involved. Molecular orbital calculations on *o*-semiquinones show that the single unpaired electron resides in a π molecular orbital.[28] The metal e_g d orbitals in these pseudooctahedral complexes are, of course, σ antibonding orbitals, while the metal t_{2g} d orbitals are of the π type. It follows, then, that the chromium(III)–*o*-semiquinone complexes would be expected to exhibit the largest magnitude of antiferromagnetic exchange interaction, because the chromium(III) complexes are d^3 complexes where all of the unpaired d electrons are in t_{2g} orbitals and can interact very effectively with the unpaired electrons of the *o*-semiquinone ligands. In the case of the high-spin iron(III) complexes, there are also three unpaired t_{2g} electrons to effect an appreciable *net* antiferromagnetic interaction, but the *net* antiferromagnetic interaction is probably reduced by virtue of the presence of ferromagnetic exchange pathways between the unpaired electrons of the *o*-semiquinone ligands and the unpaired electrons of the metal. The latter are the consequence of the presence of two unpaired e_g metal electrons in the case of the high-spin iron(III) complexes. The net antiferromagnetic interaction is quite weak for the cobalt(II) and nickel(II) complexes, because they have more unpaired electrons in e_g d orbitals than in t_{2g} d orbitals.

Acknowledgment. D.N.H. is grateful for funding from National Institutes of Health Grant HL13652 and Biomedical Research Grant RR 07030. Research at the University of Colorado is supported by National Institutes of Health Grant GM 23386 and by funds from American Cyanamid.

Registry No. $Ni(phenSQ)_2(py)_2{\cdot}py$, 76136-01-1; $Co(phenSQ)_2(py)_2$, 76136-02-2; $Ni(3,5\text{-}DBSQ)_2(bpy)$, 76136-03-3; $Co_4(3,5\text{-}DBSQ)_8$, 71370-70-2; $Co_4(phenSQ)_8$, 76172-93-5; $Ni_4(3,5\text{-}DBSQ)_8$, 76190-17-5; $Ni_4(phenSQ)_8$, 76137-18-3; $Fe(3,5\text{-}DBSQ)_3$, 70755-84-9; Fe(*o*-$Cl_4SQ)_3$, 67291-91-2; $Fe(phenSQ)_3$, 39797-84-7; $Cr(phenSQ)_3$, 68846-34-4; Cr(*o*-$Cl_4SQ)_3$, 60635-34-9.

Supplementary Material Available: Tables IV–VIII and X–XIII (calculated and observed magnetic susceptibility data) and listings of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

---

(28) (a) Pilar, J. *J. Phys. Chem.* **1970**, *74*, 4029. (b) Kuwata, K.; Shimizu, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 864. (c) Broze, M.; Luz, Z. *J. Chem. Phys.* **1969**, *51*, 738. (d) Pasimeni, L.; Brustolon, J.; Corvaja, C. *Chem. Phys. Lett.* **1975**, *30*, 249.

Contribution from University Chemical Laboratories,
Cambridge CB2 1EW, England

Donor and Acceptor Properties of Triphenylphosphine Ligands in Trigonally Distorted Tetrahedral $NiPX_3^-$ Chromophores (X = Br, I)

MALCOLM GERLOCH* and LYALL R. HANTON

Received July 28, 1980

Single-crystal paramagnetic susceptibilities are reported for $[Ph_4As]^+[Ni(PPh_3)Br_3]^-$ throughout the temperature range 20–30 K and powder susceptibilities in the range 70–300 K for $[Ph_4As]^+[Ni(PPh_3)I_3]^-$. These and the published crystal transmission spectra are analysed within the angular overlap model. Optimized parameter sets describe strong σ basicity and strong π acidity of the phosphine ligands, the magnitudes of which change somewhat in response to the differing basicity of the bromine and iodine ligands. Very small spin–orbit coupling coefficients are observed in these complexes and, in comparison with values in other systems, identify a common feature of tetrahedrally coordinated nickel(II) complexes.

Introduction

The characterization of the individual roles of σ- and π-ligand coordination in transition-metal complexes is a principal aim of current studies of spectroscopic and magnetic properties within the framework of the angular overlap model.[1] A recent analysis[2] of the single-crystal paramagnetism and optical spectra of the phosphine complexes $M(PPh_3)_2X_2$ [M = Ni(II), Co(II); X = Cl, Br] has provided a semiquantitative demonstration of considerable π acidity of the coordinated phosphine groups associated with a enhanced π basicity of the halogens. A phosphine π-acceptor role was similarly identified[3] in the low-spin, planar complex dimesitylbis(diethylphenylphosphine)cobalt(II).

The present study concerns the complexes $[Ph_4As]^+[Ni(PPh_3)X_3]^-$ (X = Br, I) which provide opportunities for comparison between (a) mono and bis coordinated phosphine complexes in "tetrahedral" nickel(II) systems, (b) bromo and iodo ligand field parameters, and (c) trigonal and tetragonal distortions in these tetrahedral chromophores. Single-crystal spectroscopic and paramagnetic properties of these compounds are reproduced within our model virtually uniquely by parameters which establish a number of interesting features: (i) The phosphine ligands act as relatively strong Lewis bases via σ bonding with the central nickel(II) ion and, at the same time, as substantial Lewis acids via π bonding. These properties are somewhat enhanced in the iodo complex with respect to the bromo one. (ii) The π-donor function is greater for the bromine ligands than for the iodines but less than observed[2] in the bis(phosphine) complexes $M(PPh_3)_2X_2$ (X = Cl, Br). (iii) The σ-donor property of the iodine ligands is less than that of the bromines which is much less than that of the phosphines. (iv) The magnetic susceptibilities of these complexes are only reproduced with a very low value for the spin–orbit coupling coefficient. This circumstance, which appears to be a common feature of tetrahedral nickel(II) systems, may reflect a participation[4] of halogen orbitals within the ground state and/or a significant role for dynamic Jahn–Teller coupling within the Ham effect.[5]

Experimental Section

The complexes $[Ph_4As]^+[Ni(PPh_3)X_3]^-$ (X = Br, I) were prepared as described in the literature.[6,7] Crystals of the bromo complex grown

---

(1) M. Gerloch, *Prog. Inorg. Chem.*, **26**, 1 (1979).

(2) J. E. Davies, M. Gerloch, and D. J. Phillips, *J. Chem. Soc. Dalton Trans.*, 1836 (1979).

(3) L. R. Falvello and M. Gerloch, *Inorg. Chem.*, **19**, 472 (1980).

(4) J. E. Collingwood, P. Day, and R. G. Denning, *J. Chem. Soc., Faraday Trans. 2*, **69** (4), 591 (1973).

(5) F. S. Ham, *Phys. Rev. A*, **138**, 1727 (1965).

0020-1669/81/1320-1046$01.25/0

Table I. Interpolated Experimental, Principal, and Average Susceptibilities[a] for $[Ph_4As]^+[Ni(PPh_3)Br_3]^-$

T/K	χ_1	χ_2	χ_3	$\bar{\chi}$	$\bar{\mu}/\mu_B$
295	38	47	64	50	3.42
275	40	51	68	53	3.41
255	42	54	74	57	3.40
235	45	58	81	61	3.40
215	48	63	89	67	3.39
195	52	69	99	73	3.38
175	56	76	112	81	3.37
155	61	85	126	91	3.35
135	68	96	147	104	3.35
115	75	111	174	120	3.32
95	85	131	214	143	3.30
75	97	162	279	179	3.28
55	111	208	385	235	3.21
35	126	292	592	337	3.07
20	133	421	958	504	2.84

[a] cgsu × 10^4; 1 cgsu = $4\pi \times 10^{-6}$ m^3 mol^{-1}.

Table II. Mean Magnetic Susceptibilities and Moments for $[Ph_4As]^+[Ni(PPh_3)I_3]^-$ [a]

T/K	68.2	86.0	119.0	169.0	218.0	268.0	297.0
$\bar{\chi}$	164	135	103	76	63	51	47
$\bar{\mu}/\mu_B$	2.99	3.03	3.14	3.21	3.30	3.31	3.36

[a] Susceptibilities (in cgsu × 10^4) corrected for diamagnetism of -552×10^{-6} cgsu.

by slow cooling of solutions in *n*-butyl alcohol, yielding both orthohombic and monoclinic forms. The present study is based on the monoclinic form, the X-ray structural analysis of which has been reported recently.[7] Magnetic susceptibilities were measured from dark green, diamond-shaped crystals weighing 2.0–3.5 mg. Satisfactory C, H analyses were obtained.

With use of our single-crystal Faraday balance,[8] susceptibilities were measured (a) for a crystal oriented $\parallel b$, yielding values of χ_1 and χ_2, (b) $\parallel a$, giving χ_3 and $\chi_{c'}$, and (c) $\parallel c$ for χ_3 and $\chi_{a'}$. The principal crystal susceptibilities are defined as $\chi_3 \equiv \chi_b$, with $\chi_2 > \chi_1$ lying in the monoclinic *ac* plane, χ_1 being oriented at an angle ϕ from *a*, measured toward *c*. Values for χ_3 measured from different crystals in the different experimental orientations agreed to within 2%, throughout the temperature range 20–300 K. In Table I are collected interpolated values of the principal and average susceptibilities corrected for a mean molar diamagnetism of $\chi_M^{dia} = -510 \times 10^{-6}$ cgsu (1 cgsu) = $4\pi \times 10^{-6}$ m^3 mol^{-1}).

By observation of the orientation of the crystal suspended $\parallel b$ in the magnetic field, the angle ϕ was estimated as ca. −63°. Using formula 1 together with the experimentally determined values of $\chi_{c'}$,

$$\sin^2 \phi = (\chi_{c'} - \chi_2)/(\chi_1 - \chi_2) \qquad (1)$$

we calculate $\phi \approx -77°$. The discrepancy is not significant in view of the approximate nature of the determination by direct observation and of the sensitivity of (1) to the ratio of susceptibility differences. Values of ϕ calculated by (1) vary by less than 3° throughout the complete experimental temperature range.

Bertini et al.[9] have described single-crystal polarized spectra for the bromo complex at 300 and 77 K and for the iodo complex at 380, 300, 195, and 77 K. Cotton et al.[6] have reported the spectrum of a solution of the chromophore in nitromethane solution.

Spectra of the iodo complex have also been reported by Bertini et al.[9] for light incident only on one face because of the thinness of those crystals. We too have been unable to grow crystals of this compound large enough for single-crystal susceptibility measurements. We are indebted to Dr. P. Thornton and Dr. C. Vuick for their measurement of the powder susceptibilities of the iodo complex using the Faraday method: the results are given in Table II. Moments of the iodo complex are found to be slightly lower than for the bromo system.

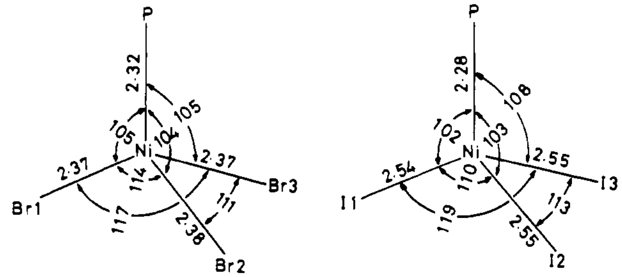

Figure 1. Coordination geometries of $[Ni(PPh_3)X_3]^-$ (X = Br,[7] I[10]).

Discussion

Eigenvalues and paramagnetic molecular and crystal susceptibilities have been calculated within the complete spin-triplet basis of d^8—^3P + ^3F—subject to the combined perturbations of interelectron repulsion, spin–orbit coupling, and the ligand field. The latter was parameterized within the angular overlap model referred to the ligand donor atom coordinates determined by X-ray analyses,[7,10] the chromophore coordination geometries of the two complex anions being summarized in Figure 1. Cylindrically symmetric π interaction is presumed for all ligands, so reducing the AOM parameter set to $e_\sigma(P)$, $e_\sigma(X)$, $e_\pi(P)$, $e_\pi(X)$ for σ and π interaction with phosphine and halogens, respectively. The parameter list is completed with the Racah B, spin–orbit ζ, and Stevens' orbital reduction k parameters, as usual.

Spectrum of $[Ni(PPh_3)Br_3]^-$

Although both calculated susceptibilities and spectral eigenvalues were monitored together throughout the analysis, we begin with a discussion of the spectral properties alone as several parameter variations affording good magnetic fits were associated with widely different eigenvalue sets. We have considered AOM parameter variations throughout the ranges $e_\sigma(P)$ 2000–7000 cm^{-1}, $e_\sigma(Br)$ 2000–5000 cm^{-1}, $e_\pi(P)$ +500 to −4000 cm^{-1}, $e_\pi(Br)$ 0–2000 cm^{-1}. As the absolute energies of components of the ^3P term are easily adjusted by variation of B, we initially focus on all components arising from ^3F.

The characteristic features of the spectra reported by Bertini et al.[9] are a peak with a shoulder at 15 600 and 14 700 cm^{-1}, a split peak at 9500 and 8800 cm^{-1}, and two further bands at 7100 and 5800 cm^{-1}. The features around 15 000 cm^{-1} are obviously to be assigned as transitions to components of the ^3P term. Bertini et al. assign the band at 7100 cm^{-1} as a spin-forbidden band subject to intensity stealing, although a similar peak at 7100 cm^{-1} in the iodo complex is ascribed to experimental beam imbalance and assigned to infrared absorptions of water vapor. It is difficult to see, from an inspection of Nielen's published[11] spectrum of water vapor, why 700 cm^{-1} should be an especially significant adsorption region. Further, the intensity of the band at 7100 cm^{-1} in the bromo complex, in view of its energy separation from other spectral features, does not convince us that this feature is to be assigned as a spin-forbidden transition. We consider that all the reported bands involve spin-allowed d–d transitions. We do, however, agree with Bertini et al. that the ground term is formally ^3E, as evidenced by their polarization studies and by the fact that all reasonable choices of AOM parameters yield an orbital doublet ground term in this chromophore geometry.

Reproduction of the observed spectrum below 13 000 cm^{-1} within the ^3F term intially centers upon the split peak at ca.

---

(6) F. A. Cotton, O. D. Fant, and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

(7) L. R. Hanton and P. R. Raithby, *Acta Crystallogr.*, in press.

(8) D. A. Cruse and M. Gerloch, *J. Chem. Soc., Dalton Trans.*, 1613 (1977).

(9) I. Bertini, D. Gatteschi, and F. Mani, *Inorg. Chem.*, **11**, 2464 (1972).

(10) R. P. Taylor, D. H. Templeton, Z. Zalkin, and W. D. Horrocks, Jr., *Inorg. Chem.*, **7**, 2629 (1968).

(11) H. H. Nielsen, *Phys. Rev.*, **62**, 422 (1942).

Table III. Comparison of Observed and Calculated Transition Energies[a] cm^{-1}) for $[\mathrm{Ph_4As}]^+[\mathrm{Ni(PPh_3)Br_3}]^-$

calcd eigenvalues		obsd spectral peaks
15584	$^3A_2$	15600
15034	^3E	14700 sh
14762		
9609	$^3A_2$	9500 split peak
7077	$^3A_1$	7100
5912	^3E	5800
5749		
5224	$^3A_2$	
469	^3E	
0		

[a] Calculated energies averaged over spin triplets. Assignments (only) correspond to idealized C_{3v} symmetry.

9000 cm^{-} This feature also appears in the spectrum of the complex dissolved in nitromethane as noted by Cotton et al.[6] The band has an unusual appearance, however. There is an obvious dependence upon temperature also, as discussed in general for both iodo and bromo complexes by Bertini et al., the splitting of the 9000-cm^{-1} band being small in the spectrum at ca. 77 K. If we require the model to place two d–d, spin-allowed transitions in this region, we must place the $^3A_2(T_d)$ and one or more components of $^3T_2(T_d)$ within ca. 900 cm^{-1} of one another. This unlikely situation is almost possible for a very limited choice of parameter values, for example, with e_σ(P) 4500, e_σ(Br) 4000, e_π(P) −4000, e_π(Br) 2000 cm^{-1}. Under these circumstances, *all* components of $^3T_2(T_d)$ are assigned to the lower component of the split band that is at 8800 cm^{-1}: we find the splitting of the $^3T_2$ term is always calculated fairly small anyway. Further, it is possible to obtain reasonably satisfactory reproduction of the observed, single-crystal paramagnetism with such a parameter set. However, the spectral fit is only fair, for we are unable to calculate two bands in this region to lie closer than 1200 cm^{-1}. At the same time, the calculated splitting of the ^3P band is about 2 times larger than that observed, and, also, such a parameter set requires B reduced to 450 cm^{-1} to reproduce the absolute energy of the ^3P components. Accordingly, we presume that the feature at ca. 9000 cm^{-1} involves a single spin-allowed transition, perhaps structured by a close-lying spin-forbidden transition with an intensity augmented by the usual intensity-stealing processes.

We also discount an assignment of the band at 9000 cm^{-1} as $^3T_2(T_d)$ with $^3A_2(T_d)$ lying at higher energy, either very weak or unobserved under the most intense band at ca. 15 000 cm^{-1}. The corresponding estimate of the tetrahedral splitting parameter Δ_{tet} would be unacceptably large.

Other choices of the AOM parameter values place one transition—$^3A_2(T_d)$—under the double peak at ca. 9000 cm^{-1}, together with two other transitions between 8000 and 4000 cm^{-1}. This constitutes a final reason for assigning the band at 7100 cm^{-1} as a spin-allowed, d–d band rather than a spin-forbidden feature or experimental artifact. We assign an orbital singlet from $^3T_2(T_d)$ to the band at 7100 cm^{-1} and a composite of the formal ^3E (from $^3T_2$) and orbital singlet (from $^3T_1$) to the band at 5800 cm^{-1}. Detailed refinement of all AOM parameters finally permitted close reproduction of all observed components of ^3F. Subsequent variation in B also yielded agreement with components of ^3P. Detailed comparison between calculated and observed transition energies is made in Table III, corresponding to the parameter set given in Table V.

Spectrum of $[\mathrm{Ni(PPh)_3)I_3}]^-$

The spectrum of the iodo complex, reported by Bertini et al., is characterized by large and unusual temperature-dependent behavior of band intensities which are associated[9] with a slightly split, orbital doublet ground term. Band maxima occur at 13 400 cm^{-1}, but with a shoulder at ca. 14 200 cm^{-1}, and at 9400 7800, 7100, and 5600 cm^{-1}. We consider all these features to reveal spin-allowed d–d transitions as noted above the further below.

Table IV. Comparison of Observed and Calculated Transition Energies[a] (cm^{-1}) for $[\mathrm{Ph_4As}]^+[\mathrm{Ni(PPh_3)I_3}]^-$

calcd eigenvalues		obsd spectral peaks
14619	$^3A_2$	14800 sh
13323	^3E	13400
13092		
9380	$^3A_2$	9400
7876	$^3A_1(^3T_2)$	7800
6899	$^3A_2(^3T_1)$	7100
5522	^3E	5600
5362		
486	^3E	
0		

[a] Calculated energies averaged over spin triplets. Assignments (only) correspond to idealized C_{3v} symmetry (and T_d symmetry in parentheses).

Table V. Angular Overlap and Racah Parameters (cm^{-1}) Reproducing Observed Spectra in Tables III and IV

chromophore	e_σ(P)	e_σ(X)	e_π(P)	e_π(X)	B
$[\mathrm{Ni(PPh_3)Br_3}]^-$	5000	3000	−1500	700	620
$[\mathrm{Ni(PPh_3)I_3}]^-$	6000	2000	−1500	600	490

Calculations have spanned the same wide parameter variations used for the bromo complex, and, as before, reproduction of the lower energy region (<12 000 cm^{-1}) comprised the initial tactic. Fitting the bands at 9400, 7800, and 5600 as components of ^3F is achieved with a virtually unique parameter set. At the same time, calculations place one further transition at ca. 7000 cm^{-1}. Any parameter set which avoids the placing of a fourth ^3F band at 7000 cm^{-1} involves a splitting pattern which is in poor agreement with the bands at 9400, 7800, and 5600 cm^{-1}. Accordingly the complete set of AOM parameters was refined to optimize fits to all four bands observed below 12 000 cm^{-1}. Reproduction of the higher energy band around 14 000 cm^{-1} requires a large reduction in B reflecting the typically large Nephelauxetic effect associated with iodine ligands. The calculated splitting of the ^3P term at ca. 1400 cm^{-1} appears to be in satisfactory agreement with the shoulder observed on that band, the formal orbital doublet being associated with the lower energy main peak and the singlet with the shoulder. Comparisons between observed and calculated transition energies in the iodo complex are given in Table IV for the optimized parameter set shown in Table V.

Some small degree of correlation between e_σ(P) and e_π(P) values is evident for good fit, larger e_σ(P) values being associated with numerically smaller, negative e_π(P), corresponding in effect to a cancellation of σ- and π-antibonding effects, of course. The limited range of this correlation is illustrated by the sets e_σ(P) 6000 cm^{-1}, e_π(P) −1500 cm^{-1} and e_σ(P) 5500 cm^{-1}, e_π(P) −2000 cm^{-1}. Variations outside these limits yield significantly worse agreement with experiment.

Best-Fit Angular Overlap Parameters

In Table V are listed the AOM and B parameters which yield essentially unique, close agreement with all spectral bands observed for bromo and iodo complex. In comparing these values among themselves and with those obtained from some other recent studies, we note several features: (i) The large, negative value for e_π(P) in both complexes (which may not be exactly equal as noted in the preceding section) clearly reflect a substantial π-acceptor role for the phosphine ligands in these complexes, at least so far as the metal antibonding d functions are concerned. Similar behavior has already been noted[2] for the bis(phosphine) complexes $M(PPh_3)_2X_2$ (M = Ni(II), Co(II); X = Cl, Br), but in that study the various parameter values could not be established quantitatively. Parameter fits in the present study are virtually unique. Independent checks have been made which establish that no other parameter sets, in particular none with positive or zero $e_\pi(P)$ values, yield satisfactory agreement with the observed spectra. (ii) The Racah B values observed in these complexes suggest three points. First, the much lower value in the iodo ion appears typical of the greater Nephelauxetic effect known[12] for iodide complexes related to bromine or chlorine ones. This may be compared with the spin–orbit coupling parameter and magnetic behavior discussed below. Second, the low value for B even in the bromo complex is presumably partly associated with the extensive π-bond network involving the phosphine ligands. It has been noted before in connection with the $M(PPh_3)_2X_2$ species[2] and with the low-spin, planar complex[3] dimesitylbis(diethylphenylphosphine)cobalt(II) that large, negative $e_\pi(P)$ parameters appear to be associated with low B values. However and third, the reduction of B in the bromo complex is less than[2] in $Ni(PPh_3)_2Br_2$, no doubt reflecting the different number of coordinated phosphine ligands in the complexes. That the B value in the present bromo complex *is* reduced by the presence of the phosphine ligand follows by comparison with the value $B = 670\ \mathrm{cm^{-1}}$ determined in our recent study[13] of the complex ion $[Ni(quinoline)Br_3]^-$. (iii) At the same time that the phosphine ligands in the present complexes appear to act as substantial π acids, the relatively large $e_\sigma(P)$ values reveal considerable σ basicity. The simultaneous large π-donor and π-acceptor properties of these phosphine groups evidenced by the present study thus reflect the usual synergic model for "back-bonding". (iv) The small e_σ value for the iodine ligands presumably reflects the longer Ni–I bond length[10] (2.55 Å) compared with Ni–Br (2.38 Å)[7] as indeed the relative positions of bromine and iodine in the spectrochemical series. Relative to phosphine, the halogens are placed well down the spectrochemical series in that the large $e_\sigma(P)$ is augmented by a large, negative $e_\pi(P)$ value while the small e_σ(halogens) are diminished by positive e_π(halogens) values. (v) The π-bonding AOM parameters for the halogens evidence some slight diminution on replacing bromine by iodine and a considerable, though only qualitatively established, reduction in $e_\pi(Br)$ as we replace the two halogens in $Ni(PPh_3)_2Br_2$ by three in the present system. (iv) The much smaller net donor capacity of the three iodines compared with the three bromines appears to be reflected in the increased σ-donor and/or π-acceptor ligand field strengths of the phosphines. The same conclusion is suggested by the reduction in the Ni–P bond length from 2.32 Å in the bromo complex[7] to 2.28 Å in the iodo one.[10]

Magnetism and Spin–Orbit Coupling

The parameter set for the bromo complex given in Table V was used to fit the single-crystal paramagnetism throughout the temperature range 20–300 K by variation of the spin–orbit coupling coefficient ζ and Stevens' orbital reduction factor k in the magnetic moment operator $\mu_\alpha = \beta(kL_\alpha + 2S_\alpha)$ ($\alpha = x, y, z$). Reproduction of the experimental data is excellent, as shown in Figure 2, and uniquely defined by the value $\zeta = 195 \pm 10\ \mathrm{cm^{-1}}$ and $k = 0.50 \pm 0.04$. This very low ζ value—compared with the free-ion value $\zeta_0 = 630\ \mathrm{cm^{-1}}$—focuses attention on what appears to be a common feature of tetrahedrally coordinated nickel(II) complexes as shown by the data collected in Table VI. Where known, the ζ/ζ_0 ratios for the corresponding cobalt(II) complexes appear normal. We consider two possible contributions to the anomalously low ζ values in the tetrahedral nickel(II) complexes.

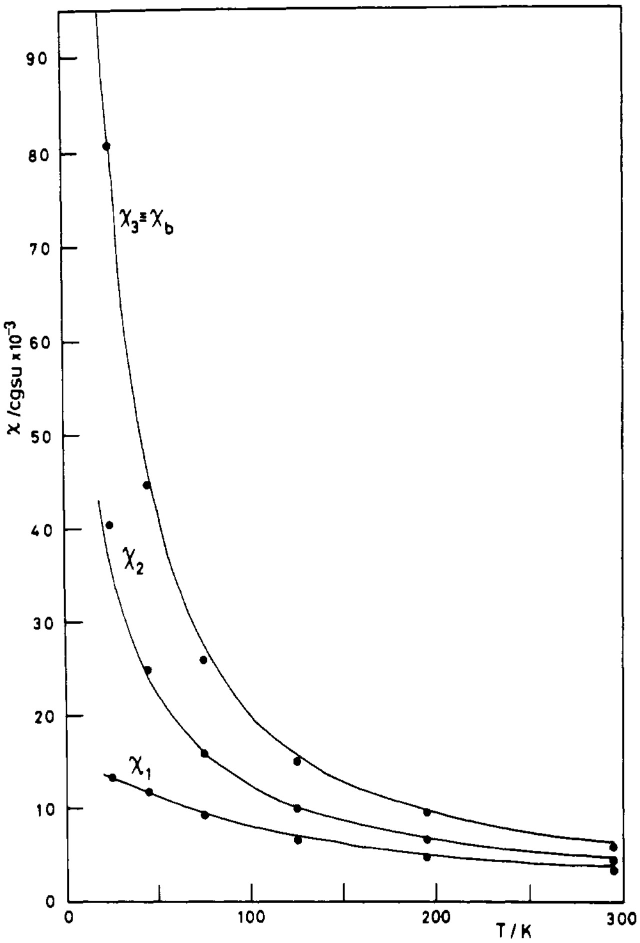

Figure 2. Comparison between observed and calculated (circles) principal crystal susceptibilities for parameter set in Table V with $\zeta = 195\ \mathrm{cm^{-1}}$ and $k = 0.5$ for $[Ph_4As]^+[Ni(PPh)Br_3]^-$.

Table VI. Spin-Orbit Coupling Coefficients ($\mathrm{cm^{-1}}$) for Tetrahedrally Coordinated Nickel(II) and Cobalt(II) Complexes[a]

	nickel system			cobalt system		
complex	ζ	ζ/ζ_0	ref	ζ	ζ/ζ_0	ref
$[M(PPh_3)Br_3]^-$	195	0.31	*d*			
$M(PPh_3)_2Cl_2$	350	0.56	2	500	0.97	2
$M(PPh_3)_2Br_2$	300	0.48	2	500	0.97	2
$[M(quinoline)Br_3]^-$	250	0.40	13	450	0.87	13
$ML_N^+Cl_3$[b]	130	0.21	15	500	0.97	15
$ML_N^+Br_3$[b]	120	0.19	15	500	0.97	15
$M(sal)_2$[c]	350	0.56	8			
MCl_4^{2-}	380	0.60	18	450	0.87	17
MBr_4^{2-}	260	0.41	16	470	0.91	17
MI_4^{2-}	15	0.02	4			

[a] $\zeta_0[Ni(II)] = 630\ \mathrm{cm^{-1}}$; $\zeta_0[Co(II)] = 515\ \mathrm{cm^{-1}}$. [b] L_N^+ = tertiary amine, *N*-ethyl-1,4-diazabicyclo[2.2.2]octonium. [c] sal = *N*-isopropylsalicyaldiminate. [d] This work.

The first concerns the effective orbital degeneracy of the ground terms in these complexes. The splitting patterns of the $^3T_1$ ground terms in several "tetrahedral" nickel complexes are compared in Figure 3. The first three complexes have coordination geometries with near threefold symmetry as indicated, not only by the reported crystal structure analyses[7,10,14]

---

(12) C. K. Jørgensen, "Modern Aspects of Ligand Field Theory", North-Holland, Amsterdam, 1971.
(13) M. Gerloch and L. R. Hanton, *Inorg. Chem.*, **19**, 1692 (1980).
(14) M. R. Manning and P. R. Raithby, in preparation.
(15) M. Gerloch and M. R. Manning, *Inorg. Chem.*, **20**, 1051 (1981).
(16) B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 1411 (1966).

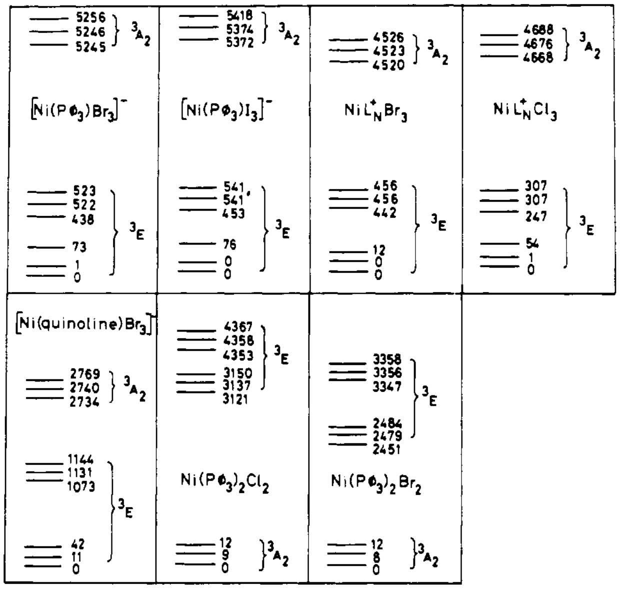

Figure 3. Splitting diagrams for $^3T_1(T_d)$ ground terms for various "tetrahedral" nickel(II) chromophores (L_N^+ = tertiary amine, *N*-ethyl-1,4-diazabicyclo[2.2.2]octonium).

but also by the nearly perfect, orbital doublet nature of the ground terms. These complexes also appear generally to possess the smaller spin-orbit coupling coefficients, although there is no clear discontinuity in ζ values as we pass to the somewhat more distorted quinoline complex or to the tetragonally distorted tetrahedra. However, one explanation of the low ζ values would be that these systems are subject to the Ham effect[5] which refers to the attenuation of orbital angular momentum phenomena within a dynamic Jahn-Teller regime.

A second cause of the low ζ values would derive from the suggestions of Collingwood et al.,[4] who showed that the sign of the coefficient of the ligand orbitals within the molecular oribtals of the formal T_1 ground state of $[NiI_4]^{2-}$ is such as to cause a contribution of spin-orbit coupling at the iodine centers to be *opposed* to that at the central metal. The data collected in Table VI are insufficiently diagnostic to establish the relative contributions of the two mechanisms proposed for the reduction in ζ. There is some evidence for the contribution from the ligand in that ζ values tend to decrease as chlorine is replaced by bromine and by iodine. Certainly, the spin-orbit coefficient established[4] in $[NiI_4]^{2-}$ is extremely low. Unfortunately, it is not possible to establish a ζ value for the present $[Ni(PPh_3)I_3]^-$ complex from the powder susceptibility data in Table II. Only anisotropy measurements provided the criterion for fixing ζ in the bromo complex. However, the similarity of μ_{eff} values for the present bromo and iodo complexes indicate that similar k values in the two systems require similar ζ values for satisfactory reproduction of the experimental data.

Table VII. Orientation of Molecular Susceptibility Tensors at 75 K for $[Ni(PPh_3)X_3]^-$ Ions, Calculated with Parameter Sets of Table V and $\zeta = 195$ cm^{-1}, $k = 0.50$ (X = Br) and $\zeta = 190$ cm^{-1}, $k = 0.5$ (X = 1)(Susceptibilities in cgsu × 10^3)[a]

	bromo complex				iodo complex		
	X	*Y*	*Z*		*X*	*Y*	*Z*
$K_1 = 917$	169.7	79.7	89.9	$K_1 = 935$	125.0	145.1	89.7
$K_2 = 934$	100.4	169.7	89.7	$K_2 = 938$	145.1	55.1	88.8
$K_3 = 3283$	90.3	90.3	179.7	$K_3 = 3270$	91.2	89.6	178.8
	a	*b*	*c'*		*a*	*b*	*c'*
X	−0.7219	0.4282	0.5436	*X*	−0.5565	−0.6864	0.4681
Y	0.4379	−0.3256	0.8380	*Y*	0.4915	−0.7262	−0.4807
Z	0.5358	0.8430	0.0475	*Z*	0.6699	−0.0374	0.7415

[a] Reference frames defined with *Z* parallel to Ni-P and with respect to orthogonalized crystallographic frames as in the bottom section of the table (direction cosines).

Molecular Susceptibility Tensors

Corresponding to the best parameter set in Table V and the ζ and k values in the preceding section, the calculated orientation of the principal molecular susceptibilities of the bromo complex are given in Table VII. Also shown is the corresponding tensor orientation for the iodo complex, calculated with $\zeta = 190$ and $k = 0.5$. The monoclinic ϕ angle calculated for the bromo complex is −84° which compares favorably with the approximate value of −77° given in the experimental section. The calculated ϕ value and orientations of molecular susceptibility tensors change throughout the temperature range 20-300 K by less than 1°.

Acknowledgment. We thank the Royal Society, London, for the award of a Rutherford Scholarship and the New Zealand University Grants Committee for financial support (both to L.R.H.).

Registry No. $[Ph_4As]^+[Ni(PPh_3)I_3]^-$, 18324-08-8; $[Ph_4As]^+[Ni(PPh_3)Br_3]^-$, 75474-42-9.

---

(17) M. Gerloch, J. Lewis, and R. Rickards, *J. Chem. Soc., Dalton Trans.*, 980 (1972).

(18) M. Gerloch and R. C. Slade, *J. Chem. Soc. A*, 1022 (1969).