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Tetrahedral Complexes of Nickel(II): Electronic Spectra, σ and π Bonding, and the Electroneutrality Principle

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Angular overlap and interelectron repulsion parameters for 13 'tetrahedrally' co-ordinated complexes of nickel(II) are critically compared and shown to describe distributions of valence electron density in σ and π bond networks which consistently reflect the operation of the electroneutrality principle. The a.o.m. and interelectron repulsion parameters were derived from analyses of spectral and magnetic properties, five of which are reported for the first time.

Introduction

During the past 25 years the inorganic chemist's interest in the electronic spectra of transition metal complexes has focussed in practice probably more upon the verification of ligand field theory and the exploitation of chromophore symmetry than on the central and chemically most legitimate aim of probing the electron distribution within the molecular bonding. More recently, however, an increasing number of analyses of spectral, and magnetic, studies have exploited the angular overlap model (a.o.m.) as a means of characterizing individual σ and π interactions between metals and ligands in co-ordination chemistry [1–6]. The angular overlap model is a ligand field approach which divides up the total effective potential experienced by a central metal into spatially discrete portions, each being associated with a separate ligand or functional group and characterized by σ and π components defined with respect to the local metal–ligand pseudosymmetry. The context of the a.o.m., first generally formulated by Schäffer and Jørgensen, within the main body of quantum chemistry, has been reviewed in some technical detail recently [7, 8].

An especially important feature of the a.o.m. is the capacity to analyse molecules having little or no symmetry in terms of parameters which refer to the various metal–ligand interactions factored out from otherwise chemically 'uninteresting' details of co-ordination geometry. Comparisons between σ and π basicity or acidity of ligands in different combinations with different metals in various geometrical arrangements are therefore made directly possible. Undoubtedly, a significant practical difficulty with the approach, however, is that the degree of parameterization may lead to correlations between different parameter values reproducing the experimental data or, indeed, a failure to establish quantitative estimates for all parameters. It is therefore especially valuable to have available analyses on a wide variety of complexes so that confidence in general quantitative trends may grow. We have reported a number of detailed studies of the single-crystal magnetic and spectroscopic properties of formally tetrahedrally co-ordinated complexes of nickel(II), recently, concerned especially with phosphine [9, 10], halogen, amine [11] and imine [12] type ligands. In the present paper we take the opportunity of drawing the results of these studies together and also of presenting analyses of the published spectra of a number of other similarly co-ordinated nickel(II) complexes. The ovarall picture that emerges from this comparative study provides a reasonably transparent, and essentially non-technical, description of the σ and π bonding in these systems as functions of both individual and group ligand properties reflecting the spirit of the electroneutrality principle.

Fitting Spectra

In this section we summarize the processes of the reproduction of the published electronic spectra of five formally tetrahedral nickel(II) complexes within the angular overlap model. We have employed our usual model and procedures [13] for the calculation of energy levels and their systematic comparison with the observed spectral bands [19]. For three paramagnetic systems, calculations have been made within the complete spin-triplet basis of the d^8 configuration, ^3P + ^3F: the full 45-fold basis of triplets and singlets was used for a fourth and also for a diamagnetic, pseudo-tetrahedral molecule. In each case the basis was diagonalized under the perturbation,

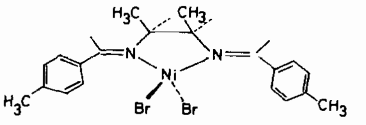
$$\mathcal{H} = \sum_{i<j} \frac{e}{r_{ij}} + V_{\mathrm{a.o.m}} + \zeta \sum_{i} l_i \cdot s_i$$

representing interelectronic repulsion, the ligand field, and spin-orbit coupling, respectively. A nominal value for ζ of 200 cm^{-1} was used throughout the analyses and not varied, in view of the gross insensitivity of the eigenvalues to this parameter. The perturbation has been included merely to indicate the extent of spin-orbit splittings in these systems. The very low value taken is typical for tetrahedrally co-ordinated nickel(II) systems, as demonstrated recently [10].

The angular overlap model of the ligand field is not restricted in any way to idealized molecular symmetry, even though many of the molecules discussed actually possess approximate high symmetry. For each complex, calculations are based upon ligands being placed and oriented exactly as defined by reported X-ray structure analyses. The present section describes the detailed fitting procedure to the five spectra, optimum parameter values having been determined independently in each case, without reference to other complexes or other techniques. The results are compared and discussed in the next section.

Dibromo[cis-endo-N,N'-di(4-methyl-benzylidene)-meso-2,3-butane diamine]nickel(II)

The crystal structure analysis of this complex has been reported by Johnston *et al.* [15] and comprises 'tetrahedral' molecules (1) with near C_{2v} symmetry.



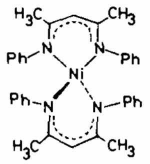
(1)

Bertini *et al.* [16] have reported the electronic adsorption spectrum of a solution of the complex in 1,2-dichloroethane, characterized by adsorption maxima at <5000, 7550, 10150, 11230, 11430 and 18630 cm^{-1}. We have parameterized the ligand field within the a.o.m. with e_σ(Br) and e_σ(N) referring to σ interaction between nickel and the bromines and imines, respectively; with $e_{\pi\perp}$(N) describing π interaction perpendicular to the plane defined by the metal and imine moiety; and with e_π(Br) for π bonding with the halogens. Wide ranges of each parameter, including the Racah B parameter, have been considered. A value around 5000 cm^{-1} for e_σ(N) is determined immediately by requiring the spectral band at 7550 to be reproduced and simultaneously placing two further components of ^3F between 8000 and 12000 cm^{-1}. The quantitative splitting pattern of the three highest-lying components of ^3F is determined by e_π(Br) for which a value near 800 cm^{-1} is optimal.

All calculations with these a.o.m values predict one ^3F component around 6000 cm^{-1} where no band is experimentally observed. It is assigned in the idealized C_{2v} symmetry, however, as $^3B_1 \rightarrow {}^3B_2$ which is electric-dipole forbidden. Approximate reproduction of all spectral bands, including one near 5000 cm^{-1}, is achieved for values of e_σ(Br) and e_π(N) which are correlated such that e_σ(Br) ~ 3000 cm^{-1} requires $e_{\pi\perp}$(N) ~ –500 cm^{-1} while e_σ(Br) ~ 5000 cm^{-1} requires $e_{\pi\perp}$(N) ~ +500 cm^{-1}. The optical parameter set in Table II was determined after final rounds in which all parameters were adjusted. B was chosen by centering all $\rightarrow {}^3P$ components under the band at 18630 cm^{-1}. The eigenvalues calculated with the optimal parameter set in Table II are listed and compared with the observed bands in Table I.

Bis[{N,N'-(1,3-dimethylpropanediylidene)-dianilinato}(1–)]nickel(II)

Healy *et al.* [17] have reported the X-ray crystal structure of this complex as containing two similar but independent molecules (2) in the asymmetric unit. The phenyl rings are inclined variously between 56 and 85° with respect to the propenediimine chains. The dihedral angle between the two chelating moieties is 98.6° so that the symmetry of this chromophore is somewhat less close to the idealized C_{2v} than that of the previous complex (1). The electronic absorption spectrum of a solution of the complex (2) in dry chloroform has been reported by Parks and Holm [18] and is characterized by band maxima at 7250, 8500, 10000 and 15870 cm^{-1}. We have parameterized the ligand field in this system by just two a.o.m. parameters, e_σ(N) and $e_{\pi\perp}$(N) for σ bonding and π bonding perpendicular to the propenediimine chelates, respectively. The best-fit parameters given in Table II yield the calculated eigenvalues in Table I. Agreement with experiment is fair only but cannot be improved with the parameter set e_σ(N), $e_{\pi\perp}$(N), B. The value for e_σ(N) is determined fairly sensitively; that for $e_{\pi\perp}$(N) is established only to the extent that any value between 0 and 400 cm^{-1} will yield satisfactory fits.



(2)

Dibromo(2,2'-biquinoline)nickel(II)

Butcher and Sinn [19] have determined the crystal structure of this complex, comprising the pseudotetrahedral molecules (3). We have recorded the unpolarized single crystal spectrum of the complex at *ca.* 5 K using a Cary 17 spectrophotometer. The spectrum in Figure 2 is characterized by major adsorp-

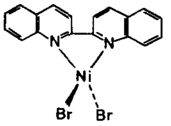
TABLE I. Comparison between Observed Spectral Bands with Those Calculated Using the Optimal Parameters Sets given in Table II. All energies in cm^{-1}, given vertically in order – calculated/observed.

xi Ni(N=C)Br$_2$	0	5243	6125	7637	9910		10489		11131		17434	18176	19052
(1)		<5000		7550		10150		11230		11430		18630	
xii Ni(N–Ph)$_2$	0	2991	3947		4251		6677		8417	10637	14358	15172	17133
(2)						7250		8500		10000		15870	
x Ni(biquinoline)Br$_2$	0	3743	4971	6020		7678		8568		9808	17303	18450	19430
(3)			<4500			7700			9800			19250	
v Ni(POP)Cl$_2$	0	4576	5441	8681		9068		10489		12181	17516	17655	18417
(4)			4900	8100		9350			11700			18200	
vi Ni(POOP)I$_2$	0	8073		12785		20041	21594	22559	24125	27187		36381	
(5)		8486		13575		20114	21830		24169	27202			
		8800	12500		13700		21200		24000	27500			

TABLE II. Angular Overlap and Racah B Parameters (cm^{-1}) for Tetrahedrally Co-ordinated Complexes of Nickel(II).

	Complex	e_σ(P)	e_π(P)	e_σ(Hal)	e_π(Hal)	e_σ(N)	$e_{\pi\perp}$(N)	e_σ(O)	$e_{\pi\perp}$(O)	B	Ref.
i[b]	Ni(PPh$_3$)Br$_3$	5000	−1500	3000	700					620	10
ii	Ni(PPh$_3$)I$_3$	6000	−1500	2000	600					490	10
iii	Ni(PPh$_3$)$_2$Cl$_2$	(4500)	(−2500)	(4500)	(2000)					(550)	9
iv	Ni(PPh$_3$)$_2$Br$_2$	(4000)	(−1500)	(4000)	(1500)					(550)	9
v	Ni(POP)Cl$_2$	5000	−1500	3600	1500					550	[a]
vi	Ni(POOP)I$_2$	(6000)	(−1500)	(2500)	(500)					(330)	[a]
vii	NiL$_N^+$Cl$_3$			3250	1000	6100	0			760	11
viii	NiL$_N^+$Br$_3$			3000	850	5900	0			720	11
ix	Ni(quinoline)Br$_3$			4500	1100	4000	−500			670	28
				3600	500	3600	−600			720	
x	Ni(biquinoline)Br$_2$			3500	850	4200	−1000			790	[a]
xi	Ni(N=C)Br$_2$			3500	800	5200	(−250)			630	[a]
xii	Ni(N–Ph)$_2$					4000	(+200)			640	[a]
xiii	Ni(sal)$_2$					(4000)	+900	(4000)	1000	(660)	12

L$_N^+$ = *N*-ethyl-1,4-diazabicyclo[2,2,2]octonium$^+$. [a]This work. [b](v) ≡ this work, molecule 4. (vi) ≡ this work, molecule 5. (x) ≡ this work, molecule 3. (xi) ≡ this work, molecule 1. (xii) ≡ this work, molecule 2. (xiii) sal ≡ *N*-isopropylsalicylaldiminato. Values in parentheses are considered to be the less well established.



(3)

tions at <4500, 7700, 9800 and 19250 cm^{-1}. Our model parameterizes the ligand field with e_σ(N), e_σ(Br), e_π(Br) and $e_{\pi\perp}$(N), the latter referring to π interaction normal to the biquinoline plane. Parameter values have not been established very sensitively, largely because components of the $\rightarrow{}^3P$ band at 19250 cm^{-1} have not been clearly resolved. The e_σ values given in Table II are not determined better than ±400 cm^{-1}, nor the e_π values better than ±250 cm^{-1}. There is no doubt, however, that $e_{\pi\perp}$(N) in this complex is substantially negative. Detailed comparison between calculated eigenvalues and observed spectral peaks is given in Table I. The band calculated at 4941 cm^{-1} is formally assigned in C_{2v} symmetry as $^3B_1 \rightarrow {}^3B_2$ and should be electric-dipole forbidden, as also the band calculated at 17,303 cm^{-1}. Bands calculated at 7678 and 8568 cm^{-1} belong to states which project [9] in C_{2v} with mixed $^3B_1/^3B_2$ character. The calculated transition at 6020 cm^{-1} is assigned as $\rightarrow{}^3A_1$ which in the spectrum of Ni(PPh$_3$)$_2$Cl$_2$, at least is observed [20] to be very weak.

The band observed at *ca.* 15,900 cm^{-1} is not assigned as a component of the $\rightarrow{}^3P$ manifold as no reasonable choice of a.o.m. parameters is able to reproduce a width for this manifold as great as

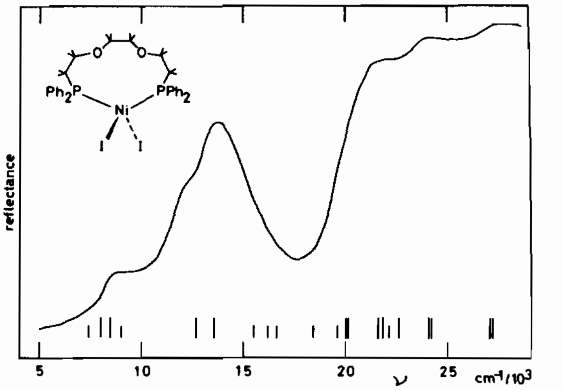


Fig. 1. Diffuse reflectance spectrum [24] of di-iodo[ethylenebis(oxyethylene)] bis(diphenylphosphine)nickel(II) at *ca.* 110 K. Eigenvalues calculated with the parameter set in Table II are shown as long bars for spin-allowed, spin-singlet transitions and short bars for forbidden, triplet bands.

3300 cm^{-1}. Accordingly, we presume that observed spectral features at 11,000, 11,500, 11,750, 13,000, 15,900, 16,800 cm^{-1} (and possibly at 5,700, 5,950, 7,250, 7,550 and 7,900 cm^{-1}, though some or all of these might be due to vibrational effects – either coupled to the spin-allowed bands and/or ligand vibrations) are to be assigned as spin-forbidden transitions. Using the full d^8 configuration as basis, we have optimized fits to these bands by variation of only the Racah F_2 and F_4 parameters, constrained so that $F_2 - 5F_4 \equiv B = 790$ cm^{-1}. Best fit was found for $F_2 = 860$ and $F_4 = 14$ cm^{-1}, for which the singlet transitions occur at 6,627, 6,635, 10,085, 11,040, 11,749, 12,853, 14,768, 15,895, 16,169, 17,631, 18,012, 18,627, 20,588, 20,690 and 29,007 cm^{-1}. The observed and calculated spectral peaks are compared in Fig. 2.

Dichloro[oxydiethylenebis(diphenylphosphine)]-nickel(II)

Greene and Sacconi [21] have reported the X-ray crystal structure of this compound which contains the distorted tetrahedral molecules (4). The diffuse reflectance spectrum of the complex, described by Sacconi and Gelsomini [22] is characterized by band maxima or shoulders at 4900, 8100 (sh), 9350,

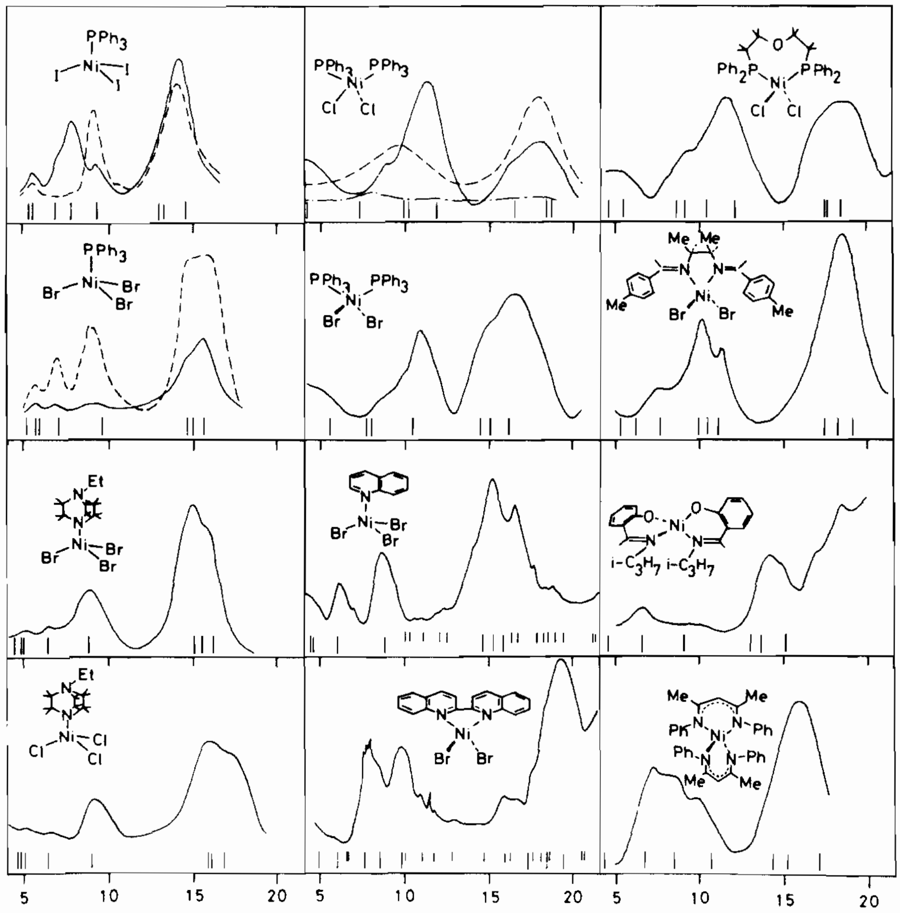
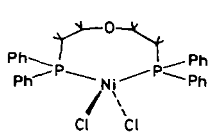


Fig. 2. Spectra for the 12 paramagnetic species in Table II. Calculated eigenvalues, using parameters listed in Table II, are shown as long bars for spin-allowed, triplet transitions and short bars for forbidden, singlet bands.

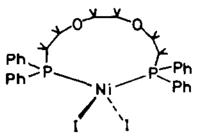


(4)

11700 and 18200 cm^{-1}. Our analysis of these data has employed the a.o.m. parameters e_σ(Cl), e_σ(P), e_π(Cl), e_π(P), together with the Racah B parameter. An important constraint in the fitting procedure was to avoid placing calculated transitions in the experimentally transparent regions around 7000 and 15000 cm^{-1}. The optimal parameter set given in Table II clearly established a large, negative e_π(P) value together with a large, positive e_π(Cl) value, the latter being determined within ±500 cm^{-1} only. The value for e_σ(Cl) is fixed within ±400 cm^{-1}. Table I lists the corresponding eigenvalues. Projection of the eigenvectors onto the representations of C_{2v} for these transitions determine the band at 5444 cm^{-1} as almost pure $^3B_1 \rightarrow {}^3B_2$, and hence electric-dipole forbidden, while those at 8676 and 9088 cm^{-1} are intimate mixtures of $\rightarrow {}^3A_1/{}^3B_2$.

Diiodo[ethylenebis(oxyethylene)] bis(diphenylphosphine)nickel(II)

A very distorted tetrahedral geometry was established for molecules (5) of this complex in the X-ray crystal structure analysis of Dapporto and Sacconi [23]. The I–Ni–I and P–Ni–P angles are 143 and 162°, respectively, while I–Ni–P angles average about



(5)

93°. The molecules are not well described as of distorted planar co-ordination, however, and considerable interest attaches to the observed diamagnetism of this complex. Sacconi and Dapporto [24] have reported the diffuse reflectance spectrum of the compound at room temperature and *ca.* 110 K. The more resolved, lower temperature spectrum is characterized by transitions at 8800, 12500 (sh), 13700, 21200, 24000 and 27500 cm^{-1}. As for the previous phosphine complex (4), we have parameterized the ligand field with the a.o.m. parameters e_σ(I), e_π(I), e_σ(P), e_π(P). However, because of the observed diamagnetism, we presume the spectrum to describe spin-singlet transitions and so our calculations have employed the complete 45-fold d^8 configuration as basis. Two interelectron repulsion parameters, the Condon–Shortley F_2 and F_4 (or Racah B and C), are now required, of course. In view of the severely limited nature of the spectral data available, we have not attempted to determine values for all a.o.m. and interelectron repulsion parameters. We have been concerned rather to see if sensible parameter sets can reproduce the diamagnetism of this complex and at the same time give a reasonable account of the observed spectrum. All calculations have been made with the ratio F_4/F_2 fixed at 0.09; this figure is in line with those ratios determined for several metal ions empirically and theoretically [4, 25], but we emphasize that the choice is only intended to serve as a rough guide. We are unable to calculate a spin-singlet ground state in this system with e parameters in the same range as for paramagnetic systems (Table II) unless we take values for B ($\equiv F_2 - 5F_4$) less than *ca.* 200 cm^{-1}. Much more reasonable nephelauxetic reductions in B can be accommodated, however, if we consider larger e values, especially for the phosphine ligators. Larger ligand field parameters for low-spin complexes, compared with their high-spin analogues have been noted before [26, 27] so the parameter set given in Table II does not appear unreasonable. The e values given there do represent a reasonable optimization with respect to the observed spectrum, given the restriction of F_4/F_2 = 0.09. The theoretical eigenvalues corresponding to this parameter set and listed in Table I correspond to the complete set of spin-singlets. The corresponding spin-triplets are calculated to lie at 1657, 2242, 7412, 9012, 15,553, 16,191, 16,626, 18,368, 19,576, 22,101 cm^{-1}. Overall, it is clear that satisfactory reproduction of the observed spectrum, shown in Fig. 1, together with the diamagnetism of this non-planar nickel(II) chromophore, are possible with a parametric description of the ligand field within 'normal' bounds.

Discussion

We collect together in Table II, a.o.m. and Racah B parameters for 13 'tetrahedral' nickel(II) complexes obtained by analyses of their spectra and magnetism. All studies of paramagnetism were based on single-crystal measurements of principal susceptibilities throughout the temperature range 20–300 K. Many of the spectral studies were of single crystals, occasionally in polarized light and often at low temperatures. It is worth emphasizing immediately, however, that the new analyses reported in the preceding section show that even studies based on rather limited diffuse reflectance or solution spectral data can be rewarding when interpreted within an a.o.m. scheme unlimited by unnecessary idealizations of molecular symmetry.

The variety of spectra is illustrated in Fig. 2, together with markers in each case illustrating the best fits listed in Table I or elsewhere. Geometrically the complexes discussed here fall into two broad classes – trigonally distorted tetrahedra, many approaching ideal C_{3v} closely; and tetragonally

TABLE III. Mean Co-ordination Bond Lengths (A).

	Complex	Ni–P	Ni–Hal	Ni–N	Ni–O	Ref.
i[a]	$Ni(PPh_3)Br_3$	2.32	2.37			32
ii	$Ni(PPh_3)I_3$	2.28	2.55			33
iii	$Ni(PPh_3)_2Cl_2$	2.31	2.21			34
iv	$Ni(PPh_3)_2Br_2$	2.33	2.34			35
v	$Ni(POP)Cl_2$	2.32	2.22			21
vi	$Ni(POOP)I_2$	2.24	2.50			23
vii	$NiL_N^+Cl_3$		2.24	2.04		36
viii	$NiL_N^+Br_3$		2.38	2.03		36
ix	$Ni(quinoline)Br_3$		2.37	2.03		37
x	$Ni(biquinoline)Br_2$		2.34	1.99		19
xi	$Ni(N{=}C)Br_2$		2.35	1.97		15
xii	$Ni(N{-}Ph)_2$			1.96		17
xiii	$Ni(sal)_2$			1.97	1.90	38

[a] Key as for Table II.

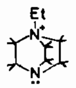
distorted tetrahedra where C_{2v} is frequently a fair idealization of the molecular symmetry. Except, of course, for the diamagnetic complex (5), all tetragonally distorted molecules in the list possess $^3B_1$ ground terms with respect to a C_{2v} idealization (or $^3B_2$, depending upon the choice of x and y axes) arising from the formal $^3T_1$ term of T_d symmetry. All trigonally distorted complexes are characterized by a near ^3E ground term with respect to the C_{3v} point group.

Of greatest interest here, however, is the opportunity the data in Table II present for the correlation of ligand field parameters and chemical bonding. We may compare phosphine ligands, occurring singly, in pairs, or as chelates; halogens; and nitrogen donors ranging imines, amines and heterocycles. While a first glance at the a.o.m. parameters in Table II may give satisfaction in terms of consistency of values, that is of their approximate transferability, a more detailed study reveals a truer chemical appreciation of how any one metal–ligand interaction is dependent to some extent on every other.

The role of phosphine ligands as π acceptors has been a matter of debate for some time. The first unequivocal demonstration from ligand field theory of phosphine π acidity towards nickel(II) and cobalt(II) concerned [9] the biphosphine complexes (iii) and (iv) in Table II. Although the a.o.m. parameter values could not be established with much precision, large negative e_π(P) values appeared to be associated with large positive values for e_π(halogen). Similar large negative e_π(P) values have been demonstrated [27] in a low-spin, planar complex of cobalt(II). Since then detailed studies of the monophosphine complexes (i) and (ii) and those of (v) and (vi) reported here appear to demonstrate that a large π acceptor role for phosphines co-ordinated to nickel(II), at least, is a general property. Recent theoretical studies [7, 8] of the angular overlap model confer considerable confidence in the quantum-mechanical basis of the approach and clearly indicate that parameter values like those in Table II do not represent artefacts on an inadequate or ill-defined model. The separation of σ and π bonding modes in metal-ligand interactions within the a.o.m. is real, although of course, each e parameter represents a local *net* property. In the monophosphine complexes (i) and (ii) the e(P) values indicate that the phosphine ligands act both as good π acceptors and strong σ donors, a view in obvious harmony with the Dewar–Chatt model of synergic 'back-bonding'. However, not only should be electroneutrality principle be invoked with respect to the phosphine ligand, but also to the metal atom. In complexes (i) and (ii), the less good donor properties (σ and π) of the iodines relative to the bromines, appear to require the phosphine ligand in the iodo complex to donate negative charge more than in the bromo system and this is reflected in the shorter Ni–P bond length observed in (ii) relative to (i); see Table III. Even though the a.o.m. parameters in the bisphosphine complexes (iii) and (IV) are less well established quantitatively, we can discern the operation of the electroneutrality principle by comparison amongst the five systems (i) to (iv). *Two* strong π accepting phosphines in (iii), (iv) and (v) apparently encourage the π donor capacity of the halogens, as compared with the situation in (i) and (ii). There appears to be some indication too that the mean donor ability of phosphines in the biphosphine complexes is less than in the monophosphine systems, this being associated with an enhanced σ donor capacity of the halogens. If the quantitative proof is less than complete, the overall evidence for synergic σ and π interaction throughout each whole molecule is persuasive. Given the limited nature of our analysis of the diamagnetic species (vi), it is especially encouraging to observe a remarkably consistent behaviour for both phosphine and halogen a.o.m. parameters which, in this highly distorted geometry, give rise to a spin-singlet ground state. The larger e_σ(P) value in the low-spin complex (vi) compared with that in the paramagnetic system (v) is in line with the shorter Ni–P bond lengths in the former, as given in Table III. As indicated earlier, our analysis does not exclude other possible parameter choices in which a larger B value is associated with even larger e parameters. The trends in e parameters in Table II will be qualitatively maintained, however.

The pattern in a.o.m. parameters for the halogens in Table II reflects the general spectrochemical trend that, for both σ and π donation, chlorine > bromine > iodine. Apart from the much greater e_π(Hal) values discussed above for (ii) and (iii), only the a.o.m. parameters for Ni(quinoline)Br_3 require comments. Two sets of best-fit parameters for this complex are entered in Table II corresponding to an ambiguity in the assignment of some spectral bands. Despite a marginal bias towards the upper set of values in the original paper [2, 8], it seems clear, by comparisons within the present set of complexes, that the lower set is to be preferred (A(2) of ref. 28). Undoubtedly, a compilation like the present Table II would have assisted the problem of spectral assignment in the quinoline complex, had it been available at that time.

Two features of the a.o.m. parameters of the complexes (vii) and (viii) deserve mention. Firstly, that the tertiary amine $\mathrm{L}_{\mathrm{N}}^{+}$ is shown to act as a strong σ donor (the analysis [11] assumed, rather than proved, that it is not involved in any π interaction with the metal atom). While the base strength of a tertiary amine might normally be expected to be less than that of a secondary amine because of the usual steric bulk of the former, the cyclic nature of the present ligand (6) surely permits a closer approach



(6)

of the nitrogen donor to the metal and hence provides for a greater base strength. However, and secondly, it is important to compare the a.o.m. parameters in Table II with those found [11] for the corresponding cobalt(II) systems. For these, $e_\sigma(\mathrm{L}_{\mathrm{N}}^{+})$ values are 4250 and 4000 cm^{-1} for the chloro and bromo complexes, respectively, with e_σ(Cl) and e_σ(Br) both at 3500 cm^{-1}. While smaller e values might be expected for the cobalt(II) system resulting from a smaller effective nuclear charge than in the present d^8 complexes, this trend is not shared by the e parameters of the halogens. However, this pattern of a.o.m. parameters reflects similar trends in co-ordination bond lengths throughout this series and has been rationalized in terms of the change in d configuration. Thus the extra electron of the d^8 system is housed in the $d_{x^2-y^2}/d_{xy}$ orbital pair (z taken parallel to Ni–N) so that the consequently reduced acceptor property of these functions weakens the nickel–halogen bonds relative to the cobalt–halogen ones. In turn the metal–amine bonds are stronger in the d^8 case. A similar argument may be applied to all the near C_{3v} molecules in Table II, so that the large axial e_σ values must in part be due to some degree of weakening of the metal–halogen bonds. Nevertheless, by comparison with the other nitrogen donors in the list, the large e_σ values observed for the tertiary amines $\mathrm{L}_{\mathrm{N}}^{+}$ must surely also reflect an intrinsically strong Lewis base behaviour of these ligands.

The a.o.m. parameters for the quinoline complexes (ix) and (x) describe a situation in which the heterocycles act as π acceptors and the bromines as π donors to an extent which reflects both the degree of quinoline π acidity and the relative numbers of nitrogen and halogen ligators. The π acidity of the quinoline ligands, especially of the biquinoline in (X) correlates well with the widely accepted stabilizing role of ligands like bipyridyl and phenanthroline on transition metals in low oxidation states. The smaller, though significant, degree of π acidity of quinoline itself in (ix) is also a characteristic of an analysis [28] of the analogous cobalt(II) complex, based on a study of single-crystal paramagnetic susceptibility, e.s.r., and electronic spectrum. Reproduction of the magnetic susceptibilities of a series [29] of antiferromagnetically exchange-coupled, binuclear cobalt benzoates has also been greatly facilitated by the recognition of such a π-acceptor role for the terminal quinoline groups.

The last three complexes listed in Table II provide an opportunity to comment upon the π functions of two Schiff base ligands, (xi) and (xiii), and of the iminoamine chelate in (xii). Chronologically, the first of these systems to be analysed [12] within the a.o.m. scheme was (xiii), bis(*N*-isopropylsalicylaldiminato)nickel(II), the study being based on complete single-crystal susceptibility measurements in the temperature range 20–300 K and, to a very limited extent, upon the diffuse reflectance spectrum. Largely because of the experimental techniques employed, the e_π parameters are better determined than the e_σ. The substantial π donor capacity of the nitrogen atoms towards the central metal atom, evidenced by e_π(N) +900 cm^{-1}, appears sensible if we compare the nominally sp^2 hybridized donor

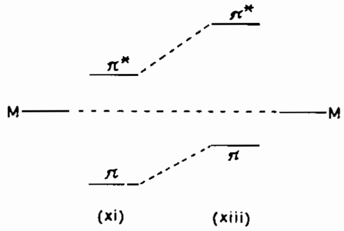
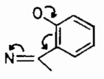


Fig. 3. Schematic representation of donor and acceptor π ligand functions for the Schiff base complexes in Table II.

atom in this complex with that in a heterocycle like quinoline, for example. However, so limited a view does not readily illuminate the small *π acceptor* role suggested by the present spectral analysis for the other Schiff base in (xi). We perceive the essential functional difference between the ligands in the two complexes (xi) and (xiii) as the presence in the latter of the oxygen *ortho* substituent on the phenyl ring. Not only do we envisage the phenolic oxygen as a π donor towards the metal atom, but also towards the imine group *via* the phenyl ring as in (7).



(7)

In so rationalizing the algebraically greater π donor capacity of the nitrogen ligator in (xiii) than in (xi), we fail to provide an explanation of the absolute π *acceptor* role in (xi). We recall, however, that a.o.m. *e* parameters represent the *net* energy shifts of appropriate metal orbitals and as such result from interactions between the metal and *both* bonding and antibonding functions of the ligand. The schematic m.o. diagram in Fig. 3 is intended to represent, in a heuristic manner only, orbital energy sets which would give rise qualitatively to the values $e_{\pi\perp}(\mathrm{N}) = -250$ and $+900$ cm^{-1} in the two complexes (xi) and (xiii). On passing from left to right, that is from the tolyl to the phenolic grouping, the nitrogen atom acquires a greater negative charge, as represented by the ground state diagram (7). The resulting decrease in ionization energy raises the energy of the π orbital to better match that of the metal and so increases the nitrogen donor function. At the same time the same increased negative charge on the nitrogen atom decreases the acceptor capacity of the group toward the metal, and this is represented by the elevated π* ligand function on the right of the diagram. Whether we should represent a decreased acceptor property of the π* orbital only by an elevated energy or by a decreased overlap with the metal – indeed probably by both – is open to discussion: however, the net effect of such changes may be represented by an *effective* energy shift of the π* function, as in Fig. 3. In the limiting case of sufficient electron transfer to the nitrogen that it be described as $-\mathrm{N}^-$, the coefficient of the nitrogen *p* orbital to the ligand molecular orbital vanishes identically, of course.

The iminoamine chelated complex (xii), though not especially well characterized by the present analysis, involves a significant but small net π donor role for the ligands. The phenyl substituents on the donor atoms do not appear [17] to take part in an extended delocalized π molecular orbital, being inclined at between 56 and 85° to the chelate planes. The π acceptor capacity of the nitrogens are therefore not expected to be as great as for those in (xi), and the small net π donor function of these ligands may be viewed as an average of those for simple amine and imine functions.

Confirmation of the bonding descriptions engendered by these analyses of the ligand-field a.o.m. parameters is afforded by the pattern of the interelectron repulsion, Racah *B* values in Table II. The phosphine complexes (i) to (v) exhibit large nephelauxetic effects especially in those molecules involving two phosphine ligands. We suppose the small interelectron repulsion manifests the substantial π bonding in relatively sparse antibonding π networks in these molecules. The particularly low *B* value in the diamagnetic complex (vi) correlates with the much shorter co-ordination bonds in this low-spin system and is comparable with the similar situation [27], with respect both to $e_\pi(\mathrm{P})$ and F_2 and F_4 values, defined in the low-spin, planar cobalt-(II) complex, *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II). By contrast, the Racah *B* parameters for the amine and quinoline complexes (vii) to (x) describe a much smaller nephelauxetic effect. The usual nephelauxetic trends for halogens is clearly shown by the *B* values in the table.

At first sight, the low values for the complexes (xi) and (xii) appear anomalous. The same is probably true of the Schiff base complex (xiii) where, despite the published value of $B = 750$ cm^{-1}, it is clear that the band assignment indicated in Fig. 2 is better, this corresponding to *B ca.* 670 cm^{-1}. Although derived only from solution spectra, in which components of the $\to {}^3P$ manifold were not resolved, it is certain that *B* values near those given in Table II are required to reproduce the experimental data. Accordingly, we believe that these low values reflect a real chemical situation which requires explanation and further confirmation. We suggest that the large nephelauxetic effects in these two molecules, and probably in (xiii), result from a fairly extensive degree of π bonding between metal and the ligands, but that this interaction involves both π and π* ligand functions, as in Fig. 3, so that the small $e_{\pi\perp}(\mathrm{N})$ values, representing the *net* π bonding *d*-orbital energy shifts, are not directly correlated with the low *B* values, reflecting a *total* π bond order.

The Magnetism of Tetrahedral Complexes of Nickel(II)

While comparing the ligand field properties of tetrahedrally co-ordinated nickel(II) complexes, it is timely to comment briefly upon their general magnetic behaviour. Years ago it was felt that a simple differentiation between tetrahedral and octahedral nickel(II) molecules would be possible by virtue of the formal T_1 ground term of the former conferring a large orbital contribution to the magnetic moment which latter should also be markedly temperature dependent. It has been known for a long time that such a diagnostic of d^8 co-ordination geometry is empirically unreliable. One reason for this, of course, is the partial quenching of the orbital moment on distortion from the ideal T_d symmetry. Nevertheless, the frequently observed, very low magnetic moments in 'tetrahedral' nickel(II) systems – occasionally lower than those observed for typical 'octahedral' molecules – have been taken as indicative of 'gross' deviation from the tetrahedral ideal. Even allowing that 'gross' is a subjective description, it remains surprising that so large a degree of orbital quenching should be associated with unexceptional tetrahedral distortions.

The reason, we believe, lies in the greatly reduced values for the effective spin–orbit coupling parameter which have recently been shown [10, 11] to be a typical feature in tetrahedrally co-ordinated nickel(II) systems. Spin–orbit coefficients determined from ten different molecules have been found to range 15 to 380 cm^{-1}, the free-ion value being $\zeta = 630\ \mathrm{cm}^{-1}$. Two, probably complementary, mechanisms for this reduction in spin-orbit parameters have been offered. One, after Collingwood *et al.* [30], refers to a sign of the mixing coefficient of ligand functions within molecular orbitals of the formal T_1 ground term which, being negative, expresses an opposed contribution to the effective ζ parameter from the ligands. This appears to be an especially significant process for heavier ligands: for example, $\zeta \sim 15\ \mathrm{cm}^{-1}$ in NiI_4^{2-}, [30]. However, much reduced ζ values, typically 200 cm^{-1}, are also observed in tetrahedral nickel(II) complexes with only lighter donors like chlorine, nitrogen or oxygen. It has been suggested [10], therefore, that a second mechanism for the reduction may arise from the Ham effect [31] which relates to a quenching of orbital angular momentum within the dynamic Jahn–Teller regime. Whatever the relative contributions of these, or any other, mechanism to this phenomenon, small spin–orbit coupling appears to be a general property of 'tetrahedral' nickel(II) species. A qualititative explanation of the low magnetic moments in these systems appears to follow.

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