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STERIC AND ELECTRONIC FACTORS INFLUENCING THE STRUCTURE OF NICKEL(II) COMPLEXES

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CONTENTS

ABBREVIATIONS

N	monodentate nitrogen base	X	halide or pseudohalide ligand
N_{anb}	aromatic nitrogen base	Y	anionic ligand
$N_{2\text{-}Rpy}$	2-alkylpyridine	Z	anionic or neutral ligand
$N \cap N$	bidentate nitrogen base	p	square planar
$O \cap O$	β-keto-enolate ligand	t	tetrahedral
R	organic residue		
acac	acetylacetonate		
aem	aminoethylmercaptide		

aep	2-(β-aminoethyl)pyridine
ampMe	2-aminomethyl-6-methyl-pyridine
BenNMe$_2$	*N*-(β-dimethylaminoethyl)formimidoyl-benzene
3-Brpy	3-bromopyridine
bia	benzimidazole
t-Buaem	*t*-butylaminoethylmercaptide
dien	bis(β-aminoethyl)amine
dpt	bis(γ-aminopropyl)amine
Et$_2$aem	diethylaminoethylmercaptide
Etaep	2-(β-ethylaminoethyl)pyridine
Et$_2$aep	2-(β-diethylaminoethyl)pyridine
Eten	*N*-ethylethylenediamine
a-Et$_2$en	*N*,*N*-diethylethylenediamine
s-Et$_2$en	*N*,*N'*-diethylethylenediamine
Etamp	2-ethylaminomethyl-pyridine
Et$_2$amp	2-diethylaminomethyl-pyridine
4-Etpy	4-ethylpyridine
Et$_2$PeSEt	β-diethylphosphinoethyl-ethylsulphide
himda	*N*-(β-hydroxyethyl)iminodiacetic acid
iquin	isoquinoline
Me$_2$aem	dimethylaminoethylmercaptide
Meaep	2-(β-methylaminoethyl)pyridine
Me$_2$aep	2-(β-dimethylaminoethyl)pyridine
Meamp	2-methylaminomethyl-pyridine
2-Mebia	2-methylbenzimidazole
2-Mebta	2-methylbenzothiazole
a-Me$_2$en	*N*,*N*-dimethylethylenediamine
Me$_4$en	*N*,*N*,*N'*,*N'*-tetramethylethylenediamine
2-Meima	2-methylimidazole
3-Meiq	3-methylisoquinoline
2-MeOBenNEt$_2$	1-[*N*-(β-diethylaminoethyl)-formimidoyl]-2-methoxy-benzene
2-MeOBenNMe$_2$	1-[*N*-(β-dimethylaminoethyl)-formimidoyl]-2-methoxy-benzene
2-MeOBtnNMe$_2$	1-[*N*-(γ-dimethylaminopropyl)-formimidoyl]-2-methoxy-benzene
2,9-Me$_2$phen	2,9-dimethylphenanthroline(1,10)
2-Mepy	2-methylpyridine
3-Mepy	3-methylpyridine
4-Mepy	4-methylpyridine
2,3-Me$_2$py	2,3-dimethylpyridine
2,4-Me$_2$py	2,4-dimethylpyridine
2,5-Me$_2$py	2,5-dimethylpyridine
2,6-Me$_2$py	2,6-dimethylpyridine
3,4-Me$_2$py	3,4-dimethylpyridine
3,5-Me$_2$py	3,5-dimethylpyridine
Me$_3$tn	1-dimethylamino-3-methylamino-propane
Me$_4$tn	1,3-bis(dimethylamino)-propane
(2-Me)$_2$ dpma	bis[6-methylpyridyl(2)-methyl]amine
(2-Me)$_3$tpma	tris[6-methylpyridyl(2)-methyl]amine
4-NH$_2$py	4-aminopyridine
peSmp	[pyridyl(2)-methyl]-[β-pyridyl(2)-ethyl]-sulphide
P(phNMe$_2$)$_3$	tris(2-dimethylaminophenyl)phosphine
Ph$_2$Asep	2-(β-diphenylarsinoethyl)pyridine
Ph$_2$Pep	2-(β-diphenylphosphinoethyl)pyridine
(Ph$_2$Pe)$_2$p	2,6-bis(β-diphenylphosphinoethyl)pyridine

$(Ph_2Pm)_2p$	2,6-bis(β-diphenylphosphinomethyl)pyridine
$PhP(phNMe_2)_2$	bis(2-dimethylaminophenyl)phenylphosphine
$Ph_2PphNMe_2$	2-dimethylaminophenyl-diphenylphosphine
pmSmp	bis[pyridyl(2)-methyl]sulphide
py	pyridine
quina	quinaldine
n-Raem	*n*-alkylaminoethylmercaptide
$salenAsPh_2$	*N*-(β-diphenylarsinoethyl)salicylaldiminate
salenNMe	*N*-(β-methylaminoethyl)salicylaldiminate
$salenNMe_2$	*N*-(β-dimethylaminoethyl)salicylaldiminate
$salenNPh_2$	*N*-(β-diphenylaminoethyl)salicylaldiminate
$salenPEt_2$	*N*-(β-Diethylphosphinoethyl)salicylaldiminate
$salenPPh_2$	*N*-(β-diphenylphosphinoethyl)salicylaldiminate
salenSMe	*N*-(β-methylthioethyl)salicylaldiminate
salep	*N*-(β-pyridyl(2)-ethyl]salicylaldiminate
salmp	*N*-[pyridyl(2)-methyl]salicylaldiminate
saltnNMe	*N*-(γ-methylaminopropyl)salicylaldiminate
saltnNMePh	*N*-(β-methylphenylamino-ethyl)salicylaldiminate
m-stien	*meso*-stilbenediamine
tpma	tris[pyridyl(2)-methyl]amine

A. INTRODUCTION

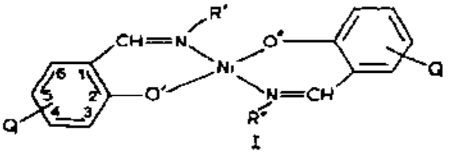
Up to the early nineteen-fifties chemists recognised only the characteristic coordination numbers six and four for nickel(II). In the first case an octahedral and in the second a square-planar or tetrahedral structure was recognised. Later Ciampolini et al. [1,2] characterised five-coordinate nickel(II) with a trigonal-bipyramidal disposition of the ligands, and Sacconi et al. [3] characterised compounds with a square-pyramidal disposition. Very recently nickel(II) chelates with a distorted trigonal-prismatic structure have been described[4]. Also, interesting new aspects resulted from the detection of the phenomena of "interallogony"[5] and "coordination polymerisation"[6].

This structural variety, together with the development of ligand field theory as a simple method of showing relationships between structure and the spectral, magnetic, and reactive behaviour of coordination compounds, has been the main reason for the active interest in the coordination chemistry of nickel(II) during the last decade. Today the extensive experimental results make it possible to explain the isomerism [7–9] of β-keto-enolate complexes of nickel(II), the structural differences [10] of compounds of the type $Ni(en)_2XY$ and the high-spin or low-spin character of five-coordinate nickel(II) chelates [11]. In this review some of these results will be summarised without attempting completeness. In particular the following problems will be treated: steric and electronic factors influencing the structures of monomeric complexes of the coordination numbers four and five; the importance of steric and electronic factors in coordination polymerisation; the interaction of ligands in mixed-ligand complexes, and the influence of the internal structures of the ligands on the structures of chelate compounds of nickel(II).

B. STERIC AND ELECTRONIC EFFECTS INFLUENCING THE STRUCTURE OF MONOMERIC COMPLEXES OF COORDINATION NUMBERS FOUR AND FIVE

(i) Chelates of salicylaldimines

The structures of nickel(II) complexes of coordination number four depend mainly on the strength of the ligand field. A strong field favours a square-planar disposition of the donor groups, whereas a weak field cannot force a change from the tetrahedral structure*, which, considering only ligand–ligand repulsions[12], is the most stable. In the salicylaldimine chelates I the ligand field is evidently of such strength that the square-planar and tetrahedral isomers have nearly the same energy.



I

Thus, *N*-alkylsalicylaldimine chelates of nickel(II) in non-coordinating solvents exhibit a temperature-controlled equilibrium between the diamagnetic square-planar and the paramagnetic tetrahedral isomers[13]. In the case of the complexes with α-branched R the ΔF values are all low (Table 1). The tetrahedral isomer is favoured by α-branching of R as observed in the solid complexes (Table 2). This is due to the decrease of the non-bonding interaction between the α-branched substituent R of the first, and the oxygen atom of the second ligand (R' and O'', and R'' and O' of compound I) in the tetrahedral isomer compared to the square-planar one[13, 14].

The structure of complexes I in the solid state, however, is not only determined by the branching of R. This is shown by the complexes with R = i-C_3H_7 and Q = H, 3-CH_3, and

TABLE 1

Thermodynamic functions for the square planar–tetrahedral equilibrium at 120°C in dibenzyl solution

R	Q	ΔF (kcal mole^{-1})	ΔH (kcal.mole^{-1})	ΔS (e.u.)
$-CH_2CH_2CH_3$	H	2.9	4.6	4
$-CH_2CH_2CH_3$	5-CH_3	2.8	4.6	4
$-CH_2CH_2CH_3$	5-Cl	2.7	5.2	6
$-CH(CH_3)_2$	H	0.52	3.2	10
$-CH(CH_3)_2$	5-CH_3	0.20	2.5	6
$-CH(CH_3)_2$	5-Cl	0.16	2.0	4

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* Unless there are specific reasons for the contrary, structural distortions will be ignored in this review.

TABLE 2

Structures of nickel(II) complexes of substituted salicylaldimines

Q	R				
	H	CH_3	n-C_3H_7	i-C_3H_7	t-C_4H_9
H	p (ref. 19)	p (refs 20, 21)[a]	p (ref. 17)	t (refs. 15, 23) (II)	t (ref 18)
5-CH_3		p (ref. 22)	p (ref. 17)	p (ref. 16)	
5-Cl				p (ref. 17)	t (ref 17)
3-CH_3		p (ref 22)	p (ref 17)	p (refs 16, 24) (III)	
3-C_2H_5				t (refs. 16, 25) (IV)	
3-Cl			p (ref 17)	p (ref. 17)	t (ref. 17)

[a] Orthorhombic (α) and monoclinic (β) forms

3-C_2H_5 (compounds II, III and IV of Table 2). Investigation of the square-planar bis(N-isopropyl-3-ethylsalicylaldiminato) palladium(II), the palladium analogue of IV, proved that the differences in the steric hindrance between the 3-methyl or the 3-ethyl and the N-isopropyl groups cannot be the reason for the square-planar structure of III and the tetrahedral structure of IV[26]; in this case lattice energy is probably the main factor determining the structure.

Structural analyses of nickel(II) chelates of substituted salicylaldimines have shown that in the square-planar allogons the Ni—N and the Ni—O distances are smaller than in the tetrahedral ones (II[23]: Ni—N = 1.970 Å, Ni—O = 1.896 Å; III[24]: Ni—N = 1.920 Å, Ni—O = 1.837 Å). On the other hand, in tetrahedral nickel(II) chelates coordinated salicylaldimine ligands have a greater "bite" (~ 2.84 Å) than in square-planar chelates (~ 2.72 Å)[27]. The Ni—Ni distance in the orthorhombic bis(N-methylsalicylaldiminato)-nickel(II)[21] proves that in complexes of this interesting type metal—metal bonds similar to that in bis-(dimethylglyoximato)nickel(II) may exist.

(ii) Complexes of the type $Ni(PR_3)_2X_2$

Complexes[28, 29] of the type $Ni(PR_3)_2X_2$ are high-spin or low-spin with a tetrahedral or a *trans* square-planar structure. Following a systematic investigation Venanzi and co-workers[12] stated that arylphosphines and bromo or iodo ligands favour the high-spin state, alkylphosphines and chloro or thiocyanato ligands the low-spin state. In the spectrochemical series the order[30] of the pertinent ligands is $I^- < Br^- < Cl^- < PR_3 < NCS^-$; i.e. in accordance with general experience ligands with a high ligand field strength produce a square-planar structure, and those with a weaker ligand field strength a tetrahedral structure.

On account of the different structures of the complexes of the type $Ni(PR_3)_2X_2$ (Table 3) we must suppose that the alkylphosphines surpass the arylphosphines in their ligand field strength. Increased π back-donation could be the reason for this. The photoelectronic spectrum[31] of $Ni(Ph_3P)_2Cl_2$ shows that the π-acceptor strength of phosphine ligands in nickel(II) complexes has not vanished, but is low[32]. Therefore a higher degree

TABLE 3

Structure and magnetic behaviour of complexes of the type $Ni(PR_3)_2X_2$

		Structure[a]			Structure	M_{eff} (B.M.)
$Ni(PEt_3)_2Cl_2$	(ref. 37)	p	$Ni(Bu^nPPh_2)_2Cl_2$	(ref. 12) (V)	t	3.35
$Ni(PEt_3)_2(NCS)_2$	(ref. 12)	p	$Ni(Bu^nPPh_2)_2Br_2$	(ref. 12) (VI)	t	3.30
$Ni(Bu^n{}_2PPh_2)_2Cl_2$	(ref. 12)	p	$Ni(Bu^nPPh_2)_2I_2$	(ref. 12) (VII)	t	3.18
$Ni(Bu^n{}_2PPh_2)_2Br_2$	(ref. 12)	p	$Ni[(C_6H_5CH_2)PPh_2]_2Cl_2$	(ref. 35)	t[b]	3.23
$Ni(Bu^n{}_2PPh_2)_2I_2$	(ref. 12)	p	$Ni[(C_6H_5CH_2)PPh_2]_2Cl_2$	(ref. 35)	p[c]	Diamagnetic
$Ni[(C_6H_5CH_2)_3P]_2Cl_2$	(ref. 35)	p	$Ni[(C_6H_5CH_2)PPh_2]_2Br_2$	(ref. 35) (VIII)	t.a.[d]	2.70
$Ni[(C_6H_5CH_2)_3P]_2Br_2$	(ref. 35)	p	$Ni[(C_6H_5CH_2)PPh_2]_2Br_2$	(ref. 35) (IX)	p[c]	Diamagnetic
$Ni[(C_6H_5CH_2)_3P]_2I_2$	(ref 35)	p	$Ni[(C_6H_5CH_2)PPh_2]_2I_2$	(ref 35)	p[e]	Diamagnetic
$Ni[(C_6H_5CH_2)_2PPh]_2Cl_2$	(ref 35)	p	$Ni[(C_6H_5CH_2)PPh_2]_2I_2$	(ref. 35)	?[f]	2.61
$Ni[(C_6H_5CH_2)_2PPh]_2Br_2$	(ref. 35)	p	$Ni(EtPPh_2)_2Cl_2$	(ref. 36)	p	Diamagnetic
$Ni[(C_6H_5CH_2)_2PPh]_2I_2$	(ref. 35)	p	$Ni(EtPPh_2)_2Br_2$	(ref. 36)	p[g]	Diamagnetic
$Ni[(C_6H_5CH_2)_2PPh]_2(NCS)_2$	(ref. 35)	p	$Ni(EtPPh_2)_2Br_2$	(ref. 36)	t[d]	3.20
			$Ni(EtPPh_2)_2I_2$	(ref. 36)	t	3.10
			$Ni(PPh_3)_2Cl_2$	(ref. 38)	t	3.41
			$Ni(PPh_3)_2Br_2$	(ref 38)	t	3.27
			$Ni(PPh_3)_2I_2$	(ref. 38)	t	3.28

[a] The compounds cited in the left-hand column are diamagnetic; [b] blue-green isomer; [c] red isomer, [d] green isomer, t.a. = interallogon; [e] red isomer without absorption band in near IR, [f] red isomer with absorption band near 900 nm, [g] brown isomer.

of σ-bonding[33] seems to be the reason for the higher ligand field strength of alkylphosphines in four-coordinate nickel(II) complexes. This correlates with the higher pK_a values of alkylphosphines in comparison to arylphosphines[34] (pK_a values: Ph_3P, 2.37, $(n\text{-}C_4H_9)_3P$, 8.43).

A stepwise substitution of alkyl by aryl groups in phosphines causes a stepwise diminution of the ligand field strength. While dialkylarylphosphines, like trialkylphosphines, form only square-planar complexes with nickel(II), the tetrahedral and the square-planar allogons of compounds of the type $[(alkyl)P(aryl)_2]_2NiX_2$ have nearly equal energy. Lattice energy and solvation energy are therefore structure-determining factors. Thus, in the solid state compounds V, VI, and VII (Table 3) have a tetrahedral structure. On the other hand, an equilibrium between the tetrahedral and the square-planar allogons is observed in benzene solution. As expected, this equilibrium is most favourable to the square-planar allogon in the case of the chloro complex V[35]. Because of the higher dipole moment of the tetrahedral form ($\mu \simeq 6$–9 D, square-planar form $\mu \simeq 1$–3.5 D), its evident stabilisation by polar solvents is clear[36]. Two isomers of the compounds $Ni[(C_3H_5)PPh_2]_2Br_2$ (ref. 35), $Ni[(C_6H_5CH_2)PPh_2]_2X_2$ (ref. 35) (X = Cl, Br, I; Table 3), and $Ni[RPPh_2]_2Br_2$ (ref. 36) (R = Et, Pr^n, Pr^i, Bu^i) are known. The complex $Ni[(C_6H_5CH_2)$-$PPh_2]_2Br_2$ is of special interest. Besides the square-planar, diamagnetic form (IX, Table 3), a paramagnetic form with an abnormal magnetic moment can be prepared (VIII, Table 3). According to the structural analysis[39] this is an interallogon. In the unit cell one square-planar and two tetrahedral molecules are present. Evidently this unusual structure permits the tightest packing of the molecules in the crystal.

This and other structural analyses[40,41] have confirmed conclusions concerning the configuration of the complexes of the type $Ni(PR_3)_2X_2$ drawn from spectral and magnetic properties. There is, however, a marked distortion in the paramagnetic tetrahedral allogons: for example[41], the angle Br–Ni–Br in $Ni(PPh_3)_2Br_2$ increases to 126.3°. This widening in comparison to the normal tetrahedral angle is attributed to the non-bonding interactions between the bromo ligands. Despite the angle of 126.3°, the Br–Br distance is 4.18 Å, only slightly greater than twice the van der Waals radius of the bromide ion.

As in the case of the salicylaldimine chelates of nickel(II) (Sect. B(i)), square-planar complexes of the type $Ni(PR_3)_2X_2$ have a shorter metal–ligand distance than is observed with the tetrahedral analogues (VIII[39]: square-planar molecule Ni–Br = 2.305 Å, Ni–P = 2.263 Å; tetrahedral molecule Ni–Br = 2.359 and 2.351 Å, Ni–P = 2.316 and 2.314 Å).

(iii) Complexes of the types $Ni(N)_2X_2$ and $Ni(N\frown N)X_2$

Complexes of the types $Ni(N)_2X_2$ and $Ni(N\frown N)X_2$ may have a polymeric octahedral or a dimeric square-pyramidal structure (Sect. C). Monomeric compounds with four-coordinate nickel(II) (Tables 4 and 5) have also been characterised. The structure of these depends to a high degree on the amine ligands. Complexes containing tertiary or secondary aliphatic mono- or bidentate amines are tetrahedral. In the case of diethylamine two isomeric compounds have been obtained[42]. Among monomeric complexes of the aromatic nitrogen heterocycles iodo compounds prevail. In most cases they have a square-planar structure, while the corresponding chloro complexes have a tetrahedral structure. Consequently the situation here is the reverse of that found with complexes of the type

TABLE 4

Structure and magnetic behaviour of monomer complexes of the type $Ni(N)_2L_2$

		Structure	μ_{eff} (B.M.)			Structure	μ_{eff} (B.M.)
$Ni(Me_2NH)_2I_2$	(ref. 42)	t	3.30	$Ni(2\text{-}Mebia)_2Cl_2$	(ref. 49) (XI)	t	3.60
$Ni(Me_3N)_2I_2$	(ref. 42)	t	3.42	$Ni(2\text{-}Mebia)_2Br_2$	(ref. 49) (XII)	t	3.43
$Ni(Et_2NH)_2Cl_2$	(ref. 42)	?	1.42	$Ni(2\text{-}Mebia)_2I_2$	(ref. 49) (XIII)	t	3.36
$Ni(Et_2NH)_2Br_2$	(ref. 42)	?	1.22	$Ni(3\text{-}Meiq)_2Cl_2$	(ref. 49) (XIV)	t	3.58
$Ni(Et_2NH)_2I_2$	(ref. 42)	?	0.96	$Ni(3\text{-}Meiq)_2Br_2$	(ref. 49) (XV)	t	3.56
$Ni(py)_2I_2$	(ref. 43)	t	3.44	$Ni(3\text{-}Meiq)_2I_2$	(ref. 49) (XVI)	p	Diamagnetic
$Ni(2\text{-}Mepy)_2Cl_2$	(ref. 44)	t	3.48	$Ni(2\text{-}Mebta)_2Br_2$	(ref. 49) (XVII)	p	Diamagnetic
$Ni(2\text{-}Mepy)_2Br_2$	(ref. 44)	t	3.47	$Ni(2\text{-}Mebta)_2I_2$	(ref. 49) (XVIII)	p	Diamagnetic
$Ni(2\text{-}Mepy)_2I_2$	(ref. 44) (IX)	p	Diamagnetic	$Ni(2,3\text{-}Me_2py)_2Cl_2$	(ref. 51) (XIX)	t	3.61
$Ni(4\text{-}Mepy)_2I_2$	(ref. 44) (X)	t	3.38	$Ni(2,3\text{-}Me_2py)_2Br_2$	(ref. 51) (XX)	t	3.54
$Ni(2,6\text{-}Me_2py)_2Br_2$	(ref. 48)	p	Diamagnetic	$Ni(2,4\text{-}Me_2py)_2Cl_2$	(ref. 51) (XXI)	t	3.60
$Ni(2,6\text{-}Me_2py)_2I_2$	(ref. 48)	p	Diamagnetic	$Ni(2,4\text{-}Me_2py)_2Br_2$	(ref. 51) (XXII)	t	3.53
$Ni(quina)_2Br_2$	(ref. 48)	p	Diamagnetic	$Ni(2,5\text{-}Me_2py)_2Cl_2$	(ref. 51) (XXIII)	p	Diamagnetic
$Ni(quina)_2I_2$	(ref. 48)	p	Diamagnetic	$Ni(2,5\text{-}Me_2py)_2Br_2$	(ref. 51) (XXIV)	p	Diamagnetic

$Ni(PR_3)_2X_2$ (Sect. B(ii)).

Lever et al.[45] have discussed the special bond type between nickel(II) and aromatic nitrogen heterocycles The latter may act not only as σ-donors, but also by using their antibonding π-orbitals, as π-acceptors. Nickel(II) is only a weak π-donor[33], but its donor strength increases if it is combined with halide ligands with a relatively low electronegativity. Therefore the group NiI_2 is more capable of π back-donation than the group $NiCl_2$. It also leads to a larger decrease in inter-electronic repulsion energy and therefore facilitates spin-pairing. Owing to this back-donation, especially in the complexes $Ni(N_{anb})_2I_2$, the mean ligand field strength increases, and the pairing energy decreases, to such a degree that the square-planar diamagnetic allogon becomes more stable than the tetrahedral one. In this connection it must also be noted that in tetrahedral nickel(II) complexes π back-donation is weaker than in octahedral or square-planar ones[46].

The degree of π back-donation, which is an electronic effect, cannot be the only reason for the formation of square-planar molecules of the type $Ni(N)_2X_2$. This is shown most clearly by comparing the compounds IX and X (Table 4). The donor strengths of 2-Mepy and 4-Mepy are only slightly different (pK_a (25°C)[47]: 2-Mepy = 5.94, 4-Mepy = 6.03). A difference in the π-acceptor strength cannot be excluded[105], but it should be low. In spite of these minimal differences in the electronic properties of the two picolines, compound IX has a square-planar structure and X a tetrahedral structure. Evidently the reason for this is a steric effect[48]. In tetrahedral complexes of the type $Ni(N_{2\text{-}Rpy})_2X_2$ there is an interaction between the substituents R chiefly where the space in the coordination sphere of the central atom available for the ligands $N_{2\text{-}Rpy}$ is reduced by two bulky iodo ligands. By contrast, even with 2,6-Me_2py as a ligand little steric hindrance is expected if the complexes $Ni(N_{2,6\text{-}Rpy})_2X_2$ have a square-planar structure and if the nitrogen ligands are arranged perpendicularly to the plane of nickel(II) and the four donor atoms.

The fine structural balance exhibited by the compounds $Ni(N_{anb})_2X_2$ is demonstrated by the complexes XI–XIII, XIV–XVI, XVII and XVIII. The ligands 2-methylbenzimidazole (2-Mebia), 3-methylisoquinoline (3-Meiq), and 2-methylbenzothiazole (2-Mebta) have a methyl group in the position α to the nitrogen donor atom. This methyl group, both in the tetrahedral and square-planar complexes of the five-membered heterocycles $Ni(2\text{-Mebia})_2X_2$ and $Ni(2\text{-Mebta})_2X_2$, is more distant[49] from the central atom than in complexes of the six-membered heterocycle 3-Meiq. Therefore, while 3-Meiq is completely analogous to 2-picoline (Table 4), steric hindrance in complexes of 2-Mebia and 2-Mepta is low even in a tetrahedral structure. Since the π-acceptor strength of 2-Mebia should not differ much from pyridine, these two nitrogen ligands should be comparable with regard to their coordination tendency. The tetrahedral configuration of complexes XI–XIII is therefore not surprising*. 2-Mebta, however, is a weak σ-donor (pK_a = 2.53) and a good

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* The complexes $Ni(py)_2Cl_2$ and $Ni(py)_2Br_2$ are octahedral polymers (Sect. C) and in this way differ from XI and XII, but the complexes $Ni(3\text{-Mepy})_2Cl_2$ and $Ni(3\text{-Mepy})_2Br_2$, which have the same structure as $Ni(py)_2Cl_2$ and $Ni(py)_2Br_2$ in the solid state, dissociate into tetrahedral monomers on dissolution in polar solvents. This shows that the octahedral polymer and the tetrahedral monomer of the complexes $Ni(N_{anb})_2X_2$ differ only slightly with regard to their energy, and that substitution at N_{anb}, though rather distant from the coordination centre, favours the tetrahedral isomer

π-acceptor[49]. Coordination only occurs with the fragments "$NiBr_2$" and "NiI_2" which have a certain capacity for π back-donation and therefore those complexes which are formed have a square-planar structure (XVII and XVIII). $Ni(2\text{-Mebta})_2Cl_2$ could not be prepared[49].

Some complexes of the type $Ni(N)_2X_2$ form tetrahedral and square-planar allogons having nearly equal energies, behaviour similar to that previously discussed in Sects. B(i), (ii). Lattice or solvation effects can therefore cause one isomer to change into the other. Thus, the square-planar complex $Ni(2\text{-Mepy})_2I_2$ dissolves without structural change in cold benzene or carbon tetrachloride[48], but in the more polar dichloromethane the tetrahedral allogon is formed[44]. Lattice effects may also be the reason for the complexes XIX–XXII having a tetrahedral structure, whilst XXIII and XXIV have a square-planar structure.

The bidentate hybrid ligands Meaep, Me_2aep, Et_2aep, Et_2amp, and Ph_2Pep contain two types of donor groups: pure σ-donors ($-NR_2$) and σ-donors which are additionally weak π-acceptors ($-PPh_2$) or intermediate π-acceptors (pyridine groups). Table 5 shows that the monomer chelates of the *N*-substituted β-aminoethylpyridines(2) and aminomethylpyridines(2) are comparable to the corresponding compounds of the *N*-substituted aliphatic diamines with regard to their structure, i.e. the pyridine donor group functions as a normal amine ligand. The same is true for the pyridine donor group in the chelates of the ligand Ph_2Pep.

(iv) Five-coordinate complexes

A coordination number of five is rather unusual in nickel(II) complexes and connected with certain steric requirements. In nickel(II) chelates the central atom can be surrounded by five bulky donor groups in such a way that a sixth donor group cannot approach near enough for bond formation to be possible. For instance, in[58] $Ni[(2\text{-Me})_2dpma]Br_2$ the two 2-methylpyridine groups have such a blocking function. However, coordination number 5 is not confined to chelate compounds of nickel(II), as shown by the anion $[Ni(CN)_5]^{3-}$. This, which is present in aqueous solutions containing excess cyanide, is one of the weakest complex species whose existence is unequivocally established. According to the general

TABLE 5

Structure and magnetic properties of monomer compounds of the types $Ni(N\cap N)X_2$ and $Ni(N\cap P)X_2$

		Structure	μ_{eff} (B.M.)			Structure	μ_{eff} (B.M.)
$Ni(Me_4en)Br_2$	(ref. 52)	t	3.26	$Ni(Me_2aep)Br_2$	(ref. 55)	t	3.43
$Ni(Me_4en)I_2$	(ref. 52)	t	3.24	$Ni(Et_2aep)Cl_2$	(ref. 55)	t	3.47
$Ni(Me_4tn)Cl_2$	(ref. 52)	t	3.37	$Ni(Et_2aep)Br_2$	(ref. 54)	t	3.35
$Ni(Me_4tn)Br_2$	(ref. 52)	t	3.32	$Ni(Et_2aep)I_2$	(ref. 54)	t	3.51
$Ni(Me_4tn)I_2$	(ref. 52)	t	3.32	$Ni(Et_2amp)Br_2$	(ref. 56)	t	3.36
$Ni(Me_3tn)Br_2$	(ref. 53)	t	3.35	$Ni(Et_2amp)I_2$	(ref. 56)	t	3.39
$Ni(Me_3tn)I_2$	(ref. 53)	t	3.35	$Ni(Ph_2Pep)Cl_2$	(ref. 57)	t	3.29
$Ni(Meaep)I_2$	(ref. 54)	t	3.39	$Ni(Ph_2Pep)Br_2$	(ref. 57)	t	3.33

rule[59] that metal complex ions which are difficult to isolate can often be isolated as salts of large ions (having an equal but opposite charge), salts of this anion could be prepared only with $[Cr(NH_3)_6]^{3+}$ and similar counterions. Evidently lattice effects stabilise $[Ni(CN)_5]^{3-}$ in these salts, and these are, as in the case of nickel(II) chelates of coordination number 5, factors which are not connected with the direct interaction between the central atom and the ligand.

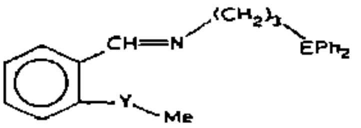
The two most symmetric arrangements of five ligands are the square pyramid and the trigonal bipyramid. Considering only the ligand–ligand repulsions the latter is the most favourable coordination polyhedron. A distorted square-pyramidal structure is only slightly less stable if the central atom is placed above the basal plane and the angle between the metal–ligand bonds and the basal plane, the "internal pyramid angle", amounts[60] to 10°.

Crystal field stabilisation energy favours the square-pyramidal arrangement (internal pyramid angle = 0°). But the stabilisation compared to the trigonal-bipyramid arrangement is low[61] (3.74 *Dq* for the high-spin; 4.12 *Dq* for the low-spin form). Thus steric requirements and lattice energies rather than electrostatic interactions are decisive for the configuration of nickel(II) complexes of the coordination number 5. The best proof for this statement is given by the two salts $[Cr(pn)_3][Ni(CN)_5]$ (ref. 62) and $[Cr(en)_3][Ni(CN)_5]\cdot 1.5\ H_2O$ (ref. 63). The anion of the first is square-pyramidal. The second compound surprisingly proved to be an interallogon composed of square-pyramidal and distorted trigonal-bipyramidal $[Ni(CN)_5]^{3-}$ in the ratio 1:1. Anhydrous $[Cr(en)_3][Ni(CN)_5]$ contains only the square-planar anion[62].

In the square-pyramidal $[Ni(CN)_5]^{3-}$ the central atom is placed 0.34 Å above the basal plane. The distances $Ni{-}C_{basal}$ are 1.862 Å, much smaller than the distance $Ni{-}C_{apical}$ (2.168 Å). In the trigonal-bipyramidal $[Ni(CN)_5]^{3-}$ the distances are: $Ni{-}C_{ax}$ = 1.837 Å (average value), $Ni{-}C_{eq}$ = 1.992, 1.907 and 1.913 Å.

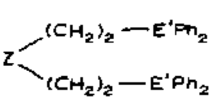
Square-pyramidal or trigonal-bipyramidal nickel(II) complexes may be of the high-spin or the low-spin type, depending upon whether the energy separation between the two highest *d*-orbitals (D_{3h}: $a_1 > e'$, C_{4v}: $b_1 > a_1$) is smaller or greater than the spin pairing energy. Sacconi and co-workers[11] have prepared and compared a great many nickel(II) chelates with the donor sets D_3X_2 and D_4X. The ligands, e.g. XXV, XXVI and XXVII, were

D_3 ligands



E = P, As
Y = NH, O S

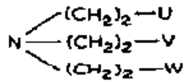
XXV



E' = As, P
Z = NH S

XXVI

D_4 ligands



U,V,W = NEt_2, PPh_2, $AsPh_2$, OEt, SMe

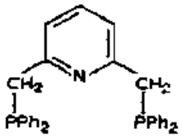
XXVII

chosen in such a way that their coordination compounds ought to have nearly the same geometry. Sacconi stated a unique relationship between the donor set and the spin state. The nephelauxetic parameter β rather than the spectrochemical Δ parameter of the donor atom is the decisive factor. In this way it is demonstrated that covalent bonding between the central atom and the ligands and the reduction of the interelectronic repulsion is decisive for the appearance of low-spin states of five-coordinate nickel(II) complexes.

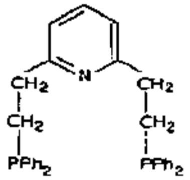
In the nephelauxetic series[64] the ligands are arranged approximately in order of decreasing polarisability and increasing electronegativity. Moreover, as the polarisability largely decides the nucleophilic reactivity of a ligand, we can understand the connection between the spin state of five-coordinate nickel(II) chelates and the sum of the electronegativities $\Sigma\chi$, and the nucleophilic reactivity constants Σn^0 of the donor groups[65]. Sacconi[11] formulated the following relation, which is also valid (with somewhat different numerical values) for cobalt(II) complexes.

Donor set D_3X_2			Donor set D_4X		
$\Sigma\chi$		Σn^0	$\Sigma\chi$		Σn^0
$\vee$	high-spin	$\wedge$	$\vee$	high-spin	$\wedge$
12.76		25.5	13.2		22.3–26
$\vee$	low-spin	$\wedge$	$\vee$	low-spin	$\wedge$
$\Sigma\chi$		Σn^0	$\Sigma\chi$		Σn^0

Chelates whose donor set yields $\Sigma\chi$ and Σn^0 values near the cross-over points given in this relationship are most interesting. In the D_3X_2 case this occurs for the donor set $PNPCl_2$ ($\Sigma\chi = 12.85$, $\Sigma n^0 = 26.76$). Here the high-spin and low-spin states should differ only slightly in energy and the transition from one state to the other should be attainable by a change of temperature. This has been confirmed by Nelson and co-workers[66,67] during their investigations of complexes of the ligands $(Ph_2Pm)_2p$ and $(Ph_2Pe)_2p$. At 294.2°K



$(Ph_2Pm)_2p$



$(Ph_2Pe)_2p$

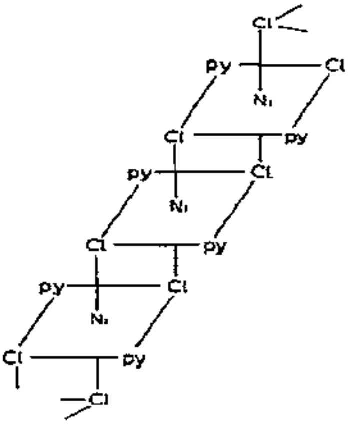
$[(Ph_2Pe)_2p]NiCl_2$ has a normal magnetic moment ($\mu = 3.16$ B.M.), but at 99.3°K a value of only 1.32 B.M. was found. As the X-ray powder diagram of this complex does not change with temperature the abnormal magnetic behaviour must be attributed to a temperature-controlled equilibrium between a singlet and a triplet state. The complex $[(Ph_2Pm)_2p]Ni(NCS)_2$ behaves very similarly.

Quantitative description of these equilibria is difficult. We must expect that in the relevant temperature range there is not only a change in the magnetic behaviour but also in the bond distances and the lattice constants. This must effect a change in the energy difference between the singlet and the triplet states which cannot, however, be described by a simple mathematical relationship. It is interesting that $[(Ph_2Pe)_2p]NiCl_2$ has a trigonal-bipyramidal configuration; $[(Ph_2Pm)_2p]NiCl_2$ with the same donor set has a square-pyramidal configuration. $[(Ph_2Pm)_2p]NiCl_2$ has a temperature-independent paramagnetism ($\mu_{eff} = 0.91$ B.M. at 293°K) like many low-spin nickel(II) complexes, and thus it differs characteristically from $[(Ph_2Pe)_2p]NiCl_2$. This demonstrates very clearly the influence of the inner structure of the ligands ($(Ph_2Pe)_2p$ forms the two six-membered chelate rings, $(Ph_2Pm)_2p$ two five-membered ones) on the configuration and properties of five-coordinate nickel(II) complexes.

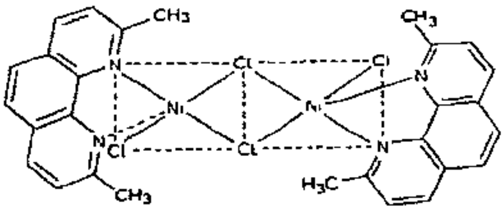
C. THE INFLUENCE OF STERIC AND ELECTRONIC FACTORS ON COORDINATION POLYMERISATION

Among the nickel(II) chelates of *N*-substituted salicylaldimines, as well as among the complexes of the types $Ni(N)_2X_2$ and $Ni(N\cap N)X_2$, four-coordinate monomers as well as coordination polymers are known. The same is true for the β-keto-enolates of nickel(II), which differ from the above-mentioned compounds in that square-planar not tetrahedral monomers are observed.

$Ni(py)_2Cl_2$ is the coordination polymer XXVIII with bridging chloro ligands, and six-coordinate central atoms[68]. Numerous other compounds, usually coloured yellow to brown, of the types $Ni(N)_2X_2$ and $Ni(N\cap N)X_2$ which according to their ligand field spectra cannot be four-coordinate, have structures[45,50,69,70] analogous to $Ni(py)_2Cl_2$. Preston and Kennard[71] have recently shown that the yellow β-isomer of $Ni(2,9\text{-}Me_2phen)Cl_2 \cdot CHCl_3$, XXIX, has a dimeric structure with a distorted square-pyramidal arrangement of the ligands. The reflection spectrum of this compound[71] differs slightly from that[72] of $Ni(py)_2Cl_2$. Therefore we must conclude that structural characterization of related compounds of the types $Ni(N)_2X_2$ and $Ni(N\cap N)X_2$ made on the basis of incomplete ligand field spectra is tenuous. The literature must be regarded with caution. We think that di-



XXVIII

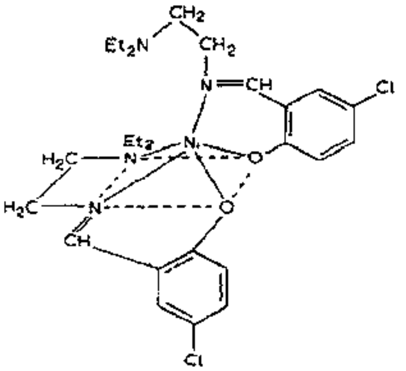


XXIX

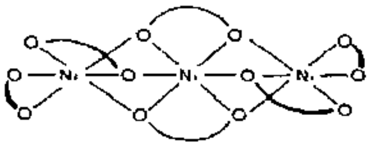
meric structures analogous to that of $Ni(2,9\text{-}Me_2phen)Cl_2$ are more common than has been supposed until now. For instance, the dissolution of $Ni(Me_4en)Cl_2$ (ref. 52), $Ni(Me_3tn)Cl_2$ (ref. 53) and $Ni(Me_2amp)Br_2$ (ref 73) in polar, weakly solvating liquids such as *o*-dichlorobenzene or acetone without structural change indicates an oligomeric and not a highly polymeric structure.

No structure analyses of polymeric nickel(II) chelates of *N*-substituted salicylaldimines[74] have yet been performed. Molecular weight determinations[75,76] have shown that the degree of association is not much higher than 2. Associated and paramagnetic *N*-arylsalicylaldimine complexes of nickel(II) absorb[76] at 7500, 10,000, 12,800 and 16,800 cm^{-1}. This correlates well with the spectrum of the compound XXX, which has a distorted square-pyramidal structure[78], one of the ligands being tridentate, the other bidentate. Therefore the associated *N*-arylsalicylaldimine chelates of nickel(II) must be assigned at least a dimeric structure with, for example, a distorted square-pyramidal arrangement of the donor groups at the two nickel atoms, and with two oxygen bridges.

Oxygen bridges also exist in the bis-β-keto-enolate complexes of nickel(II). In the solvent-free compounds XXXI coordination number 6 is reached by trimerisation[79], though dimeric compounds such as $[Ni(acac)_2py]_2$ having an octahedral structure are known[80].



XXX



XXXI

Nyholm and co-workers[81,82] have shown that the Pauling Electroneutrality Principle provides a reasonable explanation for the dependence of coordination number in complexes of transition metal ions Me^{2+} upon the nature of the ligands. With easily polarisable (for instance PR_3 and I^-) or strongly basic (NH_3, Et_2NH) ligands a large transfer of charge to the central atom is possible, and a relatively small number of ligands is needed to bring about "electroneutrality". Therefore, in spite of the high ligand field stabilisation energy for octahedral nickel(II), four-coordinate complexes of the type $Ni(PR_3)_2X_2$

(Table 3) are quite stable; while five-coordinate compounds of the type $Ni(PR_3)_3X_2$ are only known with PMe_3 as a ligand[83]. Furthermore, although there are complexes[48,50] of composition $Ni(N)_4I_2$ with coordination number exceeding 4, many four-coordinate, monomeric compounds $Ni(N)_2I_2$ and $Ni(N\cap N)I_2$ (Tables 4 and 5) are also known. Evidently in monomeric complexes of the type $Ni(N)_2X_2$ (X = halide anion of lower polarisability) the four simple ligands do not bring about "electroneutrality". Further species of type $Ni(N)_2X_2$ are added, acting as donor groups via the free electron pairs of their halide ligands. Therefore compounds $Ni(N)_2Cl_2$ and $Ni(N\cap N)Cl_2$ are frequently coordination polymers such as XXVIII or XXIX[50,52,53,73].

The *N*-aryl derivatives are the weakest donors among the substituted salicylaldiminate anions, while among the β-keto-enolate anions the trifluoromethyl compounds are weakest. This is in complete agreement with the ideas of Nyholm and co-workers[81,82] that the tendency for association is highest[74,84] precisely in the nickel(II) complexes of these ligands.

Coordination polymerisation is also influenced by steric factors, and, when the energy differences between the monomeric and associated forms are small, by lattice and solvation effects. This is demonstrated by the following examples. Substituents in the 2- and 6-positions prevent association of the complexes $Ni(2\text{-}Mepy)_2X_2$, $Ni(2,5\text{-}Me_2py)_2X_2$ etc. (Table 4). The complexes[52] $Ni(Me_2amp)Br_2$ and $Ni(Me_4en)Cl_2$ have five-membered rings and are associated in the solid state and in solution, while the compounds $Ni(Me_2aep)Br_2$ (ref. 55) and $Ni(Me_4tn)Cl_2$ (ref. 52), which have the more bulky six-membered chelate rings, are monomeric. Substitution of the EtNH group by the bigger Et_2N group causes the associated complex $Ni(Etaep)Cl_2$ to change[73] to the monomeric $Ni(Et_2aep)Cl_2$. Bis(*N*-*o*-tolylsalicylaldiminato)nickel(II) is monomeric and square-planar[85], but bis(*N*-*m*-tolylsalicylaldiminato)nickel(II) is associated ($\mu_{eff} = 3.34$ B.M.)[86].

It is thought that steric factors[7], primarily, determine the monomeric square-planar structure of bis(dipivaloylmethanato)nickel(II)[87] as opposed to the trimeric structure[79] of bis(acetylacetonato)nickel(II) There is a relation between the pK_a values of the 1,3-diketones, measured in 75% dioxan, and the structure of the corresponding nickel(II) complexes[84]. β-Keto-enolate anions of comparatively low basicity (low pK_a values of the corresponding 1,3-diketones), form trimeric, six-coordinate complexes, β-keto-enolate anions of high basicity (high pK_a values of the corresponding 1,3-diketones) form monomeric, four-coordinate compounds. The nickel(II) chelates of 1,3-diketones of medium acid strength ($13.3 < pK_a < 14.2$) exist as monomeric and trimeric isomers. Graddon[84] therefore concluded that "electronic" rather than steric effects determine the structure of β-keto-enolates of nickel(II). Certainly this applies to compounds with terminal CF_3 groups. But for the fluorine-free β-diketones it must be taken into account that the pK_a values depend not only on the inductive effect of the terminal groups (aryl or alkyl groups), but also to a high degree on the π-electron delocalisation within the β-keto-enolate anions. All these factors tend to hinder the formation of the planar conformers of these anions and in this way the π-electron delocalisation will bring about a decrease of the pK_a values For instance, for steric reasons an annelated six- or seven-membered hydroaromatic ring renders the formation of the planar conformers of the β-keto-enolate anions more difficult than does an annelated five-membered ring. Only on this basis, not on that of the inductive effect, may the great difference between the pK_a values of

2-acetylcyclopentanone, 2-acetylcyclohexanone and 2-acetylcycloheptanone (11.6; 14.1; 14.1) be understood But the steric factors hindering the formation of the planar conformers of the β-keto-enolate anion, also hinder[8] the trimerisation of the β-keto-enolates of nickel(II). Thus there is no contradiction between Graddon's experimental results and the earlier statement on the dominating influence of steric factors on the structure of fluorine-free β-keto-enolates of nickel(II).

D. POTENTIAL AND ACTUAL DENTICITY AND GEOMETRICAL ARRANGEMENT OF POLYDENTATE LIGANDS IN NICKEL(II) CHELATES

In Sects. B and C the steric and electronic influences of mono- and bidentate ligands on the configuration of nickel(II) complexes have been examined. This was always based on the premise that bidentate ligands coordinate with both donor groups, i.e. that their *potential* denticity corresponds to their *actual* denticity. In considering coordination compounds of tri- and tetradentate ligands the validity of this premise is questionable

As shown in Sect. E, in mixed-ligand complexes the "second" ligands influence the actual denticity of polydentate "first" ligands to a high degree. Here the less complicated case of complexes containing only one kind of ligand will be treated. We shall see that not only the nature of the donor atoms but also "inner-ligand" factors * are important in establishing the actual denticity. These factors also influence the geometrical arrangement of the ligands in coordination compounds. They are, for instance, the deciding factor which determines whether a meridional or a facial configuration is found for octahedral 1,2-complexes of tridentate ligands.

(i) Potential and actual denticity of polydentate ligands

β-Aminomethylmercaptide and its *N*-substituent products form diamagnetic 1,2-complexes[88] with nickel(II) whose configuration is decisively influenced by the type of the substituents. The green complexes $Ni(aem)_2$ and $Ni(n\text{-}Raem)_2$ are monomeric and have *trans* square-planar structures. Increasing the chain length of the alkyl substituents causes no essential changes in their properties, i e increasing the steric requirements without increasing the bulk in the immediate vicinity of the coordinated nitrogen atom does not alter the manner of chelation. The maroon compound $Ni(Me_2aem)_2$ also has a planar *trans* structure, but the bathochromic shift of the ligand field band in the visible region (~ 15,700 cm^{-1} for $Ni(n\text{-}Raem)_2$, 13,900 cm^{-1} for $Ni(Me_2aem)_2$) points to additional steric requirements of the coordinated tertiary amino group. Finally, the brown complexes $Ni(Et_2aem)_2$ and $Ni(t\text{-}Buaem)_2$ have polymeric, square-planar structures XXXIII with mercaptide bridges. Evidently there is no space in the immediate vicinity of the central atom for coordination of two very bulky *t*-butylamino or diethylamino groups, and these steric requirements are met by the formation of a polymeric mercaptide XXXIII. That

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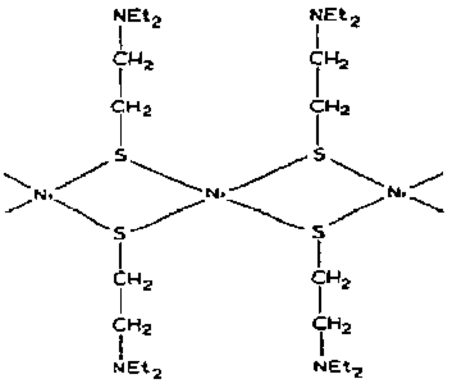
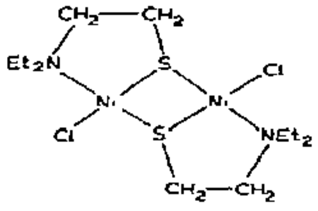
* The size of the chelate rings, the type of substitution at the donor atoms, and the rigidity of the ligands may be considered as "inner-ligand" factors.



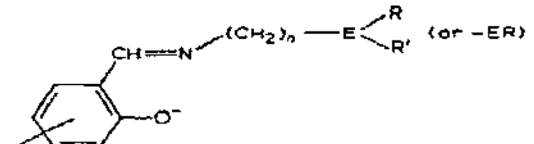
XXXIII



XXXIV

Et$_2$aem can be a bidentate ligand is demonstrated by the compound [Ni(Et$_2$aem)Cl]$_2$ (XXXIV). Only one diethylamino group is coordinated to one central atom in this case, and therefore any overcrowding is avoided.

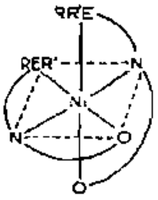
Interesting insights into the relation between the potential and the actual denticity of polydentate ligands are given by complexes of salicylaldimines which are substituted in the side chain, XXXV. As shown in Sect. B(i), salicylaldimine and its derivatives with *n*-alkyl



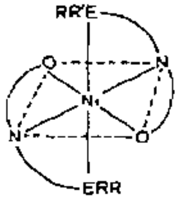
XXXV (abbreviation Q⌒N⌒ERR')

substituents at the nitrogen atom may be considered as strong ligands, causing the formation of square-planar nickel(II) chelates of the low-spin type. These complexes prove to be coordinatively unsaturated by their reaction with strong monodentate donors like pyridine, forming paramagnetic *trans* octahedral bis-adducts[89]. In nickel(II) chelates of salicylaldimines of the type XXXV, disregarding for the moment the groups −ERR′ (or −ER), the same environment is present as with nickel(II) complexes of *N*-(*n*-alkyl)-substituted salicylaldimines. Therefore the central atom is coordinatively unsaturated, and depending on the donor strength of the group −ERR′ (or −ER) the gap in the coordination sphere may be filled or unfilled. The octahedral configuration and the tridenticity of the ligands in the complexes Ni(salenNMe)$_2$ (ref. 90), Ni(salenNMe$_2$)$_2$ (ref. 77), Ni(saltnNMe)$_2$ (ref. 91), Ni(salmp)$_2$ (ref. 92), Ni(salep)$_2$ (ref. 93) and Ni(salenPEt$_2$)$_2$ (ref 94), as well as the square-planar configuration and the bidenticity of the ligands in the complexes Ni(salenNPh$_2$)$_2$ (ref. 90), Ni(saltnNMePh)$_2$ (ref. 91), Ni(salenPPh$_2$)$_2$ (ref. 95) and Ni(salenAsPh$_2$)$_2$(ref. 95) may be explained on this basis.

In certain cases steric requirements become the decisive factors affecting the configuration. In ligands of the type XXXV the imine nitrogen is sp^2-hybridised. Therefore in all complexes with ligands of the salen type ($n = 2$, formation of a five-membered chelate ring by the side chain) the donor atom E is constrained to lie in approximately the same plane as the donor atoms N and O^- and the central atom On account of this, octahedral chelates of these ligands must have a meridional *cis* configuration XXXVI, and in fact



XXXVI



XXXVII

Sacconi et al.[90] found the expected high dipole moment of 8.78 D for Ni(salenNMe)$_2$ Because of the additional methylene group in the side chain, saltn ligands are more flexible. The corresponding nickel(II) chelates can therefore have the facial configuration XXXVII with a *trans* arrangement of the ERR′ donors The latter has been proved by structure analysis[96] and the low dipole moment[91] (< 1 D) of Ni(saltnNMe$_2$)$_2$.

For *cis* octahedral complexes of the type XXXVI, considerable steric repulsion between the donor groups –ERR′ or –ER is no doubt to be expected and therefore whether they coordinate or not will depend on their donor strength and also on their bulk. Evidently their bulk prevents the coordination of two PPh$_2$ groups bound in the side chains. For this reason Ni(salenPPh$_2$)$_2$ is four-coordinate with a square-planar environment[95]. On the other hand, in Ni(salenSMe)$_2$ the small methyl substituent has only a weak influence[97] and therefore in this case even the relatively weak donor –SMe can complete the coordination sphere. The result is an octahedral structure

Ligands of the types R$_2$aem, salenER$_2$ and saltnER$_2$ coordinate in 1,2-complexes with nickel(II) according to whether the number of potential donor groups and the characteristic coordination numbers of the metal (4 or 6) correspond with one another. With 1,2-complexes of potentially tetradentate ligands, however, the number of potential donor atoms exceeds six, the highest characteristic coordination number of nickel(II) *. Therefore, non-coordinated donor groups must be taken into account, and the following inter-

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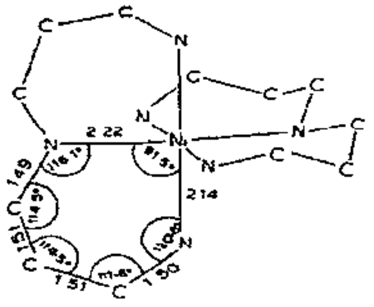
* Coordination numbers higher than 6 are known for bivalent cations of the heavier 3*d* elements[98], but they are an exception

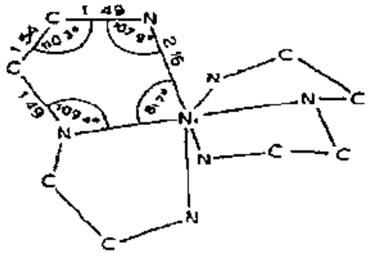
esting question arises: is one of the ligands tetradentate and the other bidentate, or are both tridentate in these 1,2-complexes? In the case of $[Ni(himda\text{-}2H)_2]^{2-}$ the question was resolved by NMR spectroscopy in the following way[99]. In aqueous solutions of paramagnetic nickel(II) chelates contact shifts for the protons bound to the carbon atoms are observed which are strongly influenced by the nearby atoms and by the conformation of the chelate rings. $[Ni(himda\text{-}2H)_2]^{2-}$ gives the same band pattern as the 1,2-complex of the anion of *N*-ethyliminodiacetic acid. As the latter anion is only tridentate both the ligands in $[Ni(himda\text{-}2H)_2]^{2-}$ must be equivalent and tridentate. The hydroxy group is not coordinated, in agreement with our knowledge of the strength of the donor groups of the anion himda-2H ($\geqslant N > -COO^- > -CH_2OH$)

(ii) Facial and meridional structures of nickel(II) chelates with tridentate ligands

The arrangement of two tridentate ligands in octahedral nickel(II) complexes can only be determined exactly by a structure analysis. Meridional environments have been proved for the cations of the salts $[Ni(dpt)_2](ClO_4)_2$, XXXVIII, and $[Ni(den)_2]Cl_2 \cdot H_2O$, XXXIX[100]. The Ni–N distances in these compounds are of interest. In the case of the



XXXVIII



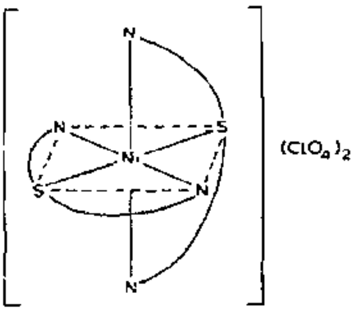
XXXIX

primary amino groups they are nearly equal (2.14 and 2.16 Å), but a notable difference exists for the secondary amino groups. Here, the Ni–N distances in the dpt complex, which contains two six-membered chelate rings, are much greater (2.22 as against 2.05 Å). This points to a weaker bond between nickel(II) and dpt compared to nickel(II) and den.

In $[Ni(dpt)_2]^{2+}$ relatively short non-bonding H...H distances are observed (2.15–2.20 Å) between the primary amino groups of the first and the methylene groups of the second ligand. Using a model it is possible to show that by twisting the chelate ring and so reducing Ni–N distances and ring strains, these H...H distances would become even shorter. For $[Ni(den)_2]^{2+}$ no steric hindrance of this type can be observed.

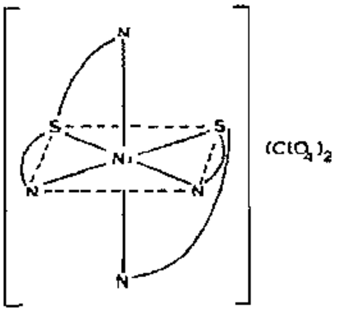
With complexes of tridentate ligands having different donor atoms important indications as to the configuration may be obtained by simple measurements. The big differences between the dipole moments of the meridional complexes $Ni(salenNMe_2)_2$ and the facial complexes $Ni(saltnNMe_2)_2$ have already been mentioned in Sect. D(i). The spectra of the two complexes also differ markedly in the region where the ν_1 band appears for strictly octahedral nickel(II) complexes. For the *cis* octahedral $Ni(salenNMe_2)_2$, one broad, asymmetric maximum (~ 10,500 cm^{-1}) is found, but for Ni(salenNMe$_2$)$_2$ four maxima (7500, 9000, 11,900 and 13,300 cm^{-1}) are observed. These differences in the band patterns are characteristic of *cis* and *trans* octahedral nickel(II) complexes with the same donor set $L_4L'_2$. Therefore they may be used to make deductions concerning the structure of such compounds

The shift of the IR frequency ν_{8a} of the pyridine ring[102, 103] in the complexes [Ni(pmSmp)$_2$](ClO$_4$)$_2$, XL, and [Ni(peSmp)$_2$](ClO$_4$)$_2$, XLI, shows that all pyridine nitrogen atoms are coordinated[104] (ν_{8a}: pmSmp and peSmp 1600 cm^{-1}, XL and XLI 1610 cm^{-1}). The magnetic moments (XL 3.16 B.M., XLI 2.92 B.M.) and the type of ligand field spectra (maxima at 11,500, 15,500 and 19,000 cm^{-1} for XL, and 11,500 and 18,300 cm^{-1} for XLI) point to an octahedral structure, XL having a *trans* and XLI a *cis* arrangement of the sulphur atoms. pmSmp contains two $-N{=}\overset{|}{C}-\underset{|}{C}-$ fragments which must be planar because of the *sp*^{2} hybridisation at the nitrogen and carbon atoms of the ring. Because of this, the whole ligand, like salenNMe$_2$, attains a certain rigidity, which very probably forces a meridional arrangement in XL and a *trans* position for the sulphur atoms. The ligand peSmp, containing an additional methylene group, like saltnNMe$_2$, is more flexible, and therefore a facial configuration of the cation [Ni(peSmp)]$^{2+}$ should become possible Evidently the *cis* configuration XLI is energetically favoured because of better possibilities for π back-donation between the central atom and the ligands.



XL

N⌒S⌒N = pmSmp



XLI

N⌒S⌒N = peSmp

E THE MUTUAL INFLUENCE OF LIGANDS IN MIXED-LIGAND COMPLEXES

In Sect. C it was shown that with complexes of the types Ni(N)$_2$X$_2$ and Ni(N∩N)X$_2$ the tendency towards coordination polymerisation via halide bridges is influenced to a large extent by the steric and electronic requirements of the ligands N or N∩N. Such an influence of the second ligands * on the denticity of the first ligands is a general phenomenon (the

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* "First ligands" are understood to be those whose function with respect to the central atom is changed by a variation of the "second ligands". Substitution at the donor atom altering the electronic and steric properties *within certain limits* (for instance the change from a pyridine to a benzimidazole complex, but not to a nitrite complex) are characterised as variation of the second ligands.

first ligands X are monodentate in the monomeric complexes $Ni(N)_2X_2$ and $Ni(N{\cap}N)X_2$, but bidentate in coordination polymers of the same composition). Further examples may be mentioned:

(*a*) The first ligands act as monodentate or "zerodentate", i.e. they do not enter the inner sphere of the central atom (cf. the complexes of the type $Ni(N)_4Y_2$, Sect. E(i)).

(*b*) The first ligands act as monodentate or as bidentate chelate ligands (cf. the nitrite and nitrate complexes, part E(ii)).

But the second ligands can also bring about a variation of the steric arrangement of the first ligands (cf. the complexes $Ni(en)_2XY$, Sect. E(i)) or of the kind of linkage between the first ligands and the central atom (cf. the nitrite complexes, Sect. E(ii)).

(i) The structure of complexes of the types $Ni(N)_4Y_2$ *and* $Ni(N{\cap}N)_2Y_2$

Complexes of the type $Ni(Rpy)_4(ClO_4)_2$ can be synthesised either by thermal degradation of the aquo complex $[Ni(Rpy)_4(H_2O)_2](ClO_4)_2$ or by reaction of $[Ni(H_2O)_6](ClO_4)_2$ with the substituted pyridine Rpy in organic solvents. In the latter case the water may be removed by reaction with 2,2-dimethoxypropane[105]. A blue paramagnetic and a yellow diamagnetic type may be distinguished (Table 6). From the visible spectra (splitting of the ν_1 band, cf. Sect. D(ii)) and the structure analysis[107] of $Ni(3,5\text{-}Me_2py)_4(ClO_4)_2$ it follows that the blue compounds have a *trans* octahedral structure with monodentate perchlorate ligands (distance $Ni\text{—}OClO_3 = 2.187$ Å). The four 3,5-Me_2py ligands form the blades of a four-bladed propeller. The angle between the average plane of each of the organic groups and the plane perpendicular to the twofold axis through the perchlorate groups and the central atom is 46.6°.

$[Ni(3,4\text{-}Me_2py)_4](ClO_4)_2$, on the other hand, is square-planar[108], the distance between the central atom and the nearest oxygen atom of each perchlorate ion amounting to 3.343 Å. Therefore we cannot speak of a coordinative bond between nickel and perchlorate. The planes of the organic ligands are perpendicular to the plane in which the nickel and the four nitrogen atoms are situated. As expected there is a shortening of the Ni—N

TABLE 6

Colours and magnetic behaviour of compounds of the type $Ni(Rpy)_4(ClO_4)_2$

		Colour	μ_{eff} (B.M.)
$Ni(py)_4(ClO_4)_2$	(ref. 105)	Blue	3.6
$Ni(3\text{-}Brpy)_4(ClO_4)_2$	(ref. 105)	Light blue	3.1
$Ni(3\text{-}Mepy)_4(ClO_4)_2$	(ref. 105)	Blue	3.5
$[Ni(3\text{-}Mepy)_4](ClO_4)_2$	(ref. 105)	Bright yellow	1.0
$Ni(3,5\text{-}Me_2py)_4(ClO_4)_2$	(ref. 105)	Blue	3.2
$Ni(4\text{-}Etpy)_4(ClO_4)_2$	(ref. 105)	Light blue	3.4
$[Ni(4\text{-}Mepy)_4](ClO_4)_2$	(ref. 105)	Yellow	Diamagnetic
$[Ni(4\text{-}NH_2py)_4](ClO_4)_2$	(ref. 105)	Yellow	Diamagnetic
$[Ni(3,4\text{-}Me_2py)_4](ClO_4)_2$	(ref. 106)	Yellow	Diamagnetic

distances in $[Ni(3,4\text{-}Me_2py)_4](ClO_4)_2$ compared to those in $Ni(3,5\text{-}Me_2py)_4(ClO_4)_2$ (1.897 and 2.093 Å).

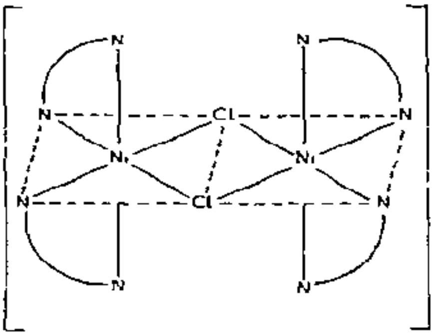
The square-planar and octahedral species of the compounds of type $Ni(Rpy)_4(ClO_4)_2$ differ only slightly with regard to their energy; therefore a change from one to the other is easily possible. Thus the blue $Ni(3,5\text{-}Me_2py)_4(ClO_4)_2$ dissolves in dichloromethane, splitting off the perchlorate ligands[106] and forming the square-planar species $[Ni(3,5\text{-}Me_2py)_4]^{2+}$; by the addition of $CHCl_3$, probably through formation of a weak hydrogen bond, the yellow $[Ni(py)_4](ClO_4)_2.CHCl_3$ is obtained[109] from the blue $Ni(py)_4(ClO_4)_2$, and blue and yellow isomers of $Ni(3\text{-}Mepy)_4(ClO_4)_2$ are known (Table 6), and may be interconverted by heating to different temperatures[105]

The reasons why the square-planar form is favoured in one case and the octahedral form in the other (Table 6) are largely unknown. Steric hindrance, for instance, is by no means an explanation of the structural differences between $Ni(3,5\text{-}Me_2py)_4(ClO_4)_2$ and $Ni(3,4\text{-}Me_2py)_4](ClO_4)_2$ in the solid state. The observation that methyl and amine substituents in the 4-position of pyridine favour the square-planar species (Table 6) is noteworthy. Probably the weak +M effect with its influence on the electron density at the nitrogen atom and, by this, on the π-interaction between nickel(II) and the pyridine ligand (cf Sect B(iii)) is decisive in favouring the square-planar species[105]. Of course, the solution behaviour shows that outer-sphere influences are also important in determining the structure of compounds of the type $Ni(N)_4Y_2$.

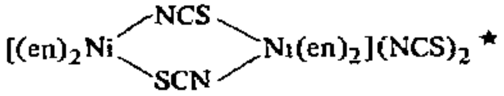
Whilst for the compounds $Ni(N)_4Y_2$ in the presence of the weak anionic donor ClO_4^- the substitution of the ligand py by 4-Mepy is sufficient to bring about the change-over from an octahedral to a square-planar structure, complexes of the same type but containing stronger anionic ligands require a greater change of the second ligands to produce the same effect. Iodide is comparable to perchlorate. No doubt $Ni(4\text{-}Mepy)_4I_2$ is octahedral in contrast to $[Ni(4\text{-}Mepy)_4](ClO_4)_2$, but $[Ni(3,4\text{-}Me_2py)_4]I_2$ and $Ni(3,5\text{-}Me_2py)_4I_2$ have the same structure[44] as $[Ni(3,4\text{-}Me_2py)_4](ClO_4)_2$ and $Ni(3,5\text{-}Me_2py)_4(ClO_4)_2$. In the case of the stronger anionic donor Br^-, the square-planar structure is only realised in one isomer of $[Ni(4\text{-}NH_2py)_4]Br_2$ (ref. 44) and $[Ni(bia)_4]Br_2$ (ref. 110). Recently it has been shown that complexes of the type $Ni(N)_4Y_2$ may have either an octahedral or a square-pyramidal structure. For $Ni(2\text{-}Meima)_4Br_2$, Goodgame et al.[72] found a *trans* arrangement of the halides. The Ni—Br distances are 2.53 and 3.57 Å. In view of the Ni—Br distance of 3.57 Å, we can hardly speak of a coordinative bond, and therefore $Ni(2\text{-}Meima)_4Br_2$ should rather be formulated with five-coordinate nickel(II). A chloro complex, isomorphous with $Ni(2\text{-}Meima)_4Br_2$, has also been isolated This shows that bulky second ligands in complexes of the type $Ni(N)_4Y_2$ may also displace chloro ligands from the coordination sphere of the central atom.

Ethylenediamine is probably the least bulky among the bidentate amine ligands. Therefore complexes of the composition $Ni(en)_2Z_2$ have no steric reasons for displacing anionic or neutral ligands from the coordination sphere of the central atom. However, two en ligands in a square-planar arrangement produce such a strong ligand field that the energy yield on the addition of two weak donors (e.g. ClO_4^- or AgI_2^- ions) in the *trans* position is small. This is demonstrated by the existence of the square-planar $[Ni(en)_2][AgI_2]_2$ (ref. 152) and of the square-planar isomer of $[Ni(en)_2](ClO_4)_2$ (ref. 111). However, if coordination of the donors Z does occur, the arrangement of two en ligands is markedly affected. Thus, for the cation of $[Ni(en)_2(H_2O)_2](ClO_4)_2$ the ligand field spectrum (maxima at 9800, 13,700, 18,400 and 22,000 cm^{-1}; splitting of ν_1) suggests a *trans* octahedral structure whilst for the cation of $[Ni(en)_2(H_2O)_2](BPh_4)_2$ (maxima at 11,000, 18,000 and $> 29{,}000\ cm^{-1}$; *no* splitting of ν_1) a *cis* octahedral structure is postulated[111]. Very probably the *trans* octahedral configuration of the cation $[Ni(en)_2(H_2O)_2]^{2+}$ is stabilised by hydrogen bonds between the aquo ligands and the perchlorate anions, i.e. by an outer-sphere effect. In the case of $[Ni(en)_2(H_2O)_2](BPh_4)_2$ such an interaction is impossible. Therefore the *cis* configuration, probably with hydrogen bonds between the aquo ligands, is favoured.

Cis structures are also observed for the dimeric complexes[112] $[(en)_2NiCl_2Ni(en)_2]Cl_2$ (XLII) and $[(en)_2NiBr_2Ni(en)_2]Br_2$. Porai-Koshits et al.[10] explain the favouring of these structures compared to the monomeric ones $[Ni(en)_2Cl_2]$ and $[Ni(en)_2Br_2]$ in this way: The lattice energy (E_1) of the salt $[(en)_2NiCl_2Ni(en)_2]Cl_2$ is considerably higher than that of the neutral complex $Ni(en)_2Cl_2$ (E_N). Therefore, E_1 together with the association energy of two fragments $Ni(en)_2Cl^+$ will over-compensate E_N and the energy of two Ni—Cl bonds $Ni(en)_2(NCS)_2$ and $Ni(en)_2(NO_2)_2$ (cf. Sect. E(ii)) have in fact a monomeric *trans* structure[10]. The considerable energies of the Ni—NCS and Ni—NO_2 bonds cannot be compensated by the lattice energy of the (hypothetical) salt



XLII


$[(en)_2Ni\begin{smallmatrix}NCS\\SCN\end{smallmatrix}Ni(en)_2](NCS)_2$ * and the energy of the association of the fragments $(en)_2Ni(NCS)^+$ or $(en)_2Ni(NO_2)^+$ by asymmetric NCS or NO_2 bridges (cf. Sect. E(ii)). However, it is not known why the fragments $Ni(en)_2Cl^+$ dimerise via *cis* dichloro bridges, rather than polymerise by *trans* chloro bridges

Substitution of ethylenediamine at the nitrogen atoms or at the carbon atoms of the bismethylene group increases the bulk and facilitates the formation of square-planar spe-

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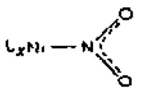
* The cation 
$[(en)_2Ni\begin{smallmatrix}NCS\\SCN\end{smallmatrix}Ni(en)_2]^{2+}$ is present[113] in 
$[(en)_2Ni\begin{smallmatrix}NCS\\SCN\end{smallmatrix}Ni(en)_2]I_2$

cies of the composition $[Ni(R_xen)_2]Y_2$. Again the donor strength of the anionic ligands has great influence on the structure, as shown by the following examples: $[Ni(a\text{-}Me_2en)_2]I_2$ is square-planar, whereas $[Ni(a\text{-}Me_2en)_2Br_2]$ and $[Ni(a\text{-}Me_2en)_2(NO_3)_2]$ are *trans* octahedral[114]. Furthermore, the complexes $[Ni(a\text{-}Et_2en)_2]Br_2$, $[Ni(a\text{-}Et_2en)_2](NO_3)_2$ and $[Ni(a\text{-}Et_2en)_2]I_2$ are square-planar. Among the halide ions only the chloride is added by the bulky cation $[Ni(a\text{-}Et_2en)_2]^{2+}$ forming[115] the octahedral species $[Ni(a\text{-}Et_2en)_2Cl_2]$.

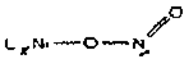
The "classical" example of a diamine ligand affecting the coordination of the first ligands in chelates of the type $Ni(N{\cap}N)_2Y_2$ in a very specific manner is *meso*-stilbenediamine, Octahedral neutral complexes $[Ni(m\text{-}stien)_2Y_2]$ and square-planar complex salts $[Ni(m\text{-}stien)_2]Y_2$ are formed depending on the donor strength of the anionic ligands. In some cases, e.g. with $Y = ClCH_2COO^-$, Cl_2CHCOO^- and Cl_3CCOO^-, two isomers have been isolated[116–118]. The characterization of a blue isomer of $Ni(m\text{-}stien)_2(Cl_2CHCOO)_2$ with six-coordinate nickel(II) and of a yellow-green "pseudo-interallogon" containing one square-planar and two octahedral species in the unit cell is of special interest[119]. The preparation of yellow $[Ni(H_2N\text{-}CH_2\text{-}CEt_2\text{-}NH_2)_2](Cl_2CHCOO)_2$ and of blue $[Ni(H_2N\text{-}CH_2\text{-}CEt_2\text{-}NH_2)_2(Cl_2CHCOO)_2]$ shows that in general *C*-substituted ethylenediamines as ligands in complexes of the type $Ni(N{\cap}N)_2Y_2$ may affect the formation of isomers[120]. A yellow, square-planar and a blue, octahedral isomer of $Ni(H_2N\text{-}CH_2\text{-}CMe_2\text{-}NH_2)_2Cl_2$ are known[121]. The latter is a dimer having a structure comparable to $[(en)_2NiCl_2Ni(en)_2]Cl_2$, XLII.

(ii) Nitrite and nitrate coordination

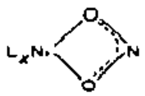
The nitrite ion has free electron pairs at the nitrogen and at the two oxygen atoms. Therefore, as Jørgenson and Werner recognised, it may be bound to a central atom by either the nitrogen or one of the oxygen atoms. Thus the possibility of formation of nitro or nitrito complexes, and in special cases of corresponding linkage isomers, arises[122]. For a long time investigation into the type of nitrite coordination remained in the field of the inert complexes of cobalt(III) and chromium(III). Only during the sixties was more attention given to the nitrite complexes of nickel(II), and thus it was found that nitrite can function both as a monodentate nitro (XLIII) or nitrito ligand (XLIV), and also as a bidentate chelate XLV or bridging ligand XLVI, XLVII. The reasons for the observed differ-



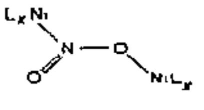
XLIII



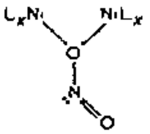
XLIV



XLV



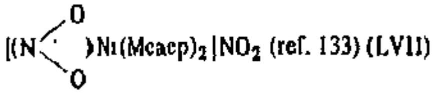
XLVI



XLVII

TABLE 7

Configuration of complexes of the types $Ni(N)_4(nitrite)_2$ and $Ni(N\cap N)_2(nitrite)_2$ in the solid state

trans-Dinitro		*trans*-Dinitrito		Chelating nitrite (XLV)
$[Ni(en)_2(NO_2)_2]$	(refs. 123, 124) (LIII)	$[Ni(py)_4(ONO)_2]$	(ref. 125)	 $[(N\langle^{O}_{O}\rangle Ni(Meaep)_2]NO_2$ (ref. 133) (LVII)
$[Ni(Meen)_2(NO_2)_2]$	(ref. 123)	$[Ni(a\text{-}Et_2en)_2(ONO)_2]$	(ref. 125)	
$[Ni(Eten)_2(NO_2)_2]$	(ref. 123)	$[Ni(a\text{-}Me_2en)_2(ONO)_2]$	(refs 125, 127) (LI)	
$[Ni(rac\text{-}stien)_2(NO_2)_2]$	(ref 123) (XLVIII)	$[Ni(s\text{-}Et_2en)_2(ONO)_2]$	(ref. 125) (L)	
		$[Ni(m\text{-}stien)_2(ONO)_2]$	(ref. 125) (IL)	
		$[Ni(Meamp)_2(ONO)_2]$	(ref. 132) (LVIII)	
		$[Ni(ampMe)_2(ONO)_2]$	(ref. 132)	

ences in the nitrite coordination have been recognised above all in connection with investigations on chelates containing ethylenediamine or other diamines as second ligand besides the first ligand, nitrite. Table 7 shows that in nickel(II) complexes the coordination of the nitrite by the nitrogen is favoured, evidently because of the higher bond energy of the Ni—N compared to the Ni—O bond (cf. the ΔH value of isomerisation reaction (1) below). In a nitro complex, however, the angular nitrite ligand needs more space in the immediate vicinity of the central atom than in a nitrito complex. Therefore the nitro configuration will be realised only in compounds[123] whose second ligands provide little or no steric hindrance to the approach of the nitrogen atom of NO_2^-. This applies to the neutral ligands of the complexes cited in the first column of Table 7; for the compounds cited in the second column the steric hindrance by the amine ligands is so great that only the nitrito configuration is possible.

There is a noteworthy difference in the configurations of the complexes XLVIII and IL, derived from the two isomer stilbene diamines. As shown by a model[125], the two phenyl substituents have an equatorial position at the chelate rings formed by *rac*-stien, but an axial position at the chelate rings formed by *m*-stien. Only in the latter case is there a non-bonding interaction between nitrite groups in the *trans* position and the phenyl substituents and therefore a constraint on the formation of a nitrito species.

The cross-over point between stable nitro and stable nitrito configuration is observed with the compounds [Ni(*s*-Et$_2$en)$_2$(nitrite)$_2$], L; [Ni(*a*-Me$_2$en)$_2$(nitrite)$_2$] LI; and [Ni(iquin)$_4$(nitrite)$_2$], LII. It follows from the IR and visible spectra[126] that LII probably contains both nitro and nitrito species in the unit cell, and that the real configuration of L and LI is determined by the relations in the second sphere (degree of solvation, packing in the crystal). In this way we can understand why these compounds exist as the nitrito isomer in the solid state, but a temperature-controlled equilibrium (1) between the nitro and nitrito isomers is established[123] in chloroform solution. Because of the decreased steric hindrance the nitrito isomer is favoured by ΔS.

$$[\mathrm{Ni}(s\text{-}\mathrm{Et_2en})_2(\mathrm{NO_2})_2] \rightleftharpoons [\mathrm{Ni}(s\text{-}\mathrm{Et_2en})_2(\mathrm{ONO})_2] \qquad (1)$$

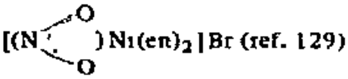
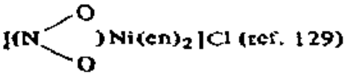
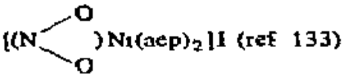
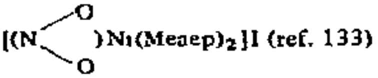
$$\Delta H = 2.3 \pm 0.6 \text{ kcal} \qquad \Delta S = 7.2 \pm 1.2 \text{ e.u.}$$

While the structures of the compounds cited in the first and second columns of Table 7 may be explained by the "classical" conception of the coordination of the nitrite ion, new structural aspects resulted from the research on the mixed anionic complexes of type Ni(N⌒N)$_2$(NO$_2$)Y (Table 8)[10]. Above all, if the second anion Y is a weak donor complex, salts with bidentate nitrite are formed. Most probably the stability of these complex salts compared with neutral complexes like [Ni(en)$_2$(NO$_2$)X] (X = Cl, Br, I) is favoured for the same reasons as are decisive for the salts [(en)$_2$NiX$_2$Ni(en)$_2$]X$_2$ (X = Cl, Br)[10] (cf. Sect. E(i)), and therefore it is not surprising that [Ni(en)$_2$(NCS)NO$_2$)], like [Ni(en)$_2$-(NO$_2$)$_2$] (LIII)[135] and [Ni(en)$_2$(NCS)$_2$] (LIV)[10], contains monodentate nitrite and thiocyanate. However, in contrast to LIII and LIV [Ni(en)$_2$(NCS)(NO$_2$)] has a *cis* structure, probably because of a specific interaction between nitrite and the thiocyanate ligands[10].

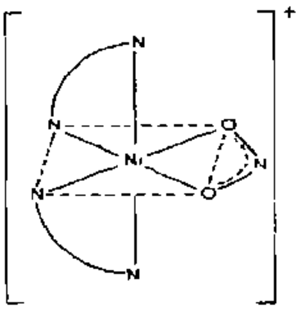
As the nitrite ion has free electron pairs both at the nitrogen and at the oxygen, several configurations are possible for complexes containing this anion as a bidentate ligand. In the

TABLE 8

Structures of octahedral complexes of the type $\mathrm{Ni(NN)_2(NO_2)Y}$

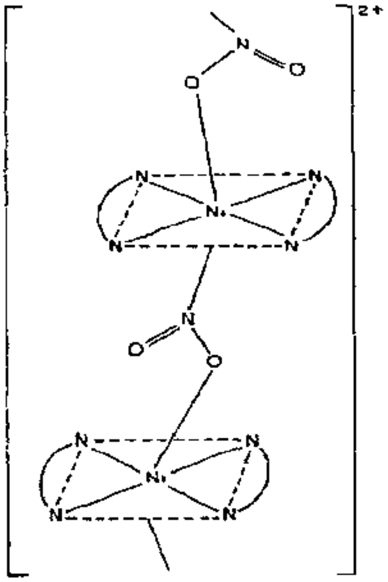
cis-Nitro	Chelating nitrite (XLV)	Bridging nitrite (XLVI)
$[\mathrm{Ni(en)_2(NCS)(NO_2)}]$ (ref 128)	 $[(\mathrm{N}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix})\mathrm{Ni(en)_2}]\mathrm{Br}$ (ref. 129)	$[(\mathrm{nitrite})\mathrm{Ni(en)_2}]\mathrm{ClO_4}$ (ref. 130)
	 $[(\mathrm{N}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix})\mathrm{Ni(en)_2}]\mathrm{Cl}$ (ref. 129)	$[(\mathrm{nitrite})\mathrm{Ni(en)_2}]\mathrm{BF_4}$ (ref. 130)
	 $[(\mathrm{N}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix})\mathrm{Ni(aep)_2}]\mathrm{I}$ (ref 133)	
	 $[(\mathrm{N}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix})\mathrm{Ni(Meaep)_2}]\mathrm{I}$ (ref. 133)	

case of the cation $[\mathrm{Ni(en)_2(nitrite)}]^+$, for instance, a four-membered chelate ring LV may be formed[129], or a coordination polymerisation to LVI, which is distinguished by delocalisation of π-electrons[131], may occur. Referred to one unit $[\mathrm{Ni(en)_2(nitrite)}]^+$, the two cationic species LV and LVI should differ only slightly in energy; the lattice forces should be decisive for the appearance of the configuration LV in the halides, and of the configuration LVI in the perchlorate as shown in Table 8.



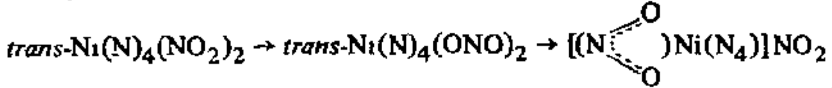
LV

N⌒N = en



LVI

If we include the chelating nitrite in the discussion at the beginning of Sect. E(ii), then the following graduation of the steric requirements in octahedral nickel(II) complexes may be supposed: 2 nitro ligands > 2 nitrito ligands > 1 chelating ligand. Therefore for mixed-ligand complexes of type $Ni(N)_4(nitrite)_2$ we shall expect the following sequence of configurations with increasing bulk of the anionic ligands.

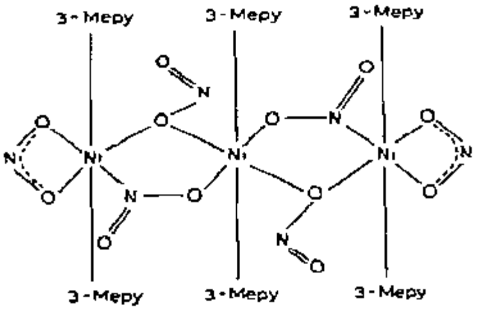


$$trans\text{-}Ni(N)_4(NO_2)_2 \rightarrow trans\text{-}Ni(N)_4(ONO)_2 \rightarrow [(N\genfrac{}{}{0pt}{}{O}{O})Ni(N_4)]NO_2$$

The most bulky anionic ligands should form only the 1,1-complexes $(N\genfrac{}{}{0pt}{}{O}{O})_2Ni(N)_2$.

This sequence is realised in practice[134] as shown by the complexes LIII, L, LVII and $(N\genfrac{}{}{0pt}{}{O}{O})_2Ni(Me_4en)$. Again the difference in the configurations of LVII and LVIII is caused by the higher steric requirements of a ligand forming a six-membered chelate ring compared to those of a ligand forming a five-membered ring (cf. Sect. D).

The purple complex $Ni(3\text{-}Mepy)_2(nitrite)_2 \cdot \frac{1}{3} C_6H_6$, LIX[135], which crystallises after some days from a solution of $Ni(3\text{-}Mepy)_4(ONO)_2$ in benzene has a very uncommon structure. It is a trimer containing both chelating and bridging nitrite of the types XLVI and XLVII. In this compound the sheet of nickel atoms and nitrite ligands is nearly planar. Thus effective delocalisation of π-electrons is possible. Probably this electron delocalisation and the distance between the coplanar pyridine ligands, which is optimal for a dispersion interaction, cause the remarkable stability of LIX.



LIX (benzene molecules have been omitted)

In the IR spectrum of LIX, the characteristic frequencies for the different types of bidentate nitrite[136] are observed:

(*a*) Maxima at 1412 and 1236 cm^{-1} → bridging nitrite type XLVI. (The lower frequency ν(NO) is shifted little from ν_{as} of the free ion (1261 cm^{-1}), but the other has moved to much higher frequency (ν_s of the free ion: 1328 cm^{-1}).)

(*b*) Maxima at 1460 and 1019 cm^{-1} → bridging nitrite type XLVII (presence of one ν(NO) at very low frequency and one at very high frequency).

(*c*) Maxima at 1299 and 863 cm^{-1} → chelating nitrite. (The two ν(NO) are shifted to lower frequencies, but δ(NO) (free NO_2^-: 828 cm^{-1}) is moved[134] to 850–880 cm^{-1}. With compound LIX probably the lower frequency ν(NO) is superimposed upon the corresponding band of the bridging nitrite type XLVI.)

There are significant differences between these characteristic frequencies of bidentate nitrite ligands and those of monodentate ones[125]. Thus for *trans*-$\mathrm{Ni(en)_2(NO_2)_2}$ maxima are found at 1333 and 1299 $\mathrm{cm^{-1}}$ (small rise of ν_s(NO) and larger rise of ν_{as}(NO)), and for *trans*-Ni(*a*-$\mathrm{Me_2en)_2(ONO)_2}$ maxima at 1387 and 1130 $\mathrm{cm^{-1}}$ (rise of ν_s(NO) and lowering of ν_{as}(NO), but to a smaller degree than with bridging ligands of type XLVII) are observed. Therefore IR spectroscopy, when reasonably used in conjunction with visible spectroscopy, proves to be very useful for structural characterisation of nitrite complexes of nickel(II).

In contrast to nitrite, monodentate nitrate can coordinate only by oxygen, and nitrate bridges analogous to XLVI are impossible. Four-membered chelate rings, however, may exist in nitrate complexes (LX).

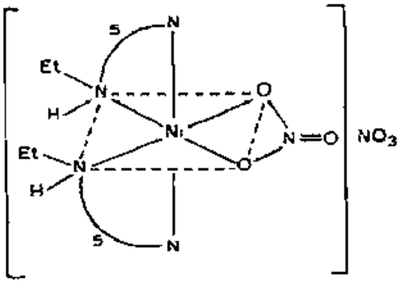
In general, the nitrate ion is a weaker ligand than nitrite. This is shown by the following facts.

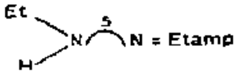
(*a*) Among the complexes of *a*-$\mathrm{Et_2en}$, [Ni(*a*-$\mathrm{Et_2en)_2(ONO)_2}$] is *trans* octahedral, having a nitrito configuration[125], but [Ni(*a*-$\mathrm{Et_2en)_2](NO_3)_2}$ is square-planar and no coordination of the nitrate ions takes place[115].

(*b*) In the ligand-field spectra of *trans* complexes of the type $\mathrm{Ni(N)_4(ONO_2)_2}$, because of the large differences between the field strength of the axial and the equatorial ligands, the ν_1 band is split[101, 114]. This is in clear contrast to the nitrito complexes $\mathrm{Ni(N)_4(ONO)_2}$, where broadening but not splitting of this band is observed. Therefore the splitting of this band and that of the asymmetric ν(NO) in the IR spectrum may be used as a proof for the *trans* structure for nitrato complexes of the type $\mathrm{Ni(N)_4(ONO_2)_2}$.

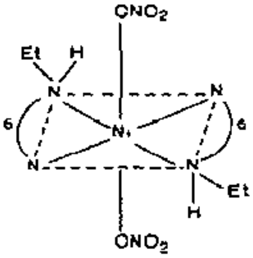
As with the nitrite complexes, the steric requirements of the second ligands are decisive in determining the configuration of the octahedral complexes[101] of the type $\mathrm{Ni(L)_4}$-(nitrate)$_2$. Small second ligands like water or en favour monodentate coordination of the nitrate. The complex $\mathrm{[Ni(H_2O)_4(ONO_2)_2]}$ shows that a *cis* configuration is possible[137], though the inter-ligand repulsions are minimised by a *trans* configuration.

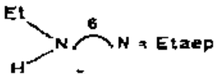
For compounds of the type $\mathrm{Ni(N)_4}$(nitrate)$_2$, more bulky amine ligands in general cause the formation of complex salts containing nitrate as a bidentate chelate ligand, viz.[138, 139] $[(\mathrm{ON}{<}^{\mathrm{O}}_{\mathrm{O}})\mathrm{Ni(N)_4]NO_3}$, LX. The *trans* octahedral $\mathrm{[Ni(Etaep)_2(ONO_2)_2]}$ with monodentate nitrate[140], and the *cis* octahedral $[(\mathrm{ON}{<}^{\mathrm{O}}_{\mathrm{O}})\mathrm{Ni(Etamp)_2]NO_3}$ with chelating nitrate[139], however, show that the electronic properties and the mutual steric interactions of the amine ligands also have an influence on the structure of the whole complex. In Sect. B(iii) the possibility of a weak π-bond between nickel(II) and pyridine ligands was discussed. Among the scarcely sterically hindered isomers of $\mathrm{[Ni(Etamp)_2}$(nitrate)$_2$], LXI is stabilised to a higher degree than the others by this π-bonding, because two out of the three filled $3t_{2g}$ orbitals of the central atom may interact with antibonding π-orbitals of the pyridine ligands[139]. By considering models we can see that when the Etamp ligands in the isomer LXI are replaced by the ligand Etaep, i.e. a substitution of two five-membered chelate rings by two six-membered ones, steric hindrance between the ethyl groups and the bismethylene fragments of the rings is present. A change to the configuration with a *trans* position of the aliphatic amino groups therefore takes place. The IR spectrum and the ligand field spectrum of $\mathrm{Ni(Etaep)_2(ONO_2)_2]}$(two maxima at 9800 and 15,500 $\mathrm{cm^{-1}}$, splitting of the ν_1-band) show that the configuration is LXII, with monodentate nitrate[140].





LXI





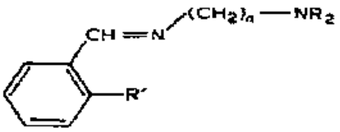
LXII

The most bulky amine ligands, like Me$_4$tn (ref. 52), Me$_2$aep (ref 140) and *N,N,N',N'*-tetramethylphenylenediamine[141], form only 1,1-complexes with nickel nitrate. A distorted octahedral structure is attained when the two nitrate ions act as bidentate chelate ligands.

(iii) Complexes of potentially tri- and tetradentate ligands

Nitrite and nitrate are potentially bidentate ligands, as shown in Sect. E(ii). Whether this bidenticity is actually realised in a mixed-ligand complex, or whether only *one* coordinative bond to the central atom is formed, depends largely on the second ligand. Very similar conditions are observed with several mixed-ligand complexes containing potentially tri- and quadridentate first ligands which in contrast to the bidentate nitrite or nitrate do not form strained four-membered rings, but form the more stable five- or six-membered rings. Sometimes the influence of the second ligands is relatively unspecific, and the actual denticity is principally determined by the steric and electronic properties of the first ligands themselves (cf. Sect. D). In other cases, however, the second ligands have a specific influence on the denticity of the first ligands and on the configuration of the whole complex. Of course, many complexes show intermediate behaviour.

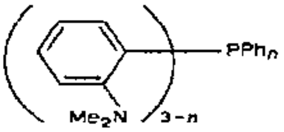
Sacconi and Bertini[142] prepared the compounds (2-MeOBenNMe$_2$)NiX$_2$, LXIII (X = Cl, Br), (2-MeOBenNEt$_2$)NiX$_2$, LXIV (X = Cl, Br, I), and (2-MeOBtnNMe$_2$)NiX$_2$, LXV (X = Cl, Br). Brick-red complexes of the types LXIII and LXV are five-coordinate, but



	n	R	R′
2-MeOBenNMe$_2$	2	Me	OMe
2-MeOBenNEt$_2$	2	Et	OMe
2-MeOBtnNMe$_2$	3	Me	OMe
BenNMe$_2$	2	Et	H

the purple complexes of the type LXIV are four-coordinate and tetrahedral. In all three cases variation of the anion has no influence on the structure. This means that the actual denticity of the ligands 2-MeOBenNMe$_2$, 2-MeOBenNEt$_2$ and 2-MeOBtnNMe$_2$ is determined by their steric requirements. the steric hindrance engendered by replacing the two methyl groups in the side chain of 2-MeOBenNMe$_2$ by ethyl groups will be sufficient to lower the denticity from 3 to 2. From the close correspondence between the reflection spectra of (2-MeOBenNEt$_2$)NiBr$_2$ and (BenNEt$_2$)NiBr$_2$ it may be inferred that the methoxy group of 2-MeOBenNEt$_2$ is non-coordinated. Of course, the nickel—oxygen bonds in chelates of the types LXIII and LXV are relatively weak. On dissolving in organic solvents, a temperature-controlled equilibrium between four- and five-coordinate species is therefore established.

Also, for the complexes (Ph$_2$PphNMe$_2$)NiX$_2$, [PhP(phNMe$_2$)$_2$]NiX$_2$, and [P(phNMe$_2$)$_3$]-NiX$_2$ (X = Cl, Br), no specific influence of the anions on the coordination of the first ligand is observed[143] In the solid state dimeric five-coordinate species with halide bridges

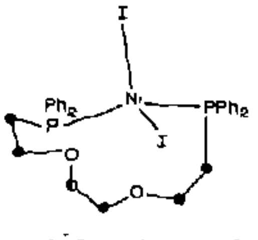


	n
Ph$_2$PphNMe$_2$	2
PhP(phNMe$_2$)$_2$	1
P(phNMe$_2$)$_2$	0

are present (cf. the structure of Ni(2,9-Me$_2$phen)Cl$_2$, XXIX). Consequently for Ph$_2$PphNMe$_2$ the actual and potential denticities correspond to each other, but for PhP-(phNMe$_2$)$_2$ and P(phNMe$_2$)$_3$ they do not. The reason for this seems to be that electron withdrawal, transmitted through the aromatic system, becomes so strong that the donor strength of the remaining dimethylamino groups declines below the limit required for a coordinative bond.

These examples show that generally an unspecific influence of the second ligands on the actual denticity of the first ligands is to be expected, if these first ligands contain weak donor groups, e.g. —O— or —N< directly bound to an aromatic residue. These weak donors, however, need not necessarily have a terminal position in the ligand. Thus, in the complex LXVI, the phosphine ligand is bidentate, and the Ni—O distance of 3.2 Å precludes a coordinative bond between the central atom and the other groups.

The complex LXVI is interesting for a further reason: the ligand Ph$_2$P(CH$_2$)$_2$O(CH$_2$)$_2$-

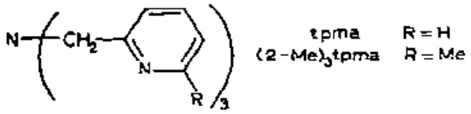


● CH_2 group

LXVI

$O(CH_2)_2PPh_2$ has nearly the same chain length as $Ph_2P(CH_2)_8PPh_2$. Therefore both phosphines, when acting as bidentate ligands, should have comparable electronic and steric influences on the central atom. However, $[Ph_2P(CH_2)_8PPh_2]NiI_2$, LXVII, is paramagnetic and tetrahedral, while the structure of the diamagnetic complex LXVI is intermediate between a square-plane and a tetrahedron. Sacconi and Dapporto[144] suggest that the different configurations of the complexes LXVI and LXVII arise through different dispositions of the chain. These different dispositions are probably due to electrostatic interaction of the oxygen atoms and the metal atom. In fact, of all the atoms in the chain, the oxygen atoms are the nearest to the metal.

Using the ligand $(2\text{-Me})_3$tpma Nelson and co-workers[145] investigated the specific influence of coordinated anions on the actual denticity of an N_4-donor. This ligand contains

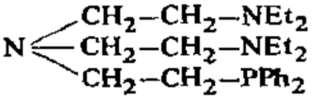


a methyl group in the position α to each pyridine nitrogen atom. Therefore steric hindrance occurs if this ligand is tetradentate. This is to be seen most clearly in a comparison of the complexes $Ni(tpma)X_2$ and $Ni[(2\text{-Me})_3tpma]X_2$ (X = Cl, Br). The former, because of the absence of steric hindrance by the α-methyl groups, have a *cis* octahedral structure with tetradentate tpma; in the latter the nickel(II) is only five-coordinate, and one of the pyridine groups of $(2\text{-Me})_3$tpma does not interact with the central atom. Nevertheless, in spite of steric hindrance the ligand $(2\text{-Me})_3$tpma may be tetradentate, as follows from the structure of the compounds $Ni[(2\text{-Me})_3tpma](NCS)_2$, $\{Ni[(2\text{-Me})_3tpma](\substack{O\\O}{>}NO)\}ClO_4$ (LXVIII), $\{Ni[(2\text{-Me})_3tpma](\substack{O\\O}{>}ClO_2)\}ClO_4$ (LXIX), $\{Ni[(2\text{-Me})_3tpma]I\}ClO_4$ (LXX) and $\{Ni[(2\text{-Me})_3tpma]Cl\}ClO_4$ (LXXI).

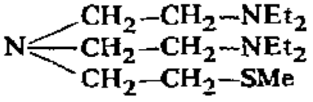
The anion NCS^- coordinating via the nitrogen is only weakly polarisable[146]. Moreover, as NCS^-, because of its linear structure, needs only a small space in the immediate vicinity of the central atom, the nickel(II) in $Ni[(2\text{-Me})_3tpma](NCS)_2$ adds the maximum number of donor groups, i.e. six. Similar conditions as to the polarisability of anions are valid for the compounds LXVIII and LXIX. Because of the overcrowding of the coordination sphere by the ligand $(2\text{-Me})_3$tpma, the addition of two more bulky anions such as perchlorate or nitrate is impossible. Therefore, only one of them is bound, forming a four-membered chelate ring (cf. Sect. E(ii)). Evidently with this type of bidentate coordination of the nitrate or perchlorate anion, a higher charge than with a normal monodentate type may be transferred to the central atom. In this way the Pauling Electroneutrality Principle can be better met (cf. Sect. C).

In the five-coordinate complexes LXX and LXXI $(2\text{-Me})_3$tpma is also tetradentate. For LXX replacement of the perchlorate by a second iodide ion has no influence on the structure and $\{Ni[2\text{-Me})_3tpma]I\}I$ contains the same cation as LXX. On the other hand there is a significant structural difference between LXXI and $Ni[(2\text{-Me})_3tpma]Cl_2$ (see above), evidently because of the low stability of the cation $\{Ni[(2\text{-Me})_3tpma]Cl\}^+$. The different behaviour of $\{Ni[(2\text{-Me})_3tpma]I\}^+$ and $\{Ni[(2\text{-Me})_3tpma]Cl\}^+$ towards excess I^- and Cl^- can scarcely be attributed to the different sizes of these anions. The acceptor character of the central atom nickel(II), which is intermediate between hard and soft, is largely determined by the properties of the ligands[146]. In the cations $\{Ni[(2\text{-Me})_3tpma]I^+\}$ and $\{Ni[(2\text{-Me})_3tpma]Cl\}^+$ the decisive influence is that of the four nitrogen donors and therefore the central atom should behave like a hard acceptor. Consequently, the hard donor Cl^- adds to the cation $\{Ni[(2\text{-Me})_3tpma]Cl\}^+$ with a simultaneous breaking of a Ni–N bond, but no addition of the soft donor I^- to $\{Ni[(2\text{-Me})_3tpma]I\}^+$ occurs.

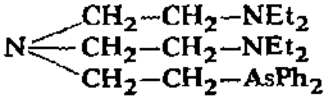
Hardness or softness of the second ligands influences more seriously the actual denticity of "hybrid ligands", i.e. of ligands containing both hard and soft donor groups. Sacconi and Morassi[147] have synthesised a series of nickel(II) complexes of the ligands N_3P, N_3S and N_3As with square-planar, square-pyramidal and trigonal-bipyramidal structures.



N_3P



N_3S



N_3As

The sulphur ligand complexes $[Ni(N_3S)X]BPh_4$ usually have coordination number 5, so that the potential and actual denticities correspond to one another. Most probably the reason for this is not a special donor quality of the –SMe group towards nickel(II), but its small steric requirement (cf. Sect. D(i)).

Both square-planar complexes and five-coordinate complexes are formed by the ligands N_3P and N_3As. With square-planar complexes of the composition $[Ni(\overline{N}N_2P)X]BPh_4$ *, LXXII[148], and $[Ni(N_3\overline{As})X]BPh_4$, LXXIII[11], the different coordination tendencies of the diphenylphosphino and the diphenylarsino groups towards nickel(II) become clearly apparent. In both cases the potentially tetradentate ligands are actually tridentate. In the compounds of type LXXII the chromophore is NiN_2PX, with one of the diethylamino groups uncoordinated, whereas in compounds of the type LXXIII, on the other hand, it is NiN_3X, with the diphenylarsino group uncoordinated **. From consideration of the complex cations $\{Ni[(2\text{-Me})_3tpma]I\}^+$ and $\{Ni[(2\text{-Me})_3tpma]Cl\}^+$ it follows that the central

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* A line over the symbol of the donor atom ($\overline{N}$, $\overline{As}$) means that this donor atom is not coordinated.

** The compound $[Ni(N_3As)I]BPh_4$ (ref. 147) with coordination number 5 is an exception. The reason for this is not clear.

atoms in the square-planar species $[\mathrm{Ni(N_3\overline{As})X}]^+$ are hard acceptors and that they can only add hard donors. Therefore the formation of the square-pyramidal $\mathrm{Ni(N_3\overline{As})(NCS)_2}$ with a non-coordinated diphenylarsino group becomes understandable.

In the cation $[\mathrm{Ni(\overline{N}N_2P)X}]^+$ the ligand $\mathrm{N_3P}$ coordinates via two hard and one soft donor atom. In this case the fourth, i.e. the anionic, ligand has a strong influence on the character of the central atom. The relatively hard ligands $\mathrm{Cl^-}$ or $\mathrm{Br^-}$ cause a "hardening" of the central atom. Therefore, under certain conditions the uncoordinated diethylamino group of $[\mathrm{Ni(NN_2P)Cl}]^+$ or $[\mathrm{Ni(NN_2P)Br}]^+$, which is a hard donor, may be added to the central atom, increasing the coordination number to five. Thus, the trigonal-bipyramidal isomers of LXXII, i.e. $[\mathrm{Ni(N_3P)X}]\mathrm{BPh_4}$ (LXXIV, X = Cl or Br), may be isolated[147]. In chloroform a temperature-controlled equilibrium between LXXII and LXXIV is established[148]. On the other hand, $\mathrm{I^-}$ causes the central atom of $[\mathrm{Ni(\overline{N}N_2P)I}]^+$ to become a soft acceptor, and coordination of the free diethylamino group does not occur either in the solid state or in a solution.

In mixed-ligand complexes of nickel(II), thiocyanate ligands particularly favour the coordination of hard donors rather than soft donors. Thus, the chromophore in $\mathrm{Ni(N_3\overline{P})(NCS)_2}$ is $\mathrm{NiN_3(NCS)_2}$, as in $\mathrm{Ni(N_3\overline{As})(NCS)_2}$, and the diphenylphosphino group is uncoordinated[149]. Besides the octahedral isomer of $\mathrm{Ni(Et_2PeSEt)_2(NCS)_2}$, a second *trans* planar isomer is known with the ligand $\mathrm{Et_2PeSEt}$ bound only by the phosphorus[150]. In the square-planar $\mathrm{Ni(Ph_2\overline{As}ep)_2(NCS)_2}$, $\mathrm{Ph_2Asep}$ is monodentate, coordinating via the nitrogen[151].

F. CONCLUSIONS

Recent investigation of nickel(II) complexes has shown that besides the characteristic coordination numbers four and six, the coordination number five with a square-pyramidal or a trigonal-bipyramidal arrangement of the ligands also occurs. The structure of a given nickel(II) complex is primarily determined by the steric and electronic effects of the donor atoms of the ligands. In many cases isomers are known differing in the geometrical arrangement of the ligands (Sect. B), in the degree of association (Sect. C), in the kind of the linkage between the ligands and the central atom (Sect. E(ii)), or in the number of coordinated anions (Sect. E(i)). Many of these isomers are energetically nearly equivalent, and therefore secondary effects such as the packing of the molecules in the crystal lattice (Sect. B(ii)) or solvation by polar or non-polar solvents determine the occurrence of a certain isomer. In other cases, above all in solution, temperature-controlled equilibria between the isomers are established (Sects. B(i), (iv), E(iii) etc.), or solid interallogons are formed (Sect. B(ii)). Such secondary effects cannot always be attributed to intermolecular interactions, but they derive from the particular structure of the ligand.

Classical coordination chemists were primarily interested in the first sphere, the coordination sphere, and they owe their successes in no small part to that wise limitation. But in the present state of knowledge interest must also be taken in the second sphere, i.e. to secondary effects mentioned above. This is necessary, first, to obtain deeper insight into the phenomenon of "coordination". Secondly, it must be mentioned once more that for metal complexes, whose actual structure is often decisively determined by such secondary effects, isomers are to be expected. The latter differ characteristically in their physical properties (magnetic moment, dipole moment, absorption spectrum etc.), but only a small quantity of energy is needed to bring about their (often reversible) interconversion.

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