrical spin system as a model for a more complex symmetrical case. In principle, the compounds investigated constitute a 20-spin system since there are 18 protons and two phosphorus nuclei. However, the methyl protons are only coupled to other nuclei to a slight extent, and they may therefore be neglected from the analysis. Moreover, all six methylene protons in one ligand are demonstrably chemically equivalent and are equally coupled to every other magnetic nucleus, provided that we consider long-range (H, H) coupling between the ligands to be zero, and they are therefore also effectively magnetically equivalent. Thus, the nuclear spin system that needs to be considered is X$_6$AA'X'$_6$, with $J_{\mathrm{XX'}} = 0$. Explicit expressions for the X transitions of the X$_n$AA'X'$_n$ case have now been given,[7] so simplification of the spin system is not necessary. However, it can readily be shown that the X transitions for an X$_n$AA'X'$_n$ system with $J_{\mathrm{XX'}} = 0$ are identical with those for an X$_{2n}$AA' system. Therefore, the compounds examined by Verkade, *et al.*,[6] could be treated as comprising X$_{12}$AA' spin systems. The reduction by these authors to X$_2$AA' spin systems is not, however, valid, as can be seen from the explicit expressions given by Harris[7] for the equivalent X$_n$AA'X'$_n$ cases. It is true that all of the X lines of the X$_2$AA' (or XAA'X') system are contained in the X$_{12}$AA' (or X$_6$AA'X'$_6$) case, but the latter has many additional lines. In particular, when $J_{\mathrm{AA'}} \gg |J_{\mathrm{AX}} - J'_{\mathrm{AX}}|$ and the X spectrum is "deceptively simple," giving approximately a triplet,[8] the extra lines of the full spin system give added width to the central band of the triplet. This fact makes the quantitative use of line widths to obtain values of J_{PP} dubious, and it may be said that the results listed by Verkade, *et al.*,[6] as crude values for J_{PP} are minimum values (which are still, of course, of some interest).



I

It is worth stressing that the "odd" appearance of spectra in these symmetrical cases[1-6] is due entirely to their symmetry. The apparent triplet appearance for the X spectrum[6,8] only occurs for strongly coupled cases, $|J_{\mathrm{AA'}}| \gg |J_{\mathrm{AX}} - J'_{\mathrm{AX}}|$, and departure from it must be considered as *normal*. The opposite extreme (a simple doublet[7]) is obtained[6,9] when $|J_{\mathrm{AA'}}| \ll |J_{\mathrm{AX}} - J'_{\mathrm{AX}}|$ and $J'_{AX} \approx 0$. The sharp outer pair of lines in the X spectrum will always be present when there is a spin system with two groups of chemically equivalent nuclei of the type X$_n$X'$_n$X''$_n$ . . . AA'A'' . . . . Spectra of such cases for phosphonitrilic compounds (NPX$_2$)$_r$ were illustrated by Allen, *et al.*[5] The sharp X doublet lines arise from A spin states with the maximum (all spins α) and minimum (all spins β) values of F_z(AA . . .). The separation of the doublet is given by

---

[1] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **4**, 419 (1965).

[2] R. G. Hayter, *ibid.*, **3**, 711 (1964), and other papers in this series.

[3] R. B. King, *ibid.*, **2**, 936 (1963), and other papers in this series.

[4] D. S. Payne, H. Nöth, and G. Henniger, *Chem. Commun.* (London), 327 (1965).

[5] G. Allen, D. J. Oldfield, N. L. Paddock, F. Rallo, J. Serregi, and S. M. Todd, *Chem. Ind.* (London), 1032 (1965).

[6] J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).

[7] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

[8] R. J. Abraham and H. J. Bernstein, *ibid.*, **39**, 216 (1961).

[9] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

$J_{AX} + J_{A'X} + J_{A''X} + \ldots$. The fractional intensity of the X spectrum that is in the sharp doublet depends on r, the number of nuclei of the A type. It can readily be shown to be $(^1/_2)^{r-1}$. Thus, for the spectra illustrated by Allen, *et al.*,[5] for $r = 3, 4, 5, 6, 7, 8$, this fraction is $^1/_4$, $^1/_8$, $^1/_{16}$, $^1/_{32}$, $^1/_{64}$, and $^1/_{128}$, thus readily explaining the apparent "disappearance" of the doublet as r increases.

School of Chemical Sciences
University of East Anglia
Norwich, England
R. K. Harris

Received September 27, 1965

Book Review

Mechanisms of Inorganic Reactions. Edited by Robert F. Gould. Advances in Chemistry Series, No. 49. American Chemical Society, Washington, D. C. 1965. 266 pp. 16 × 23 cm. $8.00.

This volume contains the proceedings of the 1964 Summer Symposium of the Division of Inorganic Chemistry. An introductory paper by J. C. Bailar, Jr., ten invited papers, and related discussions are included. The papers are more or less review in nature, and the discussions tend to be lengthy and rather more opinionated than thoughtful. Probably because of my own research interests, I particularly enjoyed the papers by Basolo and Duke. On the whole, however, the book did not come up to the expectations of this interested chemist.

One can hardly read the book without feeling the need for a new approach to the unsolved problems in coordination compound mechanisms. The need for original insight in this research area is brought sharply into focus by the number of places in this book wherein a question remains unanswered (even in principle) by either theory or experiment. Certainly we still have a long way to go before we achieve a satisfactory degree of understanding of substitutions in octahedral complexes.

The book will be useful to the chemist who deals with inorganic mechanisms, particularly those of coordination compounds. The ten papers provide up-to-date entries into ten specific systems. With most of the papers, there is an excellent list of references. It is doubtful if the book could be used as a general reference in the area of inorganic mechanisms; the reader would get a very unbalanced diet indeed.

Metcalf Chemical Laboratories
Brown University
Providence, Rhode Island
John O. Edwards

BOOKS RECEIVED

February 1966

Beat Meyer, Editor. "Elemental Sulfur, Chemistry and Physics." John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1965. ix + 390 pp. $15.00.

B. N. Figgis. "Introduction to Ligand Fields." John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1966. v + 351 pp. $9.50.