

# Correspondence

## The Magnetic Properties of Five-Coordinate Diiodotris(diphenylphosphine)nickel(II)

Sir:

The title compound was first described by Hayter in 1963 along with the corresponding chloride and bromide.<sup>1</sup> Five-coordinate structures were assigned to all three compounds on the basis of various physical measurements. The chloride and bromide are essentially diamagnetic but for the iodide a room-temperature moment of 1.48 BM was obtained. Hayter drew attention to the anomalous magnetic moment but offered no explanation. Subsequently, Bertrand and Plymale<sup>2</sup> verified Hayter's structural assignment by X-ray studies. These workers also obtained an anomalous room-temperature magnetic moment (1.29 BM) for Ni(PH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>I<sub>2</sub> which they explained in terms of a thermal population of a low-lying triplet state. From this they deduced that the magnetic "crossover" occurs at a lower field strength for nickel(II) than for cobalt(II). The reported magnetic anomaly and its suggested explanation have been carried over and used by others<sup>3,4</sup> in discussions of five-coordinate chemistry.

In the light of recent information<sup>4,5</sup> on the factors governing the spin multiplicity of five-coordinate nickel(II), it seemed surprising to us that a field of three phosphorus and two iodine atoms should produce other than a completely low-spin nickel(II) compound. This prompted a reinvestigation of Ni(PH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>I<sub>2</sub>. The compound was prepared as described by Hayter and characterized by chemical analysis and physical properties. Magnetic susceptibility measurements by the Gouy method were made over the temperature range 115–323°K. The data in Table I show that Ni(PH-

Temp, °K	$10^6 \chi_M^{\text{cor}}, ^a$ cgsu	$\mu_{\text{eff}}$ , BM
323.1	151	0.63
293.1	156	0.61
263.1	162	0.59
233.1	188	0.59
203.1	202	0.58
173.1	179	0.50
143.1	188	0.47
115.1	219	0.45

<sup>a</sup> The diamagnetic correction of  $483 \times 10^{-6}$  cgsu was calculated from Pascal's constants.

(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>I<sub>2</sub> possesses the magnetic properties expected for a normal low-spin nickel(II) compound. The small residual paramagnetism, which within experimental error is almost independent of temperature, corresponds to a room-temperature moment of  $\sim 0.60$  BM. The

very slight increase in susceptibility with decrease in temperature that was observed could be caused by a trace of paramagnetic impurity. It should be noted that the explanation of Bertrand and Plymale<sup>2</sup> for their (much larger) observed paramagnetism requires that the susceptibility should decrease with decrease in temperature. We conclude, therefore, that the previously reported<sup>1,2</sup> "anomalous" moments most probably arose from paramagnetic impurity. As yet only one five-coordinate nickel(II) compound is known to exist with high- and low-spin forms in equilibrium; this is dichloro[2,6-bis( $\beta$ -diphenylphosphinoethyl)pyridine]nickel(II).<sup>5</sup>

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## The Intramolecular Isomerization of Octahedral Complexes by Nonbond-Rupture Mechanisms

Sir:

In the past few years several papers have appeared which discuss intramolecular mechanisms, not involving bond rupture, for the isomerization of octahedral complexes. It is quite evident that there exists some confusion as to the number of such mechanistic paths which are possible and this apparent confusion has led to some misleading statements in the recent literature.

For the intramolecular isomerization of an octahedral complex containing bidentate ligands there are two roughly trigonal-prismatic activated complexes which can be involved in a nonbond-rupture mechanism. These may be referred to as either a Bailar type<sup>1</sup> (Figure 1a) or Rây and Dutt type<sup>2</sup> (Figure 1b).

It is the number of possible pathways leading to these two transition states which has been the subject of confusion. Springer and Sievers<sup>3</sup> discussed in considerable detail the mechanisms resulting in the formation of the trigonal-prismatic activated complexes. They viewed their formation from two points of view. One of these involves the twisting of opposite trigonal faces of the octahedron through an angle of 60° to form the transition state. Further twisting through another 60° leads to isomerization. This mechanism, which has been generically referred to as a Bailar twist, can lead

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(4) L. Sacconi, G. P. Speroni, and R. Morassi, *ibid.*, **7**, 1521 (1968), and references contained therein.  
(5) S. M. Nelson and W. S. J. Kelly, *Chem. Commun.*, 436 (1968).

(1) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958). Also proposed by W. G. Gehman, Ph.D. Thesis, Pennsylvania State University, 1954, and L. Seiden, Ph.D. Thesis, Northwestern University, 1957.  
(2) P. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).  
(3) C. S. Springer and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).