this species at low temperature are barely shifted from the aromatic region; the pyrrole proton signal is at 5 ppm and phenyl signals are shifted less than 2 ppm downfield. In contrast, the pyrrole proton contact shift for the presumably isoelectronic (TPP)Mn(Im)$_2^-$ is −33.6 ppm and that for (TPP)Mn(CN)$_2^-$ is −16.8 ppm at ambient temperature. Absence of significant isotropic shifts for the iron(IV) model compound and for HRP compound II has been explained by INDO–SCF[42] and extended Hückel[8] calculations that reveal efficient mixing of d_{xz}, d_{yz} orbitals with p_x, p_y orbitals of a coordinated oxo ligand. Unpaired spin density is thus localized on the oxo group at the expense of spin density transfer to the macrocycle. Data for the low-spin manganese(III) complexes can be construed as being supportive of this hypothesis. Diminished spin density at the β-pyrrole carbon atom of (TPP)Mn(CN)$_2^-$ as compared with that for (TPP)Mn(Im)$_2^-$ suggests much more efficient delocalization of spin into the cyano residue. This appears to be the case on the basis of much greater carbon-13[43] and nitrogen-15[44] chemical shifts observed for the cyano ligand vs. those for the imidazole ligand.[26] Axial ligands should thus compete with the porphyrin for unpaired spin density in the following order: oxo > cyanide > imidazolate. The oxidized cytochrome *c* peroxidase enzyme exhibits proton isotropic shifts of greater magnitude than those for horseradish peroxidase compound II.[45] Among the possible explanations for this difference is the expectation that an iron(IV) ligand such as OH$^-$ would leave greater unpaired spin on the porphyrin, as is the case for low-spin manganese(III) complexes described here.

Acknowledgment. Support from National Science Foundation Grant CHE 82-09308 is gratefully acknowledged.

---

(39) Chin, D.-H.; Balch, A. L.; La Mar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446.
(40) Simonneaux, G.; Scholz, W. F.; Reed, C. A.; Lang, G. *Biochim. Biophys. Acta* **1982**, *716*, 1.
(41) Penner-Hahn, J. E.; McMurry, T. J.; Renner, M.; Latos-Grazynski, L.; Eble, K. S.; Davis, I. M.; Balch, A. L.; Groves, J. T.; Dawson, J. H.; Hodgson, K. O. *J. Biol. Chem.* **1983**, *258*, 12761.
(42) Loew, G. H.; Herman, Z. S. *J. Am. Chem. Soc.* **1980**, *102*, 6175.
(43) Goff, H. *J. Am. Chem. Soc.* **1977**, *99*, 7723.
(44) (a) Morishima, I.; Inubushi, T. *J. Chem. Soc., Chem. Commun.* **1977**, 616. (b) Morishima, I.; Inubushi, T.; Neya, S.; Ogawa, S.; Yonezawa, T. *Biochem. Biophys. Res. Commun.* **1977**, *78*, 739. (c) Morishima, I.; Inubushi, T. *J. Am. Chem. Soc.* **1978**, *100*, 3568.
(45) Satterlee, J. D.; Erman, J. E. *J. Biol. Chem.* **1981**, *256*, 1091.

Contribution from the Department of Chemistry, University of the Western Cape, Private Bag X17,
Bellville 7530, Republic of South Africa, and Department of Physical Chemistry,
University of Cape Town, Rondebosch 7700, Republic of South Africa

Reaction Pathways from Structural Data: Dynamic Stereochemistry of Nickel Compounds

THOMAS P. E. AUF DER HEYDE*[†] and LUIGI R. NASSIMBENI[‡]

Received April 26, 1984

The principle of structure correlation is applied to the crystal structures of 78 different five-coordinate nickel complexes. The data derived map the reaction coordinate for an association reaction at planar, four-coordinate nickel centers, leading to a square-pyramidal intermediate. It is shown that this intermediate may undergo pseudorotation to a trigonal-bipyramidal conformation, in which axial dissociation may occur.

Introduction

Square-planar coordination is well established amongst the metals of the nickel triad, but it is the chemistry of platinum and palladium compounds, rather than that of nickel, that has been more extensively investigated. Complexes of square-planar geometry may undergo isomerization and substitution reactions, which have been proposed to proceed via an essentially similar associative mechanism:[1,2]

$$XML_3 + Y \rightleftarrows [XML_3Y] \rightleftarrows X + ML_3Y$$

where X, L represent any ligand donor atoms and Y is X, L, or solvent. The rate of this reaction may be determined by either the associative or the dissociative step, or a combination of both. The nature of the five-coordinate intermediate has been the subject of much discussion, with earlier suggestions[1] being that it has a trigonal-bipyramidal conformation (TBP), as opposed to a square-pyramidal (SQP) one, put forward more recently.[2] It has been suggested, and in many cases shown,[1,2] that the five-coordinate intermediate [XML$_3$Y] may undergo the fluxional behavior typical of many pentacoordinate compounds, best described by the Berry mechanism[3] shown in Figure 1. This mechanism interconverts two trigonal bipyramids (TBP) via a square pyramid (SQP) by simultaneous in-plane bends of the axial ligands (atoms 1 and 5 in Figure 1) and the equatorial ligands (atoms 2 and 4).

In this paper we apply the method of structure correlation analysis[4,5] to five-coordinate nickel complexes. We view the results as mapping the reaction coordinates for an association reaction at planar four-coordinate nickel centers resulting in a SQP intermediate, with subsequent pseudorotation and dissociation of the five-coordinate species. In terms of the structure correlation approach one examines the *gradual distortion* that a specific fragment (in this case [NiL$_5$]) undergoes in a variety of crystal environments. This distortion is then assumed to mirror the distortion which that fragment would exhibit along a particular reaction pathway. Most recently this method has been applied to an examination of the "ring-whizzing" phenomenon in complexes of the type [(Ph$_3$C$_3$)M(PPh$_3$)$_2$]$^+$, where M = Ni, Pd, Pt,[6] the stereoisomerization path for triphenylphosphine,[7] conformational dy-

---

[†] University of the Western Cape.
[‡] University of Cape Town.

(1) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.
(2) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185.
(3) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(4) Bürgi, H. B. *Angew. Chem.* **1975**, *87*, 461; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 460. Dunitz, J. D. "X-ray Analysis and the Structure of Organic Molecules"; Cornell University Press: Ithaca, NY, 1979.
(5) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.
(6) Mealli, C.; Midollini, S.; Moneti, S.; Sacconi, L.; Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 95.
(7) Bye, E.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 5893.

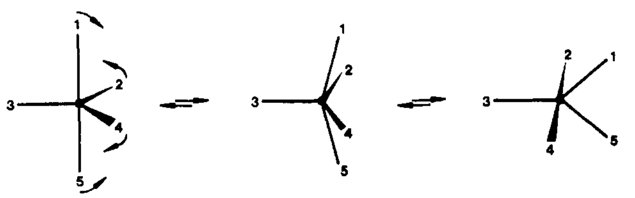

Figure 1. The Berry mechanism. In this representation ligand donor atom D_3 acts as the "pivot" for the pseudorotation.

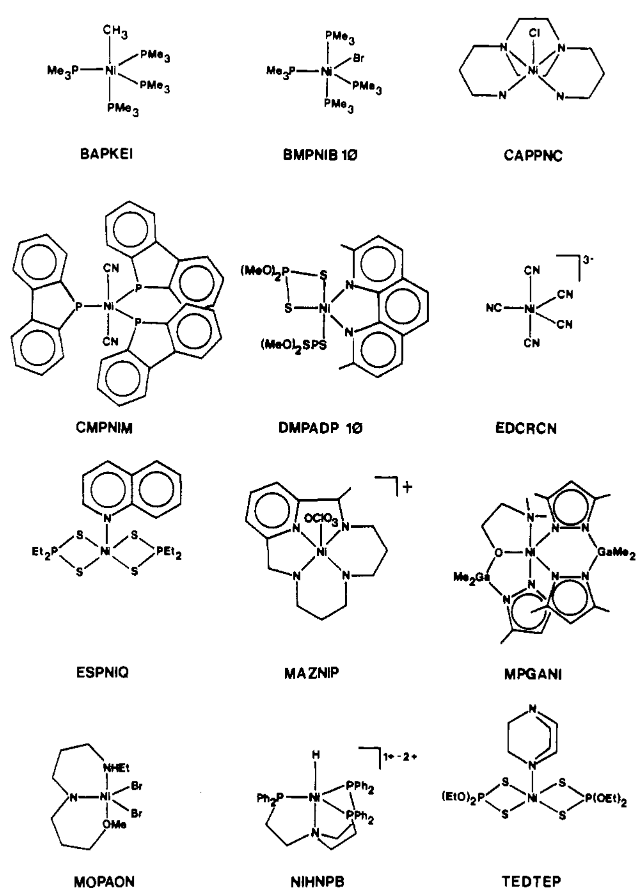

Figure 2. Structural formulas for the compounds of special interest in this study.

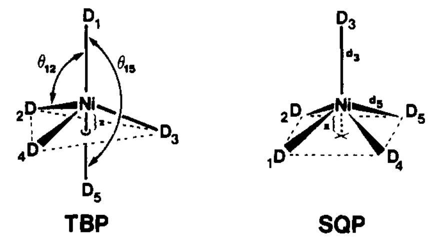

Figure 3. Analysis of molecular structure, showing angles, distances, and displacements.

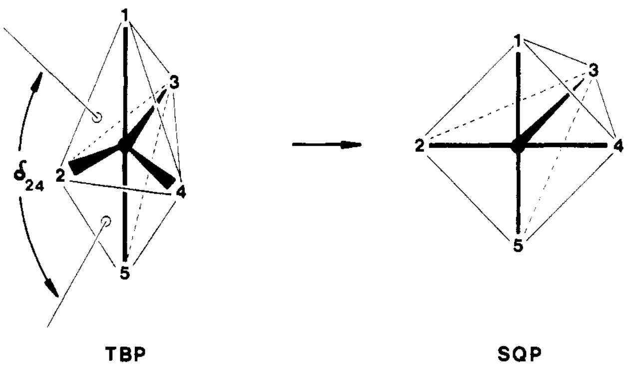

Figure 4. Edges and planes in the idealized polyhedra and definition of dihedral angles δ_{ij}.

namics of propane, di-*tert*-butylmethane, and bis(9-triptycyl)methane,[8] and nucleophilic substitution and subsequent Berry pseudorotation at tetrahedral zinc(II) centers.[9]

Data Search and Structural Analysis

The Cambridge Crystallographic Data Centre (CCDC) file contains information on the space group and positional atomic coordinates for all organic and organometallic crystal structures published.[10] A search of the March 1983 edition of this file (containing 31 982 entries) for compounds containing at least 4 non-hydrogen atoms bonded to nickel revealed 1135 such structures. After allyl complexes, porphyrin structures, and those compounds for which no atomic coordinates were available were rejected, 72 five-coordinate nickel complexes were identified. These gave rise to a total of 78 different arrangements of the ligand donor atoms about the nickel.

A cursory examination of the structures revealed large variations in nickel to ligand distances, some of which correspond to the predicted pattern,[11] and a range of conformations from TBP to SQP. Interestingly, two complexes, dicyanotris(5-methyl-5*H*-dibenzophosphole)nickel(II) (CCDC acronym CMPNIM)[12] and the pentacyanonickelate(II) anion (EDCRCN)[13] adopt both distorted-TBP and SQP conformations. Their structural formulas are shown in Figure 2.

In order to put all distances on a common scale, the sums of the respective covalent radii of nickel and the ligand atoms D_i (i = 1–5) were subtracted from the actual interatomic distances to yield distance increments d_i. In keeping with the approach outlined in our earlier paper,[9] the molecular geometries were regarded as TBP, or TBP distorted toward SQP, and were analyzed as shown in Figure 3. Ligand donor atoms D_1 and D_5 were identified as containing the largest bond angle, θ_{15}, with D_1 fulfilling the following requirements best: (i) $d_1 < d_5$ (ii) D_1 is a better leaving group, and (iii) the nickel atom is displaced toward D_1. D_2 and D_4 were then in general defined by the next largest contained angle, θ_{24}, thus in turn defining D_3. Two further parameters were also determined, these being the out-of-plane displacements z and x. The former was defined as the displacement of nickel out of the equatorial plane defined by D_2, D_3, and D_4 in the TBP. The latter is the distance between the metal and the basal plane defined by D_1, D_2, D_4, and D_5 in the SQP. Table I lists the distance increments, atom types, and displacement.

As in our earlier study of Zn(II) compounds,[9] we employed the dihedral angle method of Muetterties and Guggenberger[14] in order to define the conformations more rigorously than simply as "distorted SQP" or "distorted TBP". This method relies on the changes in the nine dihedral angles that are defined in an ideal TBP as it distorts toward a SQP via the Berry mechanism. The dihedral angles (δ_{ij}) are defined by the angles between the normals to the planes sharing a common edge (ij) in the idealized polyhedra as shown in Figure

---

(8) Bürgi, H. B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 1427.

(9) Auf der Heyde, T. P. E.; Nassimbeni, L. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, in press.

(10) Kennard, O.; Watson, D. G.; Allen, F. H.; Motherwell, F. D. S.; Town, W. G.; Rodgers, J. *Chem. Br.* **1975**, *11*, 213.

(11) (a) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365. (b) Burdett, J. K. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 113.

(12) Powell, H. M.; Watkin, D. J.; Wilford, J. B. *J. Chem. Soc. A* **1971**, 1803.

(13) Raymond, N. K.; Corfield, P. W. R.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1362.

(14) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

Table I. CCDC Acronyms, Atom Types D_i, Distance Increments d_i, Displacements x and z, Percentage Distortion TBP → SQP, Spin State S (As Far As Has Been Reported), and Charge q on the Nickel Atom for the 78 Compounds Examined (All Distances in pm)

no.	CCDC acronym	D_1	D_2	D_3	D_4	D_5	d_1	d_2	d_3	d_4	d_5	x	z	% dist	S	q
1	PEACNI 10	C	P	P	P	N	10	−1	−7	−10	54	54	25	21		2
2	BACBEM	P	P	Br	P	P	−8	−7	39	−9	−8	28	5	78		2
3	BGLNIA 10(a)	N	N	N	N	N	−4	−5	81	−5	−3	12	1	86	L	2
4	BGLNIA 10(b)	N	N	N	N	N	−4	−4	69	−4	−3	14	0	86	L	2
5	BIQN1Q	Cl	Cl	N	N	Cl	11	17	13	13	20	37	10	71		2
6	MPNBNI	Br	N	N	Br	Br	11	12	11	12	30	34	17	54		2
7	MPNCNI	Cl	N	N	Cl	Cl	11	14	12	18	22	34	10	69		2
8	BPPENI	Br	P	Br	P	N	−2	−14	35	−14	9	17	0	90	L	2
9	BPYRNI	N	N	N	N	N	−7	−6	44	−6	−7	20	0	93	L	2
10	BTCYTN	S	S	S	S	S	−8	−1	16	−8	−2	31	13	81		3
11	CAPPNC	N	N	Cl	N	N	14	14	43	20	19	34	16	91		2
12	CMPNIM(b)	P	C	P	C	P	−13	−11	1	−13	−13	50	0	59		2
13	CMPNMI	N	Cl	N	Cl	Cl	12	12	5	12	26	41	5	57		2
14	CPHEN1	Cl	N	N	Cl	Cl	12	16	15	19	18	39	6	81		2
15	CRTNCN 01(a)	C	C	C	C	C	−9	−11	18	−11	−7	30	0	97		2
16	CRTNCN 01(b)	C	C	C	C	C	−10	−11	12	−12	−8	33	−2	97		2
17	CYPSNI	N	N	1	N	N	−4	−5	30	−1	−4	24	1	83	L	2
18	DMPADP 10	S	N	N	S	S	17	12	6	5	33	42	11	53		2
19	ESPNIQ	S	S	N	S	S	17	16	15	14	17	52	2	83		2
20	DPENIA	I	As	As	As	N	32	−6	−7	−6	56	59	34	14		1
21	DPENIB	I	P	P	P	N	48	−2	−5	−5	35	59	23	15		1
22	EDCRCN(a)	C	C	C	C	C	−11	−11	19	−14	−11	33	0	95		2
23	INOPNI	I	P	O	P	N	−6	−11	75	−10	8	12	0	76	L	2
24	IPBNIB	N	N	Br	N	N	1	−3	31	0	−3	24	1	88	L	2
25	MASONI 10	O	O	O	O	O	13	13	7	13	14	39	−4	84		2
26	MAZNIP	N	N	O	N	N	−9	4	91	4	4	12	−21	74		2
27	MOPAON	N	Br	N	Br	N	10	7	11	5	41	35	16	69		2
28	MPGANI	N	O	N	N	N	15	11	9	9	32	49	6	35		2
29	MTZNIT	N	N	N	N	N	14	15	11	8	19	27	4	70		2
30	NBOSNI	S	S	S	S	S	−11	−9	103	−8	−10	13	−7	83		2
31	NICEAS 10	O	O	N	N	N	6	8	7	29	9	36	4	85		2
32	NIDSPI	I	S	S	I	P	3	−6	54	−3	−19	10	7	91	L	2
33	NIPPNS	S	P	P	P	N	11	−5	−6	−6	36	55	24	9		0
34	PEMENI	N	P	O	P	N	−6	−10	61	−10	5	14	13	89	L	2
35	PHASNI	P	As	As	As	N	4	−2	−1	0	68	58	46	7		1
36	PMENSE	P	O	P	P	O	3	14	−1	5	12	40	14	82	H	2
37	PTNNIB 10	P	P	I	S	S	−9	−13	11	1	−1	26	11	88		2
38	PYEENI	N	N	N	N	N	19	17	10	15	21	33	3	94	H	2
39	QUMQNI	Cl	N	N	Cl	Cl	10	14	15	20	23	41	5	93	H	2
40	TCAPAN 10	N	N	N	N	N	6	31	4	26	17	34	20	99	H	2
41	TEDTEP	S	S	N	S	S	19	18	22	19	20	54	0	95		2
42	TPIVNI	S	S	S	S	S	−4	−4	46	−3	−2	20	0	93		2
43	TMCAZN	N	N	N	N	N	19	20	4	19	20	33	4	97		2
44	ASPHNI	P	As	As	As	C	−10	−11	−8	−11	−9	59	19	13		2
45	ATSZNI	N	S	Cl	S	N	15	6	9	6	15	43	1	22	H	2
46	AZOCNI	N	Cl	Cl	Cl	N	24	10	8	11	25	60	1	9	H	2
47	BAPKEI	P	P	P	P	C	−10	−5	−6	−5	6	55	24	21	L	2
48	BEBPN1	P	Br	P	Br	P	−8	16	−13	11	−9	78	4	11		2
49	BMPANI	N	Br	N	Br	N	14	14	10	12	14	19	1	39	H	2
50	BMPNIB 10	P	Br	P	P	P	−6	16	−2	−5	−6	61	1	22	L	2
51	BMPONI	P	Br	P	P	P	−13	11	−7	−12	−13	58	0	12		2
52	CEBPNI	C	P	P	P	C	−16	−7	−4	−6	−13	53	3	21	L	2
53	CMPNIM(a)	C	P	P	P	C	−12	−9	−2	−8	−11	47	3	26		2
54	CMTPPN	Cl	S	S	S	P	3	−1	2	4	−20	51	6	15		2
55	CNTPNI	C	P	P	P	C	−12	−9	−5	−9	−14	52	2	22		2
56	CPEANI	Cl	P	P	P	N	−3	−12	−1	−9	6	51	9	16	L	2
57	CPEPNI	C	P	P	P	C	−11	−10	−2	−12	−9	51	0	30		2
58	DIPHNI 10	I	P	P	P	N	17	−9	−9	−9	22	56	1	7	L	2
59	EDCRCN(b)	C	C	C	C	C	−15	−7	1	−8	−13	37	0	41		2
60	ETBPNI	P	Cl	P	Cl	P	−10	15	−12	15	−10	77	1	8		2
61	IMPCNI	P	I	I	C	P	−9	7	7	−25	−8	47	0	9		2
62	IMPONI	P	I	I	P	P	−12	12	12	−14	−12	56	5	14		2
63	INPNII	1	P	N	P	N	1	−5	39	−10	12	46	13	27	L	2
64	MTRENI 10	N	N	N	N	N	6	23	16	18	13	48	19	15		2
65	NIEACL 10	O	N	N	O	N	11	26	25	10	18	62	19	24		2
66	NIHNPB	H	P	P	P	N	6	−10	−10	11	15	62	4	17		1 ~ 2
67	OXPHAD	P	P	P	P	P	−17	−11	−15	−10	−16	54	0	8		2
68	PASNIB 10	C	As	As	As	N	−10	−10	−3	−12	19	61	16	17		2
69	PEAMNI	C	P	P	P	N	4	−9	−6	−8	20	55	11	10		2
70	PEASNI	S	P	P	P	N	−12	−3	3	2	16	54	12	12		2
71	PSNPEA 10(a)	Sn	P	P	P	N	−7	−2	−1	−4	26	54	18	8		2
72	PSNPEA 10(b)	Sn	P	P	P	N	−4	−1	−7	−2	7	61	12	16		2
73	SALDNI	N	O	N	O	N	12	14	15	11	12	31	7	47		2
74	SAIMNI 10	N	O	N	O	N	8	8	17	8	10	36	0	38		2
75	TMPBNI(a)	P	Br	Br	P	P	−10	7	23	−11	−10	40	0	16		2
76	TMPBNI(b)	P	Br	Br	P	P	−10	11	20	−12	−10	39	0	19		2
77	TPENIB 10	S	P	P	P	P	1	−7	−2	−1	−15	52	20	18	L	2
78	IPESNI	P	I	I	S	P	−12	0	25	−6	−12	37	4	36		2

Table II. Values of Bond Angles (θ_{ij}, deg) and Dihedral Angles (δ_{ij}, deg) for the Idealized Structures, as Well as Absolute Differences $|\Delta|_{ij}$ and Sums of Differences $\Sigma_{ij}|\Delta|_{ij}$

	θ_{15}	θ_{12}	θ_{13}	θ_{14}	θ_{52}	θ_{53}	θ_{54}	θ_{23}	θ_{24}	θ_{34}
TBP	180	90	90	90	90	90	90	120	120	120
SQP	150	86	105	86	86	105	86	105	150	105
$|\Delta|_{ij}$	30	4	15	4	4	15	4	15	30	15

$\Sigma_{ij}|\Delta|_{ij} = 136$

	δ_{45}	δ_{25}	δ_{14}	δ_{12}	δ_{35}	δ_{13}	δ_{23}	δ_{34}	δ_{24}
TBP	101.5	101.5	101.5	101.5	101.5	101.5	53.1	53.1	53.1
SQP	118.5	118.5	118.5	118.5	76.9	76.9	76.9	76.9	0
$|\Delta|_{ij}$	17	17	17	17	24.6	24.6	23.8	23.8	53.1

$\Sigma_{ij}|\Delta|_{ij} = 217.9$

4. Table II lists the θ_{ij} and δ_{ij} values for the idealized conformations that we have chosen,[15] as well as the absolute changes $|\Delta|_{ij}$. By relation of the dihedral angles of the compounds under consideration to those in the idealized polyhedra the amount of distortion may be calculated. This is also presented in Table I.

In three previous cases where the structure correlation approach has been used to map S_N2 reactions via TBP intermediates at metal centers,[9,16,17] the effect of the d-orbital electron configuration on the pentavalent intermediate could be ignored, due to completely filled d sublevels. It has been shown, however, that the unfilled d-electron configuration may have a marked effect on the intermediate.[11] Thus for low-spin d^8 TBP conformations it has been predicted that the *axial* bonds will be stronger, and hence shorter, than the equatorial ones, while in the corresponding SQP the *apical* bond is expected to be weaker and longer than the basal ones. In the case of high-spin d^8 these rules are expected to be somewhat relaxed. For the TBP a d^9 configuration has no effect on the bond lengths, while d^7 yields a slightly stronger axial bond. Both d^7 and d^9 show slightly stronger apical bonds in the SQP than the low-spin d^8 configuration. Table I also lists the spin states (as far as they have been reported) and the charges on the nickel atom.

In the compounds examined there is a smooth progression of conformations from TBP to SQP, mimicking the Berry pseudorotation coordinate. If the compounds are viewed as distorted TBP, then d_1 and d_5 are representative of the axial bonds, while if they are viewed as distorted SQP, d_3 represents the apical bond. In order to examine the dependence of the axial bond (TBP) and the apical bond (SQP) on the degree of distortion, we plotted d_5 and d_3 against percentage distortion from ideal TBP to ideal SQP in parts a and b, respectively, of Figure 5.

From Table I and Figure 5 the following conclusions may be drawn: (i) axial d_1 and d_5 are generally smaller for low-spin d^8 than for high-spin d^8, (ii) d_1 and d_5 are shorter for d^8 than for d^9, (iii) in one case of a d^7 compound d_1 and d_5 are shorter than for the d^9 complexes, and (iv) d_3 is in general quite long for low-spin d^8 complexes, but shorter for d^9. All of these conclusions are in line with the predicted pattern.

Figure 5a hints at a reaction pathway in that the compounds represented by filled circles may be visualized as lying along some distortion coordinate, while the open circles do not. Figure 5b supports this hypothesis since the filled circles may again be seen to lie on a reaction pathway, while the empty circles are once again scattered. That the points for compounds MOPAON and CMPNIM(b) lie somewhat off the coordinate drawn might be due to considerable strain within the molecules. MOPAON, whose structural formula is shown in Figure 2, contains two six-membered rings, well recognized as being sterically hindering for five-coordinate compounds. CMPNIM

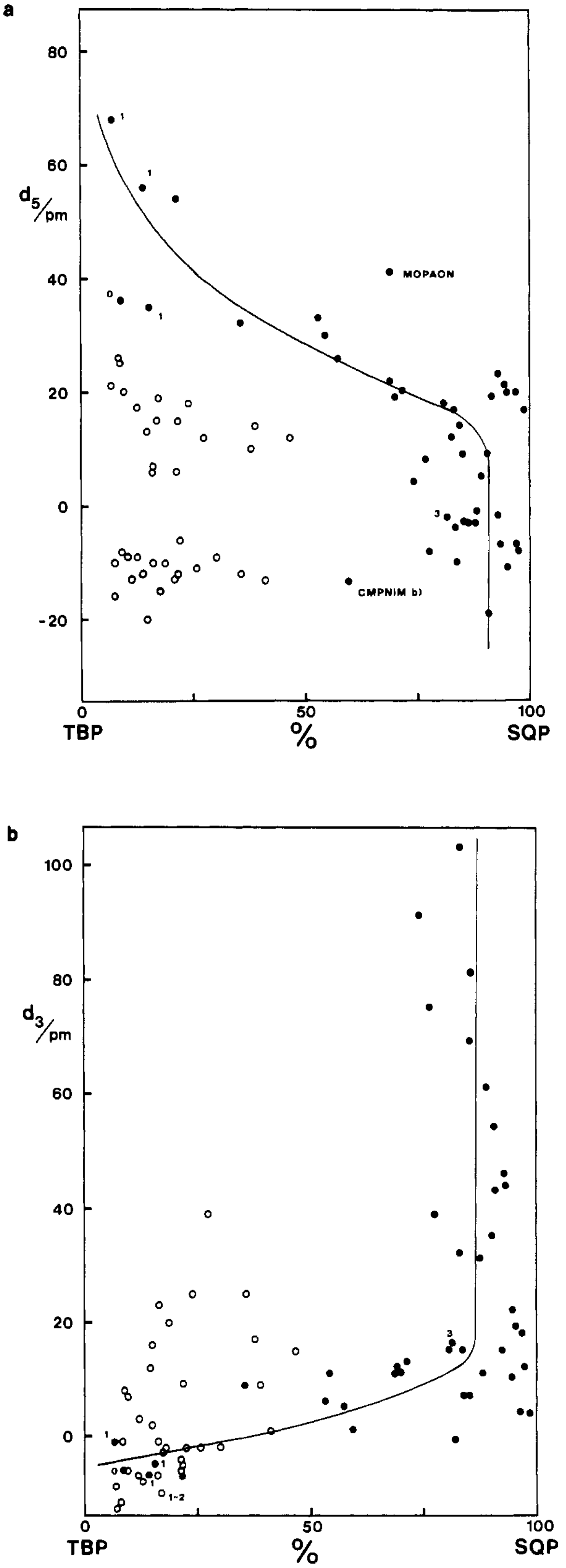

Figure 5. (a) Axial, d_5, and (b) apical, d_3, distance increments vs. percentage distortion TBP → SQP. Full circles correspond to structures considered to map the addition reaction. Empty circles correspond to compounds distorted away from this pathway. Numbers next to points refer to the charge on nickel. CMPNIM(b) and MOPAON are discussed in the text.

---

(15) We have chosen the ideal SQP as having axial–basal bond angles of 105°. This is the configuration obtained by placing Ni at the center of mass of a NiL_5 square pyramid, and it serves merely as a starting point.

(16) Bürgi, H. B. *Inorg. Chem.* **1973**, *12*, 2321.

(17) Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2971.

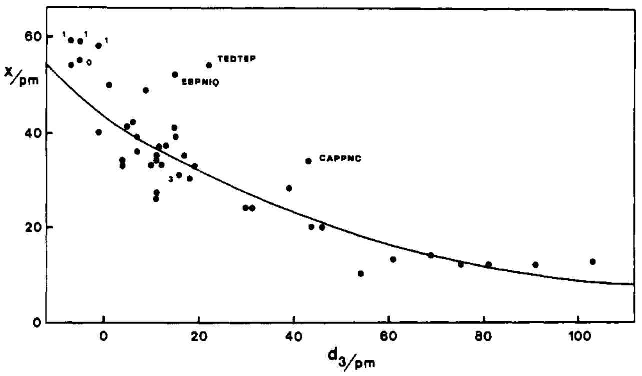

Figure 6. Dependence of out-of-plane displacement x on d_3. Numbers next to points indicate the charge on nickel. The scatter is discussed in the text; the curve is drawn to eq 1.

contains the large and bulky benzophosphole ligand, which may be expected to have some effect on the conformation. CMPNIM exists as two allogon isomers, form (a) lying well off the coordinate of Figure 5 and form (b) closer to it. The fact that it is the square-pyramidal form of the compound which lies closer to the coordinate lends credence to the assumption below.

The adherence of the compounds to the coordinate dependent on d_3, i.e. on the proximity of the apical ligand in a SQP, is in agreement with the suggestion[2] that association reactions at square-planar nickel centers proceed via a SQP intermediate. We thus identify two groups of pentavalent nickel compounds: (i) those whose distortions mirror the pattern expected in an association reaction between a square planar NiL_4 moiety and an attacking nucleophile (D_3) leading to a SQP intermediate (full circles in Figure 5, compounds 1–43 in Table I) and (ii) those which due to some combination of inter- and intramolecular restrictions are forced off this reaction coordinate (empty circles in Figure 5, compounds 44–78 in Table I).

Correlations and Reaction Pathways

Association. The association reaction leading from a square-planar, four-coordinate complex to a square-pyramidal one can best be represented by a correlation between the proximity of the attacking nucleophile (d_3) and the degree of pyramidality of the SQP (x). Figure 6 shows that as the nucleophile D_3 approaches the nickel center from infinity, so the displacement of Ni out of the basal plane increases from zero, until it reaches 44 pm in the case where $d_3 = 0$. The data have been fitted to an exponential curve such that

$$x = 44.2e^{-0.02d_3} \qquad (1)$$

whence

$$d_3 = 115.2 \log (x/44.2) \qquad (2)$$

Equation 2 is reminiscent of Pauling's formula[18] relating changes in interatomic bond distances d to bond numbers n

$$d = c \log n \qquad 0 < n < 1$$

implying that a geometrical measure for bond number n is $x/44.2$.

Although all the data in Figure 6 were used in calculating the least-squares line, it appears that for $d_3 < 10$ pm the relation between the two parameters changes, in that some of the points lie well above the line at values of $x \simeq 55–60$ pm. Indeed, an investigation of those compounds (nos. 44–78) that do not fall on the coordinates shown in Figure 5, and hence are not believed to map the association reactions, shows that in the majority of cases the x values lie in that range, i.e. appear to be constant. Moreover, from Figure 5b it seems that for $d_3 < 10$ pm the compounds distort from almost pure SQP to TBP. ESPNIQ, TEDTEP, and CAPPNC, whose structural formulas are shown in Figure 2, contain sterically hindering four- and six-membered rings, hence explaining their scatter from the line. Thus the approach of the nucleophile toward the NiL_4 moiety seems to be accompanied by increasing pyramidalization at the nickel, leading to a square-pyramidal intermediate, which then distorts, presumably via the Berry mechanism, toward a TBP when $d_3 < 10$ pm.

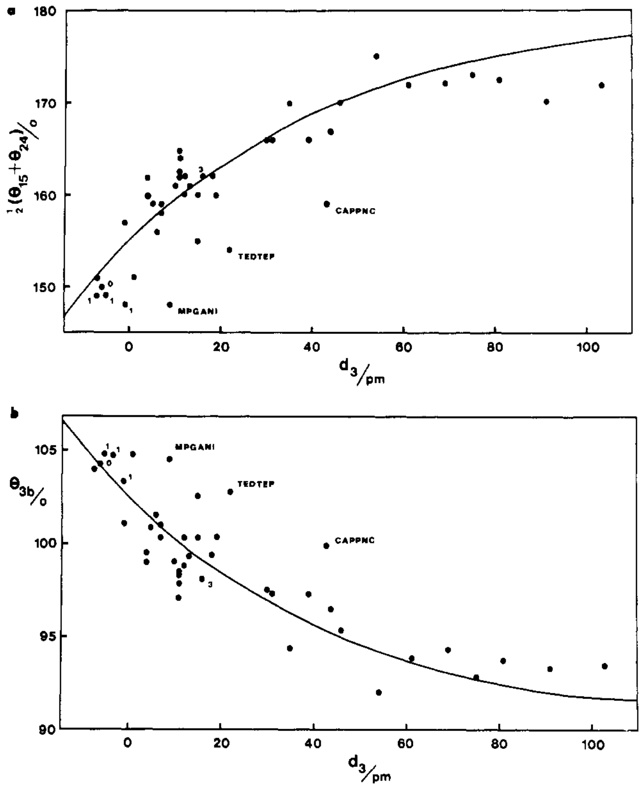

Figure 7. (a) Plot of average trans-basal angle vs. d_3 and (b) plot of average apical–basal angle vs. d_3. The scatter is discussed in the text.

There has been much discussion concerning the value of the trans-basal angle (θ_{15} and θ_{24}) in an ideal SQP, although it is generally agreed that this will depend on d-electron configuration.[11,19] Even so, Muetterties and Guggenberger[14] set the value of this angle at 156° in their study of pentavalent compounds of both main-group and transition elements. Other values have been 160, 150, and 152°, all for compounds with filled d sublevels,[20] and 164° for d^8 species.[11a] Figure 7 shows plots of the average trans-basal angle ($(\theta_{15} + \theta_{24})/2$) and the average apical–basal angle (θ_{3b}) against the proximity of the incoming nucleophile D_3. The data have been fitted to a line calculated from eq 1, assuming a bond length of 205 pm between Ni and D_1, D_2, D_4, and D_5, a value well within the range found for the compounds. The curves show that the average trans-basal angle changes from 180 to 155° as d_3 tends to zero, thus reflecting the behavior of the square-planar NiL_4 as D_3 approaches this moiety.

Structural formulas, shown in Figure 2, for MPGANI and MAZNIP show why these compounds are distorted from the coordinate shown in Figure 7. In order to examine in more detail the distortions that the NiL_4 fragment undergoes, we calculated the additional parameter ϕ, defined as the average

---

(18) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542.

(19) Gillespie, R. J. *J. Chem. Soc.* **1963**, 4679.

(20) (a) Gillespie, R. J. *J. Chem. Soc.* **1963**, 4672. (b) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

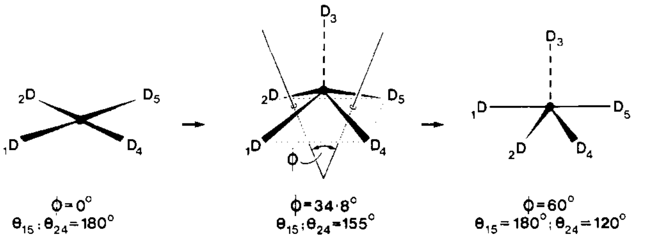

Figure 8. Definition of ϕ and diagram showing how ϕ, θ_{15}, and θ_{24} vary along the proposed reaction pathway.

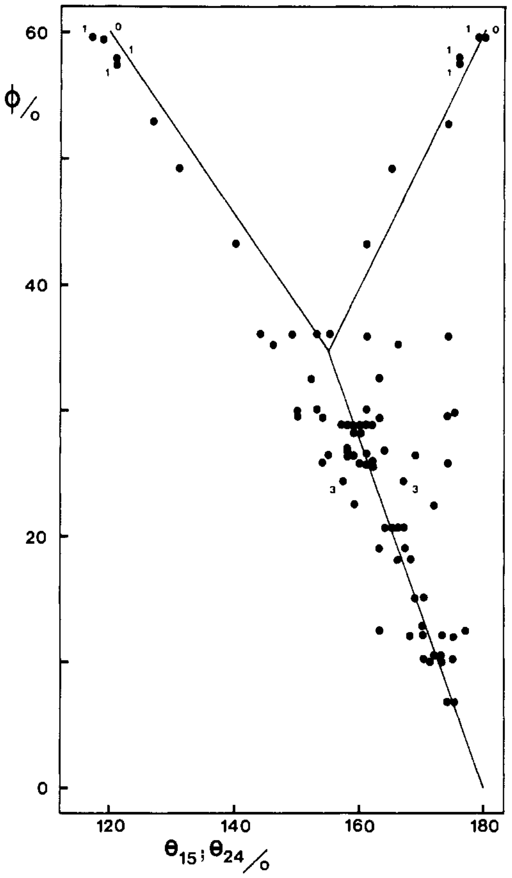

Figure 9. Plot of ϕ vs. θ_{15} and θ_{24}. The solid line corresponds to the reaction coordinate outlined in Figure 6.

angle between the normals to the pairs of planes D_1NiD_2, D_4NiD_5 and D_1NiD_4, D_2NiD_5. Figure 8 defines ϕ and shows how ϕ and the trans-basal angles vary along the pathway we have proposed. Figure 9 shows a plot of ϕ against θ_{15} and θ_{24}. The solid line represents the reaction coordinate for the scheme outlined in Figure 8. The branched part of the reaction coordinate shown in Figure 9 is, of course, the Berry coordinate, corresponding to the rotation of the SQP into a TBP.

Pseudorotation. Table II shows that the sum, over all edges, of the changes in dihedral angles accompanying the TBP → SQP transition is $\Sigma_{ij}|\Delta|_{ij} = \Sigma_{ij}|\delta_{ij}(\mathrm{TBP}) - \delta_{ij}(\mathrm{SQP})| = 217.9°$. If a compound (C) lies on the Berry rearrangement coordinate between the TBP and SQP, then its dihedral angles $\delta_{ij}(\mathrm{C})$ are related to those of the idealized polyhedra such that the sum of $\Sigma_{ij}|\delta_{ij}(\mathrm{C}) - \delta_{ij}(\mathrm{SQP})]$ and $\Sigma_{ij}|\delta_{ij}(\mathrm{C}) - \delta_{ij}(\mathrm{TBP})|$ is 217.9°. Figure 10 shows a plot of $\sum_{ij}|\delta_{ij}(\mathrm{C}) - \delta_{ij}(\mathrm{TBP})|$ vs. $217.9 - \Sigma_{ij}|\delta_{ij}(\mathrm{C}) - \delta_{ij}(\mathrm{SQP})|$, with the Berry coordinate represented by the straight line. There is considerable scatter from the minimum energy coordinate, but it is significant that those compounds not considered to map the association reaction (empty circles) exhibit less scatter than those that do (full circles). We surmise that the distortions of the compounds away from the Berry coordinate are brought about by structural restrictions imposed by a combination of steric and electronic requirements of the ligands and that these are more evident in the compounds that map the association reaction. NIHNPB is a hydride of the type MHL_4, which is pseudotetrahedral and has long been known not to pseudorotate.[21] DMPADP 10 contains a four-membered ring, as well as the large and bulky 2,9-methyl-1,10-phenanthroline ligand, thus possibly explaining its distortion. Structural formulas are shown in Figure 2.

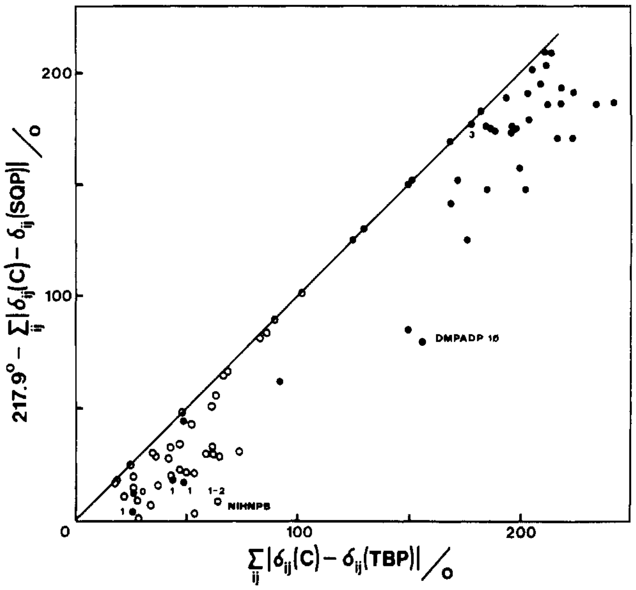

Figure 10. Diagram showing Berry coordinate (solid line) and adherence of the compounds to it. Full circles correspond to structures mapping the association reaction.

In our modeling of the Berry coordinate we have followed our previous study[9] and that of Holmes[20b] in defining our SQP as having trans-basal angles of 150° for the purpose of calculating $\delta_{ij}(\mathrm{SQP})$ values.[15] We recognize, however, that whereas the geometry of the TBP is fixed, this is not the case for the SQP. The values of the SQP dihedral angles are dependent on the apical–basal angle chosen, and the scatter of the points in Figure 10 will also be dependent on this.

Dissociation. Theoretical considerations have rather vaguely implied equatorial dissociation of a TBP intermediate[1] or apical dissociation of a SQP intermediate[2] in substitution and isomerization reactions, respectively, with experimental evidence seeming to support the latter. However, in at least four cases[22,23] departure of an axial ligand in a TBP has been indicated. We apply a method outlined by Dartiguenave et al.[22] to map the geometrical reaction coordinate for the gradual removal of an axial ligand in a TBP along the C_3 axis, i.e. the transition from a trigonal bipyramid with C_{3v} symmetry to a monocapped tetrahedron. This method involves calculating the normalized shift parameter $s = (\bar{d}_{\mathrm{eq}} - 3z)/\bar{d}_{\mathrm{eq}}$ and correlating it with the sum of the angles at the central metal atom along ($\sum\theta_{1\mathrm{e}}$) and around ($\sum\theta_{\mathrm{ee}}$) the threefold axis, respectively. $\bar{d}_{\mathrm{eq}}$ is the averaged metal to equatorial ligand distance, $\sum\theta_{1\mathrm{e}} = \theta_{12} + \theta_{13} + \theta_{14}$, and $\sum\theta_{\mathrm{ee}} = \theta_{23} + \theta_{34} + \theta_{24}$. This method was originally introduced in support of a suggestion that the compound BAPKEI, whose structural formula is

---

(21) Muetterties, E. L. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *10*, 46.

(22) Gleizes, A.; Kerkeni, A.; Dartiguenave, M.; Dartiguenave, Y.; Klein, H. F. *Inorg. Chem.* **1981**, *20*, 2372.

(23) (a) Saint-Joly, C.; Mari, A.; Gleizes, A.; Dartiguenave, M.; Dartiguenave, Y.; Galy, J. *Inorg. Chem.* **1980**, *19*, 2403. (b) Meier, P. F.; Merbach, A. E.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chem.* **1979**, *18*, 610. (c) Lukosius, E. J.; Coskran, K. J. *Inorg. Chem.* **1975**, *14*, 1926.

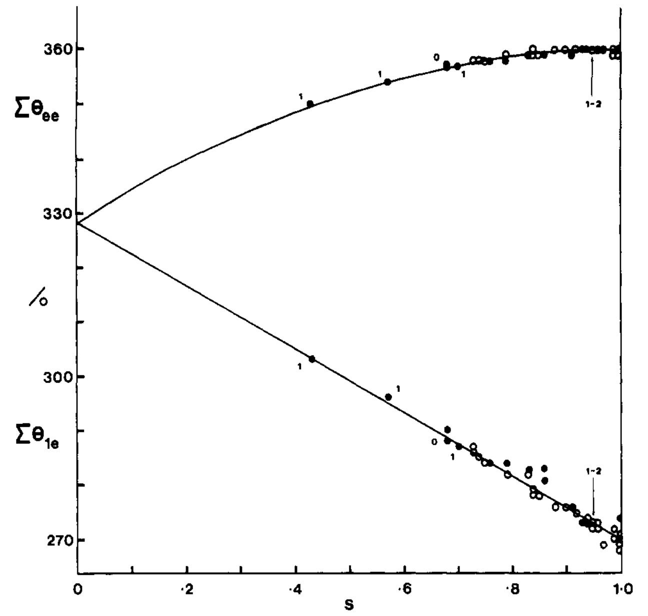

Figure 11. Diagram showing $C_{3v} \rightarrow T_d$ transition for compounds that map the association reaction (full circles) and those that do not (empty circles). $\sum\theta_{1e}$, $\sum\theta_{ee}$, and *s* are defined in the text. The calculated reaction coordinate is shown by the solid line.

shown in Figure 2, lies along the reaction pathway for homolytic Ni–CH_3 bond cleavage leading to a tetrahedral Ni(I) species.

Figure 11 shows a plot of $\sum\theta_{1e}$ and $\sum\theta_{ee}$ vs. *s* for those compounds not considered to map the association reaction (empty circles), as well as for the more trigonal-bipyramidal conformations of the second group (full circles). The solid line indicates the calculated coordinate, and it seems as if both groups adhere to it equally well. The fact that it is the Ni(I) species that are in general furthest removed from the C_{3v} toward the T_d conformation supports, first, the suggestion originally made[22] and, second, our assumption that there may be an element of axial departure in a TBP intermediate.

Since we are mapping essentially a substitution reaction that occurs via an associative step, it is of interest to correlate the approach of the nucleophile with the departure of the leaving group. In the analysis of the molecular geometries we assigned ligand D_1 the better leaving group qualities, while in the derivation of Figure 10 we assumed D_5 to be the leaving group.

Figure 12 shows the correlation between d_3, d_1, and d_5, and although scattered, the plots do show a trend. It appears that the approach of D_3 to the NiL_4 fragment is accompanied at first by very little, if any, lengthening of the axial bonds. However, small decreases of d_3 below ca. 20 pm seem to bring about large increases in d_1 and d_5. This trend suggests that the formation of the SQP intermediate precedes any departure of a leaving group, which may occur once the SQP → TBP transition has taken place, thus allowing the nucleophile to bond more closely to nickel.

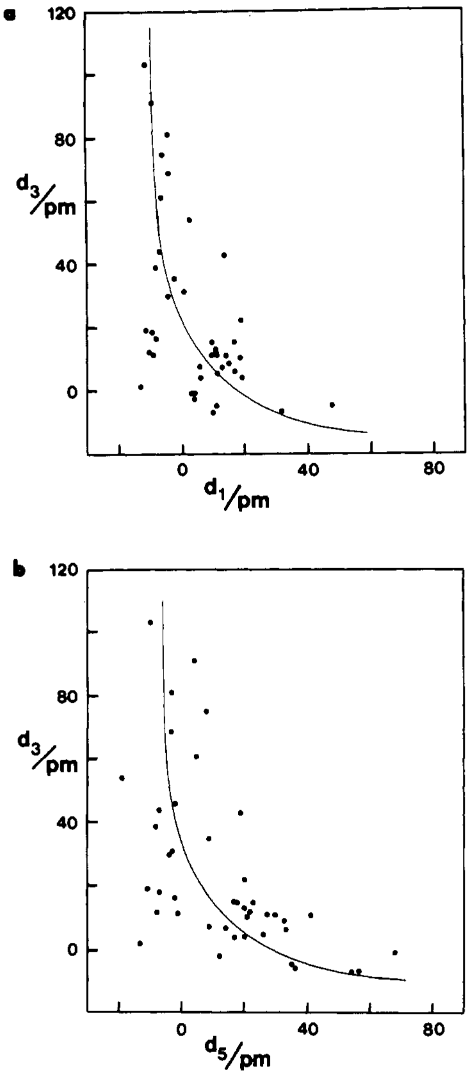

Figure 12. Correlation of (a) d_3 with d_1 and (b) d_3 with d_5, for the compounds mapping the association reaction.

Discussion and Experimental Observations

The correlations presented here are consistent with the sequence of reversible steps outlined in Figure 13, all of which have been previously proposed on the basis of experimental evidence. Associative steps, in some cases rate determining, leading to five-coordinate intermediates have been suggested for a number of substitution and addition reactions. Thus, for example, substitution of the ligands in square-planar dithiocarbamate and dithiophosphate complexes, by ethylenediamine and cyanide ion, has been rationalized in those terms,[24] as well as the substition of X^- by various nucleophiles in complexes of the type *trans*-$[Ni(PEt_3)_2(o\text{-tol})X]$, where X = Cl, Br, I, N_3, NO_2 and tol = tolyl.[25] A preequilibrium involving a five-coordinate species has been indicated for ligand substitution reactions in bis(*N*-R-salicylaldiminato)nickel(II) complexes.[26] The rate of addition of 1,10-phenanthroline to bis(thioacetylacetonato)- and bis(dithiophosphato)nickel(II) complexes is dependent on the rate of formation of a pentavalent intermediate,[27] as is the addition of L to $[HNiL_3]^+$, where L = $P(Et)_3$.[28] The concept of such an intermediate is not limited only to addition and substitution reactions, but it has also been invoked in a mechanistic interpretation of intermolecular ligand exchange in the series of complexes *trans*-$[NiRXL_2]$[29] and in the study of the interchange between coordinated and uncoordinated acetyl groups in [3,3′-(ethylenebis(nitrilomethylidyne))bis(2,4-pentanedionato)]nickel.[30]

Fluxional behavior of five-coordinate nickel species is well established in vitro and has been proposed to occur in vivo as

---

[24] Hynes, M. J.; Brannick, P. F. *J. Chem. Soc., Dalton Trans.* **1977**, 2281.

[25] Cusumano, M.; Ricevuto, V.; Romeo, R.; Trozzi, M. *Atti Accad. Peloritana Periocolanti, Cl. Sci. Fis., Mat. Nat.* **1974**, *54*, 157; *Chem. Abstr.* **1976**, *85*, 37574.

[26] Schumann, M.; Holtum, A. V.; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1982**, *21*, 606.

[27] Fayyaz, M. U.; Grant, M. W. *Aust. J. Chem.* **1978**, *31*, 1439.

[28] English, A. D.; Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 422.

[29] Wada, M.; Nishiwaki, K. *J. Chem. Soc., Dalton Trans.* **1983**, 1841.

[30] Funke, L. A.; Melson, G. A. *Inorg. Chem.* **1975**, *14*, 306.

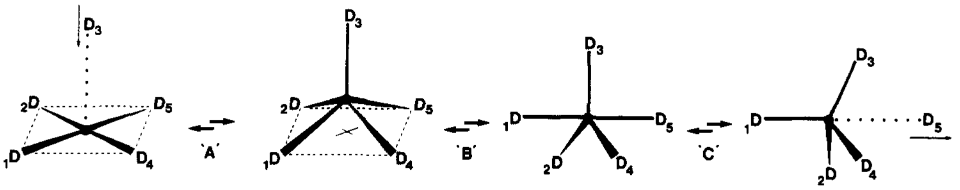

Figure 13. Diagram of reaction sequences mapped in this study: A = reversible dissociation of a SQP; B = the Berry mechanism; C = reversible dissociation of a TBP.

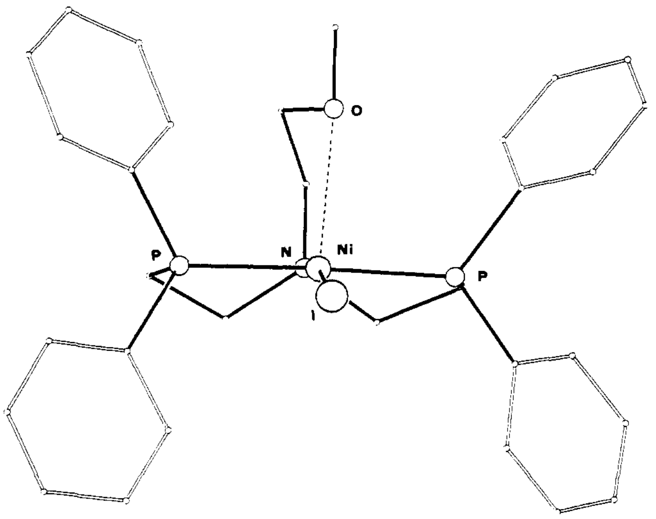

Figure 14. Perspective view of INOPNI, showing near-planarity of base (P, Ni, N, P, I) and extremely long apical Ni–O bond.

well, in that it has been suggested[31] that the nickel complex with human serum albumin is five-coordinate and is in slow exchange. Complexes of the type $[ML_5]$ (L = phosphite, PMe_3) have been studied[32,33] and shown to undergo intramolecular ligand exchange, presumably via the Berry mechanism. Similarly an investigation of the C_{2v} complexes $[NiX(PMe_3)_4]^+$ (X = Cl, Br, I), the bromide of which was used in this study (compound BMPNIB 10—structural formula in Figure 2), revealed a "double Berry mechanism" with one of the equatorial phosphines acting as the pivot.[34] A fluxional five-coordinate intermediate has also been suggested[35] for the carbonylation reaction of halobis(ligand)organonickel(II) complexes.

In a series of papers[23a,b,34–36] the results of studies on the dissociation of complexes of the type $[ML_5]^{2+}$, $[ML_4X]^+$, and $[ML_3X_2]$, where X = Cl, Br, I, CN and L = tertiary phosphine or phosphite, are presented. In the case of $[ML_3(CN)_2]$ and $[ML_4X]^+$ apical departure of L from a SQP intermediate takes place, corresponding to step A of the reaction sequence in Figure 13. However, in $[ML_5]^{2+}$ and $[ML_3X_2]^+$, where X is a halide, L leaves from the axial position of a trigonal bipyramid, corresponding to step C. Dissociation of a SQP complex is also indicated in the reaction of $[Ni(diars)_2Br]^+$ with CN^- (diars = *o*-phenylenebis(dimethylarsine)) and for the intermediate in the octahedral $\rightleftharpoons$ square-planar interconversion of $[Ni(bbh)L_2]$ (L = pyridine; bbh = biacetyl bis(α-hydroxybenzylidene)hydrazone(2–)).[38]

Our conclusion regarding the mechanism of the reaction is the same as that put forward by English, Meakin, and Jesson[28] in their detailed study of ligand association reactions at square-planar nickel. Finally we would like to mention a study of the compound identified by the CCDC acronym INOPNI,[39] a perspective view of which is presented in Figure 14. On the basis of the electronic spectra, neither a square-planar nor a five-coordinate conformation could be unambiguously assigned. Indeed, the crystal structure of the compound reflected this, in that it revealed an extremely long bond in the apical position of an almost flat square pyramid. It is remarkable to what extent the behavior of the $[NiL_5]$ fragment in crystals mirrors its generally accepted mode of behavior in solution.

Acknowledgment. We wish to thank the Council for Scientific and Industrial Research and the Universities of the Western Cape and Cape Town for financial assistance. This paper is dedicated to the memory of the late Prof. Earl L. Muetterties.

---

(31) Sarkar, B. *Coord. Chem.* **1980**, *21*.

(32) Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5751.

(33) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

(34) Dartiguenave, M.; Dartiguenave, Y.; Gleizes, A.; Saint-Jolly, C.; Galy, J.; Meier, P.; Merbach, A. E. *Inorg. Chem.* **1978**, *17*, 3503.

(35) Grimes, C. G.; Pearson, R. G. *Inorg. Chem.* **1974**, *13*, 970.

(36) Lukosius, E. J.; Coskran, K. J. *Inorg. Chem.* **1975**, *14*, 1922.

(37) Sweigart, D. A. *Inorg. Chim. Acta* **1977**, *23*, 413.

(38) Cusumano, M. *J. Chem. Soc., Dalton Trans.* **1976**, 2133.

(39) Dapporto, P.; Morassi, R.; Sacconi, L. *J. Chem. Soc A* **1970**, 1298.