

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.¹ 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 Plymale² 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(C₆H₅)₂)₃I₂ 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^{3,4} in discussions of five-coordinate chemistry.

In the light of recent information^{4,5} 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(C₆H₅)₂)₃I₂. 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-

TABLE I

Temp, °K	$10^6 \chi_M^{00r, a}$ cgsu	μ_{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

^a The diamagnetic correction of 483×10^{-6} cgsu was calculated from Pascal's constants.

(C₆H₅)₂)₃I₂ 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 ~ 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 Plymale² for their (much larger) observed paramagnetism requires that the susceptibility should decrease with decrease in temperature. We conclude, therefore, that the previously reported^{1,2} "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(β -diphenylphosphinoethyl)pyridine]nickel(II).⁵

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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 type¹ (Figure 1a) or Rây and Dutt type² (Figure 1b).

It is the number of possible pathways leading to these two transition states which has been the subject of confusion. Springer and Sievers³ 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

(1) R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).
(2) J. A. Bertrand and D. L. Plymale, *ibid.*, **5**, 879 (1966).
(3) J. F. Steckhaus and T. Layloff, *ibid.*, **6**, 2185 (1967).
(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).

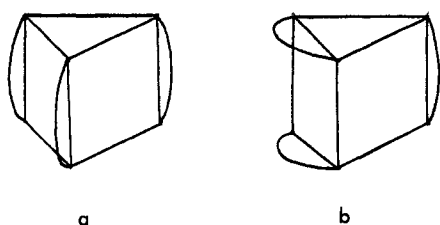


Figure 1.—(a) Bailar type of transition state; (b) Rây and Dutt transition state.

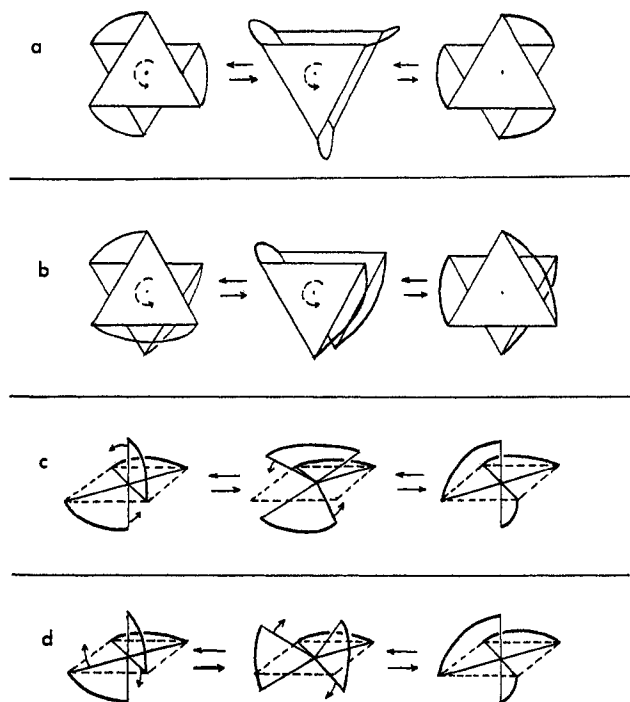


Figure 2.—(a) Bailar twist to produce a Bailar type of transition state; (b) Bailar twist to produce a Rây and Dutt transition state; (c) Rây and Dutt type of twist to produce a Bailar transition state (Springer-Sievers mechanism); (d) Rây and Dutt type of twist to produce a Rây and Dutt transition state.

to either type of transition state depending upon which pair of trigonal faces is chosen for the rotation. The Bailar twist is illustrated by Figure 2a and b.

Springer and Sievers viewed the formation of the two transition states as also being the result of a mechanism which consists of holding one chelate ring stationary while the other two rings swing in opposite directions. As first proposed,² this leads to a Rây and Dutt intermediate. Springer and Sievers pointed out that the same type of motion in the opposite direction would lead to a Bailar transition state. The Springer-Sievers and Rây-Dutt mechanisms, both of which will be referred to generically as Rây and Dutt type of mechanisms, are illustrated by Figure 2c and d.

Springer and Sievers recognized that the Bailar twist and the Rây and Dutt type of twist are really equivalent although their statement to this effect was not put quite so strongly. Their attention was focused primarily on the changes in donor-metal-donor (D-M-D) angles during the rearrangement process and it was never stated explicitly that the Bailar-twist mechanism and the Rây and Dutt type of mechanism are *completely*

identical and that they only appear different because they view the intramolecular twisting process from two different perspectives.

It should be made clear that the differences which appear to exist, from a consideration of the variations in D-M-D angles, are purely artificial. The formation of a Bailar transition state in which the ring D-M-D angles have been compressed may be viewed as the result of a Bailar twist in which the distance between the rotating trigonal faces remains fixed. The motion described by this mechanism is completely equivalent at every point to the motion which occurs during the application of a Rây and Dutt type of twist in which the chelate rings are not rigid and where the ring D-M-D angles decrease. Likewise, the formation of a Bailar transition state in which the ring D-M-D angles are 90° may be looked upon either as resulting from a Bailar twist in which the rotating trigonal faces move apart along the C_3 axis or as the result of the operation of a "rigid-ring" Rây and Dutt type of mechanism. Again, the two mechanisms are identical at each point along the path to the transition state. This exact equivalence holds for any set of D-M-D angles as well as for the formation of a Rây and Dutt transition state.

The apparent general lack of recognition that the differences between the Bailar twist and the Rây and Dutt twist are not real is manifest in at least two places in the very recent literature. Muetterties,⁴ in an analysis of intramolecular rearrangements in six-coordinate species, referred to these two paths as being distinct for tris chelates. In another instance, Broomhead, Dwyer, and Meller⁵ described models to illustrate the Bailar twist and the Rây and Dutt twist. In their article, intended for the teaching of inorganic racemization mechanisms, they failed to make any mention of the complete equivalence of these two paths.

This correspondence does not mean to suggest that one view of the intramolecular twisting mechanism be discarded in favor of another. Indeed, the two perspectives of the nonbond-rupture mechanism complement one another. Rather, it is aimed at correcting what may be an important misunderstanding. It should be absolutely clear that there is basically but one twisting mechanism which can lead to two different types of transition state depending upon its mode of execution.

(4) E. L. Muetterties, *J. Am. Chem. Soc.*, **90**, 5097 (1968).

(5) J. A. Broomhead, M. Dwyer, and A. Meller, *J. Chem. Educ.*, **45**, 716 (1968).

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The 3d Orbitals of Phosphorus and Sulfur¹

Sir:

Since the 3d orbitals of phosphorus and sulfur are not occupied in the normal states of the free atoms,

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