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THE INFLUENCE OF GEOMETRY AND DONOR-ATOM SET ON THE SPIN STATE OF FIVE-COORDINATE COBALT (II) AND NICKEL (II) COMPLEXES ★

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CONTENTS

A INTRODUCTION

The nature of the donor atoms in five-coordinate complexes of cobalt(II) and nickel(II) has been shown to be an important factor in determining whether the metal atom is in a high- or low-spin state [1]. In fact the magnetic cross-over point for five-coordinate complexes does not depend only on the dipolar strength of the donor atoms, i.e. on $Dq = \mu B_4/6$ (ref. 2), but also on their nephelauxetic effects. A strong reduction of the interelectronic repulsion term, which can well be as large as 50%, brings the low-spin terms closer to the high-spin ground term, so that a lower Dq value is required to reach the cross-over point. Accordingly, some bromo and chloro complexes are found high-spin whereas the iodo analogues, with smaller Dq and β values, are found to be low spin [3]. Both Dq and β ligand field parameters are related to the covalent and π-bond character of the metal donor bonds, as the antibonding character of the metal orbitals is a measure of Dq, at least for octahedral complexes. On the other hand the electron delocalization onto the ligands is believed [4] to determine the value of β. According to Basolo and Pearson [5a] the nucleophilic reactivity constant n° is strictly related to polarizability and to π-bonding properties of nucleophiles. Therefore the nucleophilicity n° as well as the electronegativity of

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the donor atoms have been suggested as parameters related to the spin state of the complexes [1], although the latter parameter does not take into account the type of hybridization of a given donor atom. Recently a correlation between the optical ligand electronegativity and the complex geometry has been treated by Hollebone [5b].

B SPIN STATE OF THE COMPLEXES AND OVERALL ELECTRONEGATIVITY AND NUCLEOPHILICITY OF DONOR ATOMS

If the donor atoms sets are placed in order according to the sum of individual χ and n° values, the complexes are clearly divided into the high- and low-spin categories, with a small region of overlap where both spin types may be found Tables with the donor sets ordered in this way, which collect the values for magnetophores formed by tri- and tetradentate ligands, have been published [1]. They have been found to be useful in predicting the spin state of a given magnetophore, in assigning its coordination number of in identifying the donor atoms where alternative possibilities would be expected to give different spin states

The effects of stereochemistry on spin state have, by contrast, received little attention [6]. A sufficient number of X-ray crystallographic determinations has now been reported to permit a discussion of these effects [7].

As it is well known, five equivalent donor atoms can be symmetrically arranged around a central metal ion in one of the two limit structures, C_{4v} and D_{3h}, which can be interconverted by means of simple angular distortions through geometries with C_{2v} symmetry (Fig. 1) From a general point of view one would expect that the spin state of the complexes may depend on the symmetry of the magnetophores However a ligand field treatment of cobalt(II) and nickel(II) ions has shown that the energy difference between the lowest high- and low-spin levels is approximately equal for all the above dispositions of the five donor atoms * (Fig 1).

These results can be extended with some approximations to the five-coordinated magnetophores having non-equivalent donor atoms. All the magnetophores, then, can be ordered according to the electronegativity or nucleophilicity sum of the donor set independently of the ligand skeleton or stereochemistry of the complex, as illustrated in Table 1, which reports almost all the known donor sets of five-coordinated complexes of cobalt (II) and nickel(II).

Both Σn° and $\Sigma\chi$ correlate well with the spin state, and this shows that the previous assumption that the spin state is independent of molecular geometry is fully justified. The cross-over ranges, which are quite narrow, are practically coincident for cobalt(II) and nickel(II). The positions of N_2S_3 and NS_4 donor sets can be considered undetermined because the n° values for sulphur in dialkyldithiophosphates and -phosphinates are not known [5a] In any case, the S donor atoms are unusual in strongly changing the relative σ and π contributions to the coordination bond depending on the ligand bond system.

We have excluded from Table 1 certain complexes that have "irregular" structure. Thus, while most metal–ligand bond lengths are close to a value which may be termed "standard",

* Ligand field calculations have been performed using the well known weak scheme inclusive of configuration interactions. The energy separation of the free ion term has been reduced by 25%

there are some compounds in which it is known that one metal–ligand bond is significantly longer than the "standard", the difference may be as much as ca. 30% of the "standard" bond length in some cases [65, 66, 73, 108]. The donor atom in an elongated metal–ligand bond can be considered as partially coordinated to the metal so that the effective coordination number is somewhere between five and four.

TABLE 1

Overall nucleophilicities and spin state for five-coordinate cobalt(II) and nickel(II) complexes [a]

Set		Σn°	Co	Ref	Ni	Ref
O_5		12 00	H	8, 9, 10a, 11, 12	H	8a, 10, 11
O_3N_2		13 40	H	13	H	14, 15
O_2N_2Cl		14 04	H	16	H	16
O_2N_3		14 10	H	17, 18a	H	18b, 18c, 19, 20
$ONCl_3$		14 62			H	21a
ON_2Cl_2		14 68	H	22	H	22, 23
ON_3Cl		14 74	H	16	H	16
O_2N_2Br		15 18	H	16	H	16
Cl_5		15 20			H	24
N_2Cl_3		15 32			H	25
$ON_3(NCS)$		15 35	H	16	H	16
N_3Cl_2		15 38	H	26–35	H	26a,27a,28,29a,30–32,35,36
N_4Cl		15 44	H	37–39	H	37, 39, 40
N_5		15 50			H	41
ON_3Br		15 88	H	16	H	16
$ON_2(NCS)_2$		15 90	H	22		
$N_4(NCS)$		16 05	H	42		
O_2N_2I		16 42	H	16	H	16
N_4Br		16 58	H	37–39, 40a, 43, 44	H	37, 39, 40a, 45
$N_3(NCS)_2$		16 60	H	16, 31–33, 34a, 46, 47	H	16, 46, 48
ON_2Br_2		16 96	H	22	H	22, 23, 49
N_2SCl_2		17 01	H	50, 51	H	50, 52, 53
N_3SCl		17 07	H	16, 46	H	16, 46
ON_3I		17 12	H	16	H	16
N_3Br_2		17 66	H	26a,28,29a,30–33, 34a,35	H	26a,28,30,31,33,35,36,54
$N_3S(NCS)$		17 68	H	16, 46	H	16, 46
N_4I		17 82	H	37–39, 40a, 42	H	37, 39
N_3SBr		18 21	H	16, 46	H	16, 46
$N_2S(NCS)_2$		18 23	H	50, 52, 53	H	50, 52
N_2S_2Cl		18 70	H	16, 46	H	16, 46
N_3AsCl		19 09	H	46, 55		
N_2SBr_2		19 29	H	50, 51	H	50, 52, 53
$N_2S_2(NCS)$		19 31	H	16, 46	H	16, 46
N_3SI		19 45	H	16, 46	H	16, 46
N_2S_2Br		19 84	H	16, 46	H	16, 46
N_3I_2		20 14	H	26a, 30–32, 34a	H	26a, 28, 30, 31, 36
N_3AsBr		20 33	H	46, 55		
NS_3Cl	(Me)[b]	20 33	H	56		

TABLE I (continued)

Set		Σn°	Co	Ref	Ni	Ref
NS_3Br	(i-Pr)	20.42	H	57	H	57
N_2OPCl		20 43	H	58		
$ONAsBr_2$		20 61			H	3
$N_2OP(NCS)$		21 04	H	58		
N_2PCl_2		21 07	H	57		
N_2S_2I		21 08	H	16, 46	H	16, 46
N_3PCl		21 13			H	46, 55
N_2SI_2		21 17	H	51	H	52, 53
N_2AsBr_2		21 31			H	3
N_3AsI		21 47	H	46, 55	H	46, 55
NS_3Br	(Me)	21 47	H	56		
N_2OPBr		21 57	H	58		
NS_3I	(i-Pr)	21 66	H	57	H	57
N_3PBr		22 27			H	46, 55, 59
$N_2P(NCS)_2$		22 29	H	60		
$ONPBr_2$		22 65			H	3
NS_3I	(Me)	22 71	H	56		
N_2SPCl		22 76	H	58		
N_2OPI		22 81	H	58		
$SNAsBr_2$		22 94			H	3
$ONAsI_2$		23.09			H	3
N_2PBr_2		23 35	H	57	H	3
$N_2SP(NCS)$		23 37	H	58		
N_2S_2Cl		23 44			H	16, 46, 61
N_2AsI_2		23 79			H	3
N_2SPBr		23 90	H	58		
PS_2Cl_2		24 33			H	62
NAs_2Br_2		24 96			H	63
$SNPBr_2$		24.98			H	3
$ONPI_2$		25 13			H	3
N_2SPI		25 14	H	58		
$SNAsI_2$		25 42			H	3
N_2PI_2		25 83	H	57	L	3
PS_3Cl		26 02			L	64
NOP_2Cl		26 12			L	65
As_2SBr		26 59			L	63
PS_2Br_2		26 61			L	62
$PS_3(NCS)$		26 63			L	64a
$NOP_2(NCS)$		26.73	L+H	65	L	65, 66
NP_2Cl_2		26 76	H	67–69	H+L	68–70
N_2P_2Cl		26.82	L	71	L	71
NOP_2Br		27.26			L	65
$N_2P_2(NCS)$		27 43			L	54
NAs_2I_2		27.44			L	63
$SNPI_2$		27.46			L	58
NAs_3Br		27 53			L	63, 72
N_2P_2Br		27.96	L	46, 55	L	46, 55, 71
PS_3I		28.40			L	64a
NOP_2I		28 50			L	65, 73
PSe_3Cl		28 51			L	74

TABLE 1 (continued)

Set		Σn°	Co	Ref	Ni	Ref
As_3Br_2		28 61			L	75
NAs_3I		28 77			L	63, 72
$P_4(NCS)$		28 81	L	76		
NP_2Br_2		29.04	L+H	67–69, 77a	L	68–70, 77
As_2SI_2		29 07			L	63
PS_2I_2		29 09			L	62, 78
$PSe_3(NCS)$		29.12			L	74
N_2P_2I		29 20	L	71	L	71
P_2S_2Cl	(PhEt)	29.38	L	79		
P_2S_2Cl	(Et)	29 50			L	80
PSe_3Br		29.65			L	74
As_4Cl	(Ph)	30 04			L	81, 82
P_2S_2Br	(PhEt)	30 52	L	79	L	79
P_2S_2Br	(Et)	30 64			L	80
$As_4(NCS)$	(Ph)	30 65			L	82
PSe_3I		30 89			L	74
As_3I_2		31 09			L	75
As_4Br	(Ph)	31 18			L	82
P_2S_2Br	(PhMe)	31 22	L	83	L	62
NP_2I_2		31 52	L	67–69, 77a	L	68–70, 77a
As_4Cl	(PhMe)	31 62			L	84
P_2S_2I	(PhEt)	31 76	L	79	L	79, 85
P_2S_2I	(Et)	31 88			L	80
$As_4(NCS)$	(PhMe)	32 23			L	84
As_4I	(Ph)	32 42			L	82
P_3Cl_2		32 45			L	86
NP_3Cl		32 51			L	72, 87
As_4Br	(PhMe)	32 76			L	84
P_2Se_2Br	(PhMe)	32 88	L	83	L	62
$NP_3(NCS)$		33 12	L	87	L	87
P_2SI_2		33 15	L	77	L	85
As_4Cl	(Et)	33 20			L	88
NP_3Br		33.65			L	72, 87
$As_4(CN)$	(Ph)	34.00			L	82
As_4I	(PhMe)	34 00			L	89
As_4I	(PhMe)	34.10			L	84
P_2As_2Cl	(Ph)	34 12	L	83	L	90
$P_2As_2NO_2$	(Ph)	34 30			L	90
As_4Br	(Et)	34 34			L	88
PAs_3Cl	(Et)	34 51			L	91
PAs_3NO_2	(Et)	34 69			L	91
P_3Br_2		34 73	L	92	L	86
$P_2As_2(NCS)$		34 73			L	90
NP_3I		34 89	L	87, 93	L	72, 87, 94
$(CN)_5$		35 00			L	95, 96
$PAs_3(NCS)$	(Et)	35 12			L	91
P_2As_2Br	(Ph)	35 26	L	83	L	90
P_5		35 40			L	97
As_4I	(Et)	35 58			L	88
PAs_3Br	(Et)	35 65			L	91

TABLE 1 (continued)

Set		Σn°	Co	Ref	Ni	Ref
SbP_3Cl		36 06			L	98
$NP_3(CN)$		36 47	L	56		
P_2As_2I	(Ph)	36 50	L	83	L	90
PAs_3I	(Et)	36 89			L	91
$P_3(CN)_2$		36 95			L	99–102
$As_4(CN)$	(Et)	37 16			L	88
P_3I_2	(Ph)	37 21			L	86
As_5		37 70			L	103
P_4Cl	(Ph)	38 20	L	76, 81, 104	L	82, 105
$PAs_3(CN)$	(Et)	38 47			L	91
P_4Br	(Ph)	39 34	L	76	L	105
$P_3(CN)_2$		39 49			L	106
$P_3(CN)_2$		40 43			L	107
P_4I	(Ph)	40 58	L	76		

[a] The value of n° for isothiocyanate was taken as three units less than that of thiocyanate (R.G Pearson, personal communication) This will not require any substantial change in the published order.
[b] Substituent at the peripheral donor atoms

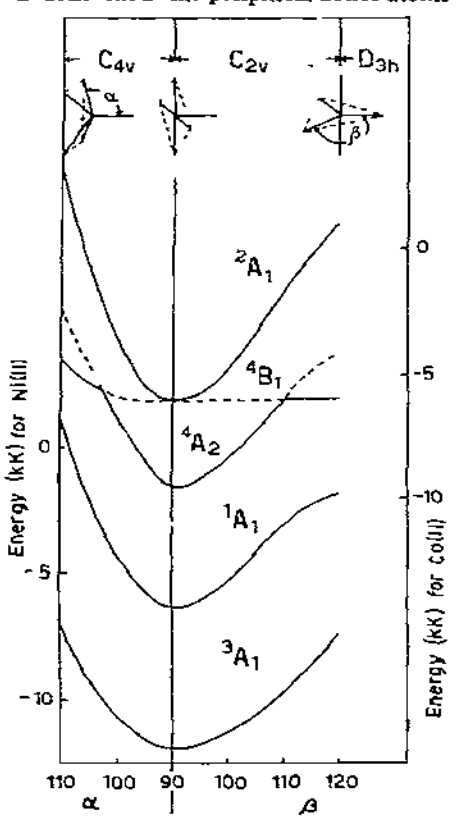

Fig 1. Lowest high- and low-spin levels for cobalt(II) (upper) and nickel(II) (lower) in D_{3h}, C_{4v} and intermediate C_{2v} symmetries $Dq = 1.2$ kK, $\beta = 0.80$

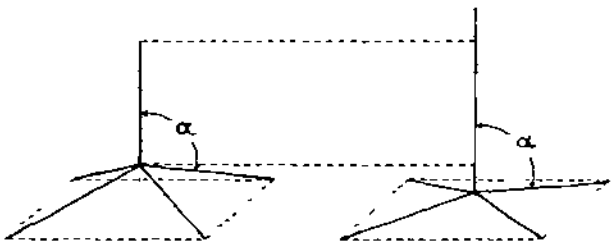

Fig 2 Axial elongation observed in some square pyramidal complexes

C AXIAL ELONGATION IN SQUARE PYRAMIDAL COMPLEXES

Square pyramidal complexes are susceptible to lengthening of the axial bond with simultaneous shortening of four basal bonds, which in the limit results in a square-planar four-coordinate complex (Fig. 2). Since square-planar cobalt(II) and nickel(II) complexes are invariably low spin, and a square-pyramidal complex may be high spin, the extent of apical bond lengthening is expected to have a decisive effect on the spin multiplicity in some cases

The apical angle α (Fig 2) has been found to be ca 100° in square pyramidal complexes with five "standard" bonds. The lengthening of the apical bond is then usually accompanied by a decrease in the apical angle towards 90°

The apical angle may be plotted against another measure of distortion, the ratio of axial : "standard" bond lengths (axial elongation) as shown in Fig. 3 Most points on this plot lie close enough to a single curve to indicate that either axial elongation or apical angle may be used as a measure of distortion from a "regular" configuration.

Average standard five-coordinate bond lengths (Å) were taken as follows. Ni—O = Co—O = 2.0, Co—O^- = 1.94 (LS), Ni—S = 2.26 (LS), 2.38 (HS), Ni—N_{sp^2} = 2.04 (HS), 1.92 (LS), Co—N_{sp^2} = 2.12 (HS), 1.94 (LS), Ni—N_{sp^3} = 2.10 (HS); Co—P = 2.23 (LS); Ni—As = 2.29 (LS); Ni—Cl = Co—Cl = 2.31 (HS), Ni—Br = 2 40 (LS), Co—Br = 2.43 (LS); Ni—NCS = 1 96 (HS)

The largest distortions are found for the magnetophores such as $NiNOP_2I$ (ref. 73) or $NiNOP_2(NCS)$ (ref. 66) in which the apical M—O bond is 0 6 or 0.4 Å longer than the "standard"

If the energies of the high- and low-spin states are calculated by a ligand field treatment such as to fit the curve in Fig 3, using Ballhausen's method to calculate B_2 and B_4 as functions of bond length [109], it is found that the low-spin state is favoured by increasing axial distortion (Fig 4) Thus, the highly distorted complexes of C_{4v} symmetry may be low spin when they would expected to be high spin on the basis of the Σn° or $\Sigma\chi$ criterion The overall n° and χ values for complexes of cobalt(II) and nickel(II) whose structure has been ascertained by an X-ray crystallographic determination are given in Tables 2 and 3, including those omitted from Table 1.

The low-spin complexes with magnetophores placed by the Σn° criterion in the high-spin region are all grossly distorted from a regular configuration. For example, the com-

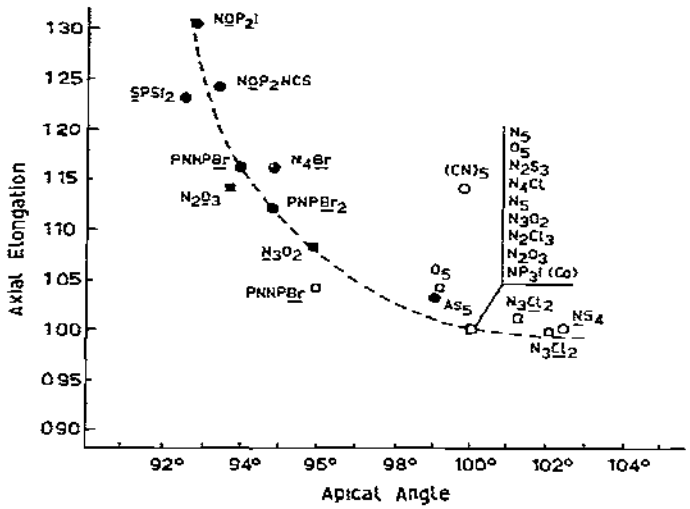

Fig 3 Axial elongation vs the apical angle for square pyramidal complexes ○, high-spin nickel, ●, low-spin nickel, ○, high-spin cobalt, ■, low-spin cobalt Apical atoms underlined.

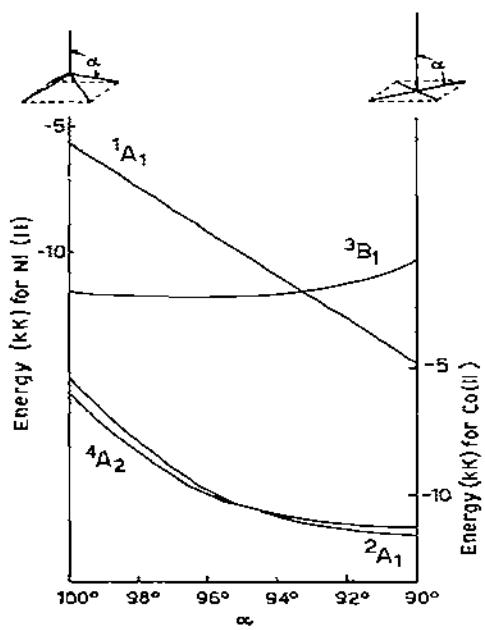

Fig. 4. Energy of the lowest high- and low-spin levels for cobalt(II) (lower) and nickel(II) (upper) plotted vs. α. The α values are related to the axial elongation through the plot of Fig. 3. Dq (basal) = 1.4 kK for nickel and 1.5 kK for cobalt, $\beta = 0.8$ and 0.7 for nickel and cobalt respectively.

TABLE 2

X-ray structure and spin state of five-coordinate cobalt(II) complexes

Set	$\Sigma\chi$	Σn°	Square pyram	Elong ratio	Intermed	Trig bipyr.	Axial angle	Ref.
O_5	17 50	12 00	H	1 04		H	92°, 93°	8b, 9b
O_3N_2	16 64	13 40	L	1 14		H		110, 13a
O_2N_3	16 21	14 10	H	1 00				18b, 18c, 111
			L	1.08				
N_3Cl_2	14.87	15 38	H	1 00, 1 01				26b, 27b, 29b, 34b
$N_2O(NCS)_2$	15 71	15 90				H	96 6°	57
N_4Br	15.02	16 58				H	99°, 91°	43, 44
$N_3(NCS)_2$	15 35	16 60				H	96 4°	47
N_3PCl	14.10	21 13				H	100°	57
$N_2P(NCS)_2$	14 34	22 29			L + H 97°	H	98°	57
NOP_2Cl	13 52	26 12				H	103°	65
N_2P_2Br	13 00	27 96	L	1 04				57
N_2P_2I	12 47	29 20				H	103°	57
NS_4	12 83	31 50	L	1 03				112
NP_3Cl	12 08	32 51				H	104 6°	113
NP_3Br	11 99	33 65				H	106°	57
P_3Br_2	11 66	34 73				L	90°	92b
NP_3I	11 46	34 89	L	1 00		H	106°	93
P_4Cl	11 07	38 20				L	94°	104

TABLE 3

X-ray structure and spin state of five-coordinate nickel(II) complexes

Set	$\Sigma\chi$	Σn°	Square pyram	Elong ratio	Intermed	Trig bipyr	Ref
O_5	17 50	12 00	H	1 0			10b
O_3N_2	16 64	13 40	H	1.0	H		14, 15
O_2N_3	16 21	14 10	H	1 0		H H H	18b, 18c, 19a, 20
$ONCl_3$	15 06	14 62				H	21b
Cl_5	14 15	15 20	H	1 0			24
N_2Cl_3	14 63	15 32	H	1 0			25
N_4Cl	15 11	15 44	H	1.09			40b
N_5	15.35	15.50	H	1 0			41b
$N_4(NCS)$	15 35	16 05				H	57
N_4Br	15 02	16 58	L	1.16		H	45, 114
$N_3(NCS)_2$	15 35	16 60	H				48
ON_2Br_2	15 12	16 96			H		49
N_3Br_2	14 69	17 66			H		54
N_2S_2Cl	13 85	23 44				H	61
PS_3Cl	12 21	26.02				L	64b
$NOP_2(NCS)$	13 76	26 73	L	1 24			65b, 66

TABLE 3 (continued)

Set	$\Sigma\chi$	Σn°	Square pyram	Elong ratio	Intermed	Trig bipyr.	Ref
N_2S_3	13.46	27 50	H	1 00			115
N_2P_2Br	13.00	27 96	L	1 16			55b, 57
NOP_2I	12 90	28 50	L	1 30			73
As_3Br_2	12 08	28 61	L	1.11			75b
NP_2Br_2	12 67	29 04	L	1 11			77b
PS_2I_2	11 36	29 09	L	1 25			78
N_2P_2I	12 47	29 90				L	57
NS_4	12 83	31 50	H	1 03			116
NP_3Cl	12 08	32 51				L	57
NP_3I	11 46	34 89				L	94
$(CN)_5$	12 50	35 00	L	1 14, 1 16		L	95b, 96
P_5	10 30	35 40				L	97
S_5	12 20	35 50	L	1 25			117
$P_3(CN)_2$	11 18	36 95			L		102b
P_3I_2	10 60	37 21				L	92b
As_5	11 00	37 70	L	1 03			103b
$PAs_3(CN)$	11 16	38 47				L	91b
$P_3(CN)_2$	11 18	39 49				L	106
$P_3(CN)_2$	11 18	40 43	L			L L	107b, 107c

plexes $[Ni(mac)Br]^+$ (ref. 114) and Cosal-en (ref. 110) have an elongated square pyramidal structure and are low spin whereas the complexes $[Ni(Me_6tren)Br]^+$ (ref 45) and Cosal-Me (ref 13b), which have the same magnetophores NiN_4Br and CoN_2O_3 respectively, are trigonal-bipyramidal in structure, and are high spin *.

More examples of distorted square-pyramidal nickel complexes will be found in the Tables than of distorted square-pyramidal cobalt complexes. This can be understood by considering the effect of elongation of the axial bond (z axis) upon the d electrons, the main result of which is to decrease the antibonding character of the electrons in the d_{z^2} orbital. Low-spin nickel(II) complexes which have two electrons in this orbital therefore gain more energy as a result of axial elongation than do cobalt(II) complexes which have only one electron in the d_{z^2} orbital In agreement with this hypothesis, the complex of nickel with the open-chain ligand *N*,*N'*-bis(2-diphenylphosphinoethyl)-*N*,*N'*-dimethylethylenediamine ($Ph_2P{\cdot}CH_2CH_2{\cdot}N(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$, PNNP) having the formula [57, 71] $[Ni(PNNP)Br]Y$ ($Y = Br, PF_6$), is markedly distorted (elongation ratio 1 15, α 94°) whereas the cobalt analogue is almost regular (elongation ratio 1 04, α 97°)[57,71] (Fig. 5).

* mac = 2, 12-dimethyl-3, 7, 11, 17-tetraazabicylo [11, 3, 1] heptadeca-1 (17), 2, 11, 13, 15-pentaene; sal-en = *N*, *N'*-ethylene-bis(salicylaldimine), sal-Me = *N*-methyl(salicylaldimine), tren = tris(2-aminoethyl)-amine.

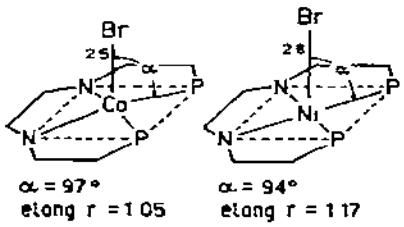

Fig 5. Structures of the [M(PNNP)] magnetophores

D. TETRAHEDRAL DISTORTION IN TRIGONAL BIPYRAMIDAL COMPLEXES

Turning to trigonal bipyramidal complexes of cobalt(II), a distortion is frequently found in which, as one of the apical bond distances increases, the configuration tends towards tetrahedral (Fig 6).

X-ray data show that the angle γ is often larger than 90° and correspondingly the distance between metal and apical atoms is greater than usual The distortion may be so large [73] that γ may nearly reach 109°28′, e g., 106°, with an elongation ratio reaching ca. 1 3.

A plot of γ against M–N apical bond lengths in cobalt and nickel complexes is presented in Fig. 7. Most of the complexes in this figure have tetradentate tripod-like ligands with a nitrogen atom at the apex of the tripod in a state of sp^3 hybridization, i e , N_3P, N_2P_2, NOP_2 and NP_3 donor sets The donor sets N_4P refer to the bis-isothiocyanate complexes with the tridentate ligand *N*,*N*-diethyl-*N*′-(2-diphenylphosphinoethyl) ethylenediamine

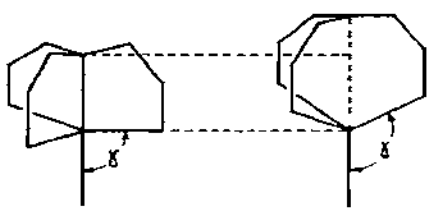

Fig 6 Tetrahedral distortion of trigonal bipyramidal cobalt(II) complexes

($Et_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2CH_2{\cdot}PPh_2$, HNNP) and its *N*′-methyl analogue (MeNNP) (refs. 57, 60). The set N_4O refers to *N*,*N*-diethyl-*N*′-(2-diphenylphosphineoxide-ethyl)-ethylenediamine ($Et_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}POPh_2$) (ref 57). As can be seen from Fig 7, the M–N bond length increases in parallel with the extent of distortion towards a tetrahedral configuration This kind of distortion is limited in practice to complexes of cobalt(II).

Since tetrahedral complexes of cobalt(II) can be only high spin, distortion towards a tetrahedral configuration should favour the high-spin state. Ligand field calculations show that the separation of the $^4A_2$ and ^2E levels increases steadily as γ tends to 109° 28′, as illustrated in Fig 8. For a practical example of this, compare the two complexes Co(HNNP) $(NCS)_2$ and Co(MeNNP) $(NCS)_2$. The difference between the two complexes,

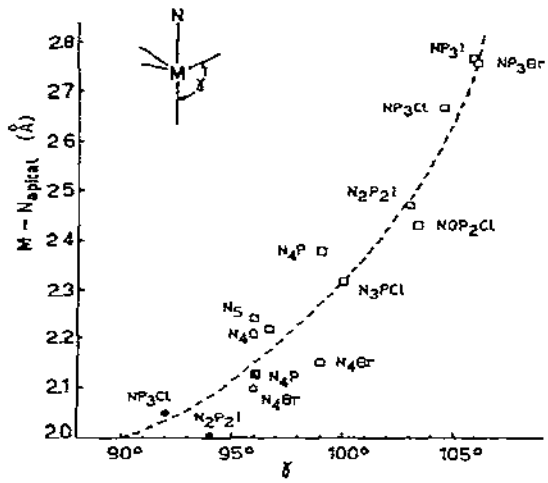

Fig. 7. M–N apical bond lengths vs γ angle in tetrahedrally distorted trigonal bipyramidal magnetophores

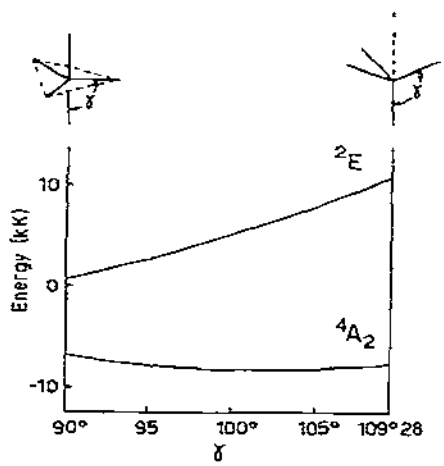

Fig. 8 Energy of the lowest high- and low-spin levels for cobalt(II) complexes vs γ values which are related to the tetrahedral distortion through the plot of Fig 6 Dq = 1.2 kK, β = 0 8

which have a N_4P donor set, consists in an *N*-H group in the former in place of an *N*-CH_3 in the latter The former complex is trigonal-bipyramidal with a small distortion and exhibits a spin equilibrium (μ_{eff} = 2.16 B M at 77°K, 4.32 B.M. at 418°K). The latter compound is severely distorted, with a cobalt-apical nitrogen bond length ca. 0.3 Å longer than in the former complex, and exists only in the high-spin state (μ_{eff} = 4.47 B M at 294°K) [57, 60] (Fig. 9).

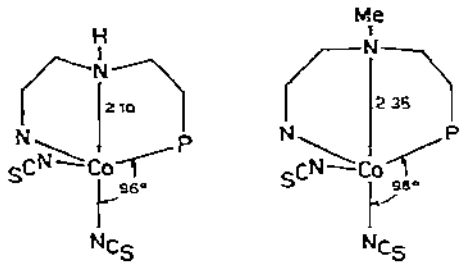

Fig. 9 Structures of the $Co(HNNP)(NCS)_2$ and $Co(MeNNP)(NCS)_2$ complexes

The square-pyramidal iodo complex of cobalt(II) with the tripod ligand tris (2-diphenylphosphinoethyl) amine, $[Co(NP_3)I]^+$, has a "standard" geometry with $\alpha = 100°$ and is low spin [87,93]. In contrast, the other form of the same complex cation, which has a distorted trigonal bipyramidal structure, $\gamma = 106°$, is high spin [57,87]. The cobalt(II) magnetophores with NP_3Cl, NP_3Br, NOP_2Cl and N_2P_2I donor sets derived from tripod ligands are also high spin These are strongly distorted towards tetrahedral with γ between 100° and 106°, as shown in Fig 10 It appears that, starting from the tripod ligand with donor set N_4 ($\gamma = 99°$), both γ and the apical distance increase with the number of equatorial phosphorus atoms Clearly, the Σn° or $\Sigma\chi$ criteria may fail when this type of distortion is present

The particular way in which complexes of nickel tend to adopt an elongated square pyramidal configuration while complexes of cobalt tend to take a distorted tetrahedral structure is well illustrated by the X-ray structures of the two "umbrella-shaped" complexes $[M(N_2P_2)I]I$ (Fig 11) The nickel complex is diamagnetic, the cobalt complex is high-spin The cations of both complexes are distorted trigonal-bipyramidal. The cobalt complex undergoes distortion towards tetrahedral when the cobalt atom lies ca. 0.5 Å

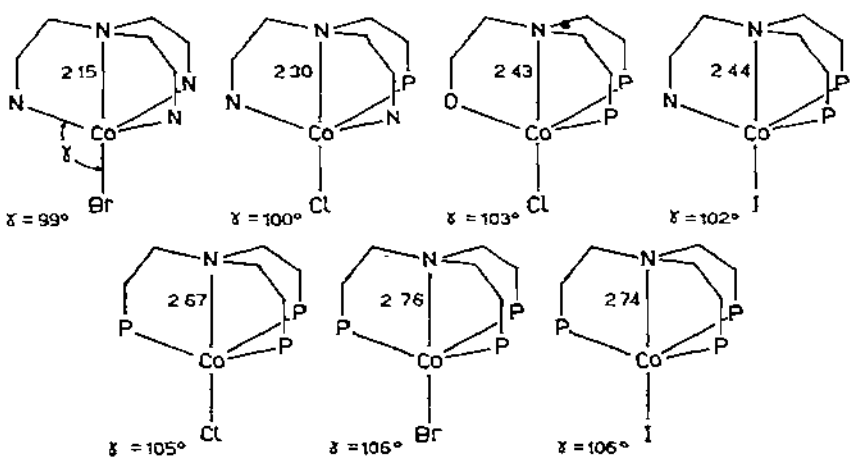

Fig 10 Structures of tetrahedrally distorted trigonal-bipyramidal cobalt(II) complexes

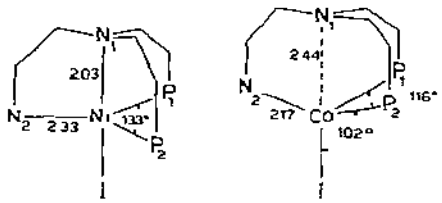

Fig 11. Structures of $[Ni(N_2P_2)I]$ I and $[Co(N_2P_2)I]$ I complexes.

below the equatorial plane, and thus much nearer to the apical iodine atom The Co—N(1) distance is unusually long. By contrast the nickel atom is only 0 13 Å below the equatorial plane, and it is the Ni—N(2) distance which is long, i e. the nickel complex tends to an elongated square pyramid with the N(2) atom at the apex Since the two compounds are isomorphous the different distortions cannot be attributed to solid state effects, but must be caused by the intrinsic electronic requirements of the two metal ions

E CONCLUSIONS

To sum up, the Σn° and $\Sigma\chi$ values of a donor set provide a generally useful datum with which to predict the spin state of a five-coordinate complex The prediction may fail, however, if the complex is strongly distorted towards a four-coordinate structure. indeed an unexpected spin state probably indicates that distortion is present The most common distortion of five-coordinate complexes consists of the lengthening of one metal—donor bond so that the complex tends towards the limiting tetrahedral or planar stereochemistry The effects of these distortions on magnetic properties can now be fairly well understood

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