Principal Crystal and Molecular Paramagnetic Susceptibilities of Bis-(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)nickel(II) †

By **Denis A. Cruse** and **Malcolm Gerloch,*** University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

The principal crystal susceptibilities of the five-co-ordinate title complex have been measured in the range 20—300 K by the Faraday technique. Complete sets of values for χ_1, χ_2, and χ_b, the principal susceptibilities of the monoclinic crystals, have been obtained, together with representative values of the susceptibility parallel to *a'*, the normal of *b* and *c*, from which the value of ϕ, the angle subtended by χ_1 and *a*, was determined. The crystal susceptibilities have been fitted by calculations within a complete d^8 basis, using the angular-overlap model (a.o.m.) to represent the ligand field. Values for the a.o.m. parameters as well as those for spin–orbit coupling and orbital-reduction factors are critically compared with those recently obtained for the closely similar four-co-ordinate complex, bis-(*N*-isopropylsalicylideneiminato)nickel(II). It is suggested that the present study furnishes some evidence that current techniques in magnetochemistry may reveal mesomeric effects separate from inductive ones. The orientation of the molecular magnetic ellipsoid with respect to the square-pyramidal type molecular geometry is calculated and discussed.

WE have recently described [1] the paramagnetic susceptibilities of a nominally tetrahedrally co-ordinated Schiff base complex of nickel(II) and their interpretation within the angular-overlap model (a.o.m.) of Jørgensen and Schäffer as adapted by Gerloch and McMeeking.[2] The main attraction of the theoretical approach is the parameterization of the ligand field with respect to individual metal–ligand σ and π interactions rather than the simple symmetry-based expansion coefficients referring to the molecule as a whole. Further, no approximations were made with respect to the actual very low symmetry in that molecule. At this stage of development we are concerned to explore bonding characteristics in different molecules as revealed by their magnetic properties but at the same time to test the efficacy of the model itself. Both aims are served by investigations of molecules bearing chemical or structural similarities. We report here the measurement and interpretation of the magnetic properties of a five-co-ordinate nickel(II) complex with closely similar ligands to those in the tetrahedral complex above.

Bis(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)nickel(II) is a high-spin five-co-ordinate molecule with the structure [3] shown in Figure 1. The relations with the structure [4] of bis(*N*-isopropylsalicylideneiminato)nickel(II) are that, in the present molecule, the salicylaldehyde is chloro-substituted in the *para* position and that the co-ordinationally neutral *N*-isopropyl substituents of the imine nitrogen atoms are replaced by tertiary amines. As shown by Orioli *et al.*,[3] one, but only one, of these tertiary amines co-ordinates with the nickel atom and establishes the five-co-ordinate species in Figure 1. The Ni–N(imine) bond lengths are essentially equal, averaging 1.98 Å; similarly the Ni–O bonds average 1.94 Å. The Ni–N(amine) bond is much longer at 2.20 Å. From the point of view of our ligand-field model, therefore, the present five-co-ordinate molecule may be regarded approximately as the previous four-co-ordinate one with an additional amine group as a fifth ligand, once allowance for chelate orientations is made.

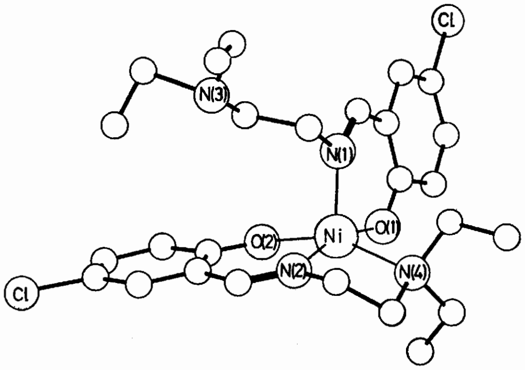

FIGURE 1 Molecular structure of bis(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)nickel(II)

The co-ordination shell of the nickel approximates that of a square-based pyramid but it is interesting to note that the presumably more weakly bound amine group occupies a basal rather than an axial site: the reasons for this are unexceptional, as discussed by Orioli *et al.*[3] The nickel atom is reported to lie 0.36 Å above the best plane of N(2),N(4),O(1),O(2). In addition to our interest in those bonding features in this molecule which may be inferred from the magnetic properties, we enquire also into the orientation of the principal magnetic susceptibilities with respect to this nominal C_{4v} geometry.

EXPERIMENTAL AND RESULTS

Bis(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)-nickel(II) was prepared by the literature method [5] and recrystallized from chloroform solution. Satisfactory C, N, and H analyses were obtained. Susceptibility measurements were made on dark green block-like crystals weighing 5—6 mg, oriented by standard, *X*-ray oscillation, and Weissenberg techniques.

Principal susceptibilities were measured by the Faraday technique in the range 20—300 K using the apparatus and

---

† No reprints available.

[1] D. A. Cruse and M. Gerloch, *J.C.S. Dalton*, 1977, 152.

[2] M. Gerloch and R. F. McMeeking, *J.C.S. Dalton*, 1975, 2443.

[3] P. L. Orioli, M. Di Vaira, and L. Sacconi, *J. Amer. Chem. Soc.*, 1966, **88**, 4383.

[4] M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *Acta Cryst.*, 1964, **17**, 1157.

[5] L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, 1965, **4**, 943.

procedures described recently.[1] The crystals are monoclinic[3] so that complete data were obtained from two different crystal mountings. (*a*) With crystal axis *b* vertical, direct measurements of χ_1 and χ_2, as defined previously,[6] were obtained by rotation of the magnet. Although no direct measurement of ϕ, the angle subtended by *a* and χ_1, was attempted, it was noted that this angle does not change within experimental error (±3°) throughout the temperature range. (*b*) With crystal axis *c* vertical, direct measurements of $\chi_b = \chi_3$ throughout the full temperature range were made, together with several measurements of $\chi_{a'}$, the susceptibility perpendicular to *b* and *c*. The results are collected in Table 1 in interpolated form to permit comparison between axes and with other work. Using relation (1) we calculated the value of ϕ at

TABLE 1

Interpolated experimental principal and average crystal susceptibilities (c.g.s. units × 10^{-6}) and average moments of bis(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)nickel(II). (Susceptibilities are corrected for diamagnetism, $\chi_d = 3.68 \times 10^{-4}$ c.g.s. units)

T/K	χ_1	χ_2	χ_3	$\bar{\chi}$	$\bar{\mu}$/B.M.*
295	4 100	4 950	3 920	4 320	3.19
285	4 230	5 110	4 040	4 460	3.19
275	4 370	5 280	4 170	4 610	3.18
265	4 510	5 470	4 320	4 760	3.18
255	4 670	5 670	4 470	4 940	3.17
245	4 850	5 900	4 640	5 130	3.17
235	5 050	6 140	4 820	5 340	3.17
225	5 260	6 410	5 020	5 570	3.16
215	5 490	6 690	5 240	5 810	3.16
205	5 740	7 010	5 490	6 080	3.16
195	6 040	7 370	5 770	6 390	3.16
185	6 360	7 760	6 060	6 730	3.15
175	6 670	8 180	6 370	7 080	3.15
165	7 030	8 650	6 710	7 470	3.14
155	7 460	9 180	7 090	7 910	3.13
145	7 940	9 790	7 530	8 420	3.12
135	8 470	10 520	8 030	9 010	3.12
125	9 080	11 370	8 610	9 690	3.11
115	9 840	12 390	9 280	10 500	3.11
105	10 730	13 570	10 040	11 450	3.10
95	11 840	15 130	11 050	12 670	3.10
85	13 180	17 060	12 290	14 180	3.10
75	14 850	19 560	13 820	16 080	3.10
65	16 900	22 720	15 660	18 430	3.09
55	19 770	27 250	18 100	21 710	3.09
45	23 440	33 110	21 150	25 900	3.05
35	29 070	44 350	25 570	33 000	3.04
25	37 920	64 040	31 770	44 580	2.99
20	43 460	79 180	35 390	52 670	2.90

* 1 B.M. ≈ 9.27×10^{-24} A m^2.

$$\sin^2(\beta - 90 - \phi) = (\chi_{a'} - \chi_1)/(\chi_2 - \chi_1) \qquad (1)$$

several temperatures throughout the temperature range. The calculated value $\phi \sim 25°$ varies by less than 3° in this range, which variation is within the experimental error (*ca.* ±3—5°) for the ϕ angle determined in this way, depending as it does on a ratio of differences.

DISCUSSION

Definitions of Parameters.—Calculations, using the model described elsewhere,[2] were performed within the complete d^8 45-fold basis using $|J,M_J\rangle$ quantization. The Racah parameters *B* and *C* for interelectron repulsion, ζ for spin–orbit coupling, and *k* as an orbital-reduction factor are included as in earlier studies.[1] The ligand field, parameterized within the framework of the angular-overlap model (a.o.m.), is described as follows. We presume the two Schiff base salicylideneiminato-ligands to be equivalent except, of course, for their orientations. This approximation is based on the essential equality of the co-ordinate bond lengths as described in the introduction. The parameterization scheme for these ligands follows the conventions described[1] for the 'tetrahedral' *N*-isopropyl molecule. Thus, σ bonding is represented by e_σ(O) and e_σ(N) and π bonding for the oxygen atoms in the plane of the aromatic ring by $e_{\pi y}$(O) and normal to the appropriate plane by $e_{\pi x}$(O); $e_{\pi y}$(N) refers to π bonding in the plane Ni–N=C, and $e_{\pi x}$(N) that normal to this plane. Most calculations assume $e_{\pi y}(\mathrm{N}) = 0$, on the assumption of an essentially sp^2 hybridized state for the imine nitrogen atom, as has been demonstrated[1] for the tetrahedral molecule, but this was checked later. The tertiary amine group is presumed not to π bond and its influence is simply represented by $e_\sigma(\mathrm{N_T})$.

Fitting Observed Susceptibilities.—Susceptibilities are fairly insensitive to interelectron repulsion parameters so values for *B* and *C* were initially set at 850 cm^{-1} and 4.5 *B* respectively, by reference to the spectral interpretation of a five-co-ordinate arsine oxide complex.[7] The free-ion spin–orbit coupling parameter value is 630 cm^{-1} and the value found for the *N*-isopropyl tetrahedral system was 375 cm^{-1}. Here we have considered ζ values in the range 350—650 cm^{-1}. Orbital-reduction factors were allowed to range from 0.4 to 1.0. The e_σ values for O and N atoms of the Schiff bases in the tetrahedral molecule were found to be *ca.* 4 000 cm^{-1}: here we have considered the range 3 000—5 000 cm^{-1} independently for both. The long Ni–N$_\mathrm{T}$ bond length (2.20 Å) suggests smaller e_σ values for amine bonding and the range 1 900—3 400 cm^{-1} has been studied. It is more difficult to fix π-bonding parameters and, after preliminary calculations and by comparison with values obtained for the tetrahedral system, we have considered $e_{\pi x}$(O) and $e_{\pi y}$(O) in the range 500—1 700 cm^{-1}, $e_{\pi x}$(N) as 300—1 300 cm^{-1}, with $e_{\pi y}$(N) initially held at zero (but see later).

Within these limits, our usual trial-and-error mapping procedure revealed a single, but broad, region in poly-parameter space within which better than 5% agreement between observed and calculated susceptibilities is possible. Further, within this region the calculated ϕ value is 14 ± 3° as compared with the observed value of 25 ± 5°: outside this region the agreement with the observed ϕ value is poor. The fitted region is summarized in Table 2.

Comparisons, Spectrum, and Conclusions.—We now seek to sharpen the fitting region of Table 2 by recourse to theory, comparison with the tetrahedral molecule, and consideration of the electronic spectrum. We begin with some general theoretical observations.

A major attraction of the a.o.m. is the way that the

---

[6] M. Gerloch and P. N. Quested, *J. Chem. Soc.* (*A*), 1971, 2308.

[7] M. Gerloch, J. Kohl, J. Lewis, and W. Urland, *J. Chem. Soc.* (*A*), 1970, 3269.

parameters are chosen to refer to individual ligands and bonding modes rather than to the complex as a whole: indeed the efficacy of the model rests on just this. In systems involving the weak covalency of transition-metal complexes this approach blends well with familiar ideas of localized valence-bond types of chemical interaction. However, in common with all ligand-field models, whatever the superposition properties of the approach, the totality being constructed is an effective potential acting on the central metal. In some measure at least, a view of the complex *as a whole* is inescapable. The consequences of holohedrized symmetry, discussed by Schäffer and Jørgensen,[8,9] make a particularly clear example of this. We are using a pure centrosymmetric basis of *d* orbitals (although the argument extends to any *pure l* bases) so that no mathematical distinction results between the cases of M–L and L′–M–L′ in which L′, having a.o.m. parameters exactly one half of those for L, are placed on opposite sides of the metal atom. Indeed, if we have two ligands on exactly opposite sides of the central metal, regardless of whether they lie at equal distances from the metal atom, then the model can only recognize the *sum* of their a.o.m. parameters. While this is always true for σ bonding, it is also true for π bonding if the orientation of the π bonds on these opposite sides are parallel.

TABLE 2

Parameter ranges within which observed susceptibilities of bis(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)nickel(II) may be fitted to within 5%

Parameter	Maximum range (cm^{-1})	Comment
B	850	Fixed, insensitive
C	$4B$	Fixed, insensitive
ζ	475—525	Very sensitive
e_σ(O)	4 000—4 800	
e_σ(N)	3 000—3 600	A slight degree of positive correlation
e_σ(N_T)	2 100—2 900	
$e_{\pi y}$(N)	0	Fixed (to be confirmed)
$e_{\pi x}$(N)	600—1 100	Some positive correlation
$e_{\pi x}$(O)	1 200—1 700	
$e_{\pi y}$(O)	500—900	
k	0.55—0.65	Sensitive

With this in mind, referring to the present co-ordination geometry of Figure 1, we note that, to the extent that ligands in the ' basal plane ' of the five-co-ordinate molecule are opposite one another, we might expect some lack of factoring of some of the parameter values. The situation is complex, however. One O donor atom lies roughly opposite the imine N from the other Schiff base, while the second O atom lies ' opposite ' the tertiary amine. There are similar difficulties with respect to the π bonding. All this demonstrates two important points in the use of the a.o.m. First, some degree of correlation between the various fitting-parameter values is to be expected; *i.e.* a fitting region in polyparameter space might well be broad and non-spherical (non-hyperspherical ?). But secondly, the low symmetry of molecules like the present one and the axiomatic linking of parameters referring to similar chemical species (*i.e.* the Schiff bases are presumed equivalent) both serve to place an increasing number of conditions on the parameter values. These will, in general, sharpen the fitting region, increase the factorizability of parameters, and thus generally increase the efficiency of the a.o.m.

We may attempt to limit the fitting region further by comparison with our results[1] from the tetrahedral *N*-isopropyl system. The values $e_\sigma(N) = 3\,600$, $e_\sigma(O) = 4\,200$, and $B = 850$ cm^{-1}, appropriate for the tetrahedral molecule, fall within the initial fitting region of Table 2. Additionally we fix $e_\sigma(N_T)$ as 2 100 and $\zeta = 500$ cm^{-1} and concentrate attention on the π-bonding parameters. Fits were investigated for $e_{\pi x}$(N) in the range 700—1 000 cm^{-1}, $e_{\pi x}$(O) 1 100—1 700 cm^{-1}, and $e_{\pi y}$(O) 600—1 200 cm^{-1}, all in steps of 100 cm^{-1}. Throughout each of these ranges agreement with experiment was satisfactory ($\pm 5\%$), but, as indicated by the correlations in Table 2, all the fits were not equally good. The best agreement with the observed susceptibilities occurs for the π-bonding parameters in Table **3**.

TABLE 3

Best-fit π-bonding parameters (cm^{-1})

	This molecule	' Tetrahedral ' *N*-isopropyl system
$e_{\pi x}$(N)	900	930
$e_{\pi y}$(N)	0	0
$e_{\pi x}$(O)	1 300	660
$e_{\pi y}$(O)	900	1 000

The essentially zero value for $e_{\pi y}$(N), supporting a description of the imine N as sp^2 hybridized, was confirmed by monitoring fits with this parameter allowed to vary: a similar result was found for the *N*-isopropyl molecule. From Table **3** we observe good agreement between the four- and five-co-ordinate molecules (although *exact* agreement would not be expected for molecules with different co-ordination numbers), except that the $e_{\pi x}$(O) parameter, referring to π donation from the oxygen atom in a direction perpendicular to the salicylaldehyde plane, is much larger in the five-co-ordinate molecule. While we cannot attach too high a reliability to the values in Table 3, following our remarks about the spread of fitting values, we do observe a clear indication of greater π donation from the phenolic oxygen in the five- than in the four-co-ordinate molecule. Although the parameter values given in Table 3 represent agreement with experiment to better than 2% in magnetic susceptibilities the values are not unique. The breadth of the fitting region in Table 2 is some indication of this, although that region corresponds to a 5% fit with experiment. Refining the fits in the manner just described, but with e_σ values for O and N differing by 300 cm^{-1} from the ' tetrahedral ' values, for example, produces results similar to those in Table **3**, differing by ± 150 cm^{-1} at most. The most important point, which the present analysis has demonstrated only semi-quantitatively, is that $e_{\pi x}$(O) is greater in the present

---

[8] C. E. Schäffer and C. K. Jørgensen, *Met. Fys. Medd. Dan. Vid. Selsk.*, 1965, **34**, 3.

[9] C. E. Schäffer, *Structure and Bonding*, 1968, **5**, 68.

five-co-ordinate system than in the 'tetrahedral' molecule and that the relative magnitudes of $e_{\pi x}(\mathrm{O})$ and $e_{\pi y}(\mathrm{O})$ are reversed in the two systems. This can be seen to be true from the totally unprejudiced results in Table 2: the parameter values in Table 3 represent 'best values' obtained after the assumption that other common factors of the two molecules can be represented by common parameter values. We are currently engaged on studies of related molecules in order to confirm this conclusion and remove doubts that it may reflect the uptake of experimental and/or model errors. Meanwhile, the magnitude of the present effect does warrant an interpretation.

An explanation is not difficult to find, at least at a qualitative level: namely, we are observing the greater mesomeric effect of the chlorine *para*-substituent of the phenol moiety with respect to hydrogen. While chlorine is generally regarded as inductively electron attracting (σ), it is equally common to regard it as mesomerically electron donating (π). The release of electron density into the ring may then increase the π-donor function of the phenolic oxygen atom, this being reflected in the greater $e_{\pi x}(\mathrm{O})$ value. Alternatively, we may take the view that the energies of the filled ligand π orbitals have been more closely matched with those of the metal by the chlorine substitution, so increasing the magnitude of the M–L π interaction. There is, at least, a potentially useful avenue here for further work.

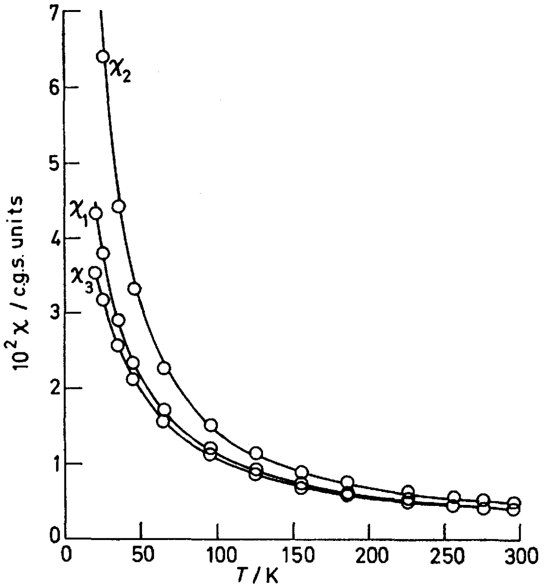

FIGURE 2 Comparison between observed (circles) and calculated principal crystal susceptibilities of bis(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)nickel(II) for the parameter set: $B = 800$, $C = 4B$, $\zeta = 500$, $e_\sigma(\mathrm{O}) = 4\,200$, $e_\sigma(\mathrm{N}) = 3\,600$, $e_\sigma(\mathrm{N})_\mathrm{T} = 2\,100$, $e_{\pi x}(\mathrm{N}) = 900$, $e_{\pi y}(\mathrm{N}) = 0$, $e_{\pi x}(\mathrm{O}) = 1\,300$, $e_{\pi y}(\mathrm{O}) = 900$ cm^{-1}, and $k = 0.60$

Attempts to establish the parameter values more exactly by recourse to the electronic spectrum have not been successful. The reflectance spectrum is reported [5] to have bands at *ca.* 7 700, 9 800, 12 800, and 16 200 cm^{-1}. The lowest two bands can be fitted by components of the ^3F term for all the parameter values in Table 2. The third band cannot be fitted as a spin triplet. As a spin singlet (it is the weakest of all the reported bands, although not obviously a spin singlet on intensity criteria), it lies at an energy typical of spin-forbidden transitions in nickel(II) complexes, and can be fitted with ease, but with little significance for the present work, by variation of the Racah C parameter. The fourth band can be fitted to components of the ^3P term with some adjustment of the B value in Table 2, which has little effect on the calculated magnetic properties. Altogether, therefore, the spectrum is compatible with the magnetic work but does not serve to improve the earlier parameter estimates.

Using the parameter values in, and used to set up, Table 3 we have plotted the comparison between observed and calculated crystal susceptibilities in Figure 2. The corresponding calculated *molecular* susceptibilities are listed in Table 4. The orientation of the principal molecular susceptibilities varies by less than 2° throughout the whole fitting region and over the experimental temperature range. With respect to the orthogonal crystal axes *a*, *b*, and *c'* the orientations (°) are:

	a	*b*	*c'*
K_1	61	30	86
K_2	146	61	106
K_3	106	86	17

TABLE 4

Calculated principal molecular susceptibilities (c.g.s. units × 10^{-6}) of bis(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)nickel(II) using the parameter set listed in Figure 2

T/K	K_1	K_2	K_3	T/K	K_1	K_2	K_3
295	3 840	4 140	4 740	145	7 470	8 200	9 760
285	3 960	4 280	4 910	135	7 970	8 790	10 510
275	4 100	4 430	5 090	125	8 500	9 460	11 400
265	4 240	4 590	5 280	115	9 230	10 250	12 440
255	4 400	4 760	5 490	105	10 020	11 180	13 700
245	4 570	4 950	5 710	95	10 900	12 300	15 250
235	4 750	5 150	5 950	85	12 090	13 680	17 190
225	4 950	5 370	6 220	75	13 480	15 400	19 680
215	5 170	5 610	6 510	65	15 210	17 610	23 020
205	5 410	5 870	6 840	55	17 420	20 560	27 690
195	5 670	6 160	7 190	45	20 330	24 670	34 650
185	5 950	6 485	7 590	35	24 210	30 750	46 010
175	6 270	6 840	8 040	25	29 210	40 520	67 270
165	6 620	7 240	8 540	20	31 740	47 850	86 170
155	7 020	7 690	9 110				

TABLE 5

Angles (°) subtended by principal molecular susceptibilities (calculated) with respect to various molecular directions of bis(5-chloro-*N*-β-diethylaminoethylsalicylideneiminato)nickel(II)

Direction	K_1	K_2	K_3
Vector Ni–N(1)	19	73	77
Ni–N(2)	67	67	31
Ni–N(4)	89	41	52
Ni–O(1)	80	66	40
Ni–O(2)	64	23	60
Bisector N(2)–Ni–N(4)	76	76	12
N(4)–Ni–O(1)	83	35	84
O(1)–Ni–O(2)	78	68	23
O(2)–Ni–N(2)	54	22	75

These directions bear no obvious relation to the molecular geometry. The nearest approach to ' unique directions ' are K_1 lying 19° from Ni–N(1) and K_3 lying 12° from the bisector of N(2)–Ni–N(4). Table 5 lists a number of angles subtended by the principal directions of the susceptibility ellipsoid.

This result need occasion no surprise in view of the low molecular symmetry but does serve to emphasize again[10] the intractability of problems such as this molecule within earlier models in which true molecular geometry had to be replaced by higher-symmetry approximations. A description here of the molecular magnetic properties in terms of a C_{4v} square-based pyramid is clearly wrong in any approximation.

We thank the S.R.C. for support for the Faraday balance and for the award of a research studentship (to D. A. C.).

[6/1996 *Received, 27th October*, 1976]

---

[10] M. Gerloch, R. F. McMeeking, and A. M. White, *J.C.S. Dalton*, 1975, 2452.