plex; (b) rotations of the NO_2 group, creating an opportunity for the formation of a Co–ONO bond. Of course, in the solid state only the second way practically competes with the primary recombination.[33]

Acknowledgment.—The authors are indebted to Professor V. Carassiti for his interest in this work and for his helpful criticism.

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(33) As far as the cage effect is concerned, our mechanism is similar to the general mechanism proposed in order to interpret the photochemistry of coordination compounds: A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958). For a critical discussion of Adamson and Sporer's mechanism, see ref 1.

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New Stilbenediamine Complexes of Nickel(II)

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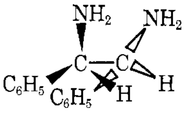
The preparation and electronic spectra are reported of the paramagnetic compounds [Ni(*ms*-1,2-diphenylethylenediamine)$_2$-L_2]$(ClO_4)_2$ (L = pyridine or β-picoline) and [Ni(*rac*-1,2-diphenylethylenediamine)$_2$(DMSO)$_2$]$(ClO_4)_2$·2DMSO, and of the diamagnetic complexes Ni(*ms*- or *rac*-1,2-diphenylethylenediamine)$_2(ClO_4)_2L_2$ [L = $(C_6H_5)_3PO$ or $(C_6H_5)_3AsO$], Ni(*ms*-1,2-diphenylethylenediamine)$_2(ClO_4)_2$(DMSO)$_4$, and Ni(*ms*-1,2-diphenylethylenediamine)$_2(ClO_4)_2$(α-picoline)$_2$. It is suggested that in the diamagnetic compounds the nickel ions may be six-coordinate. The preparation of [Ni(*ms*-1,2-diphenylethylenediamine)$_3$]$(ClO_4)_2$ is also reported. The *Dq* values of *ms*- and *rac*-1,2-diphenylethylenediamine in the tris-chelate cations are very similar ($\sim$11,000 cm^{-1}) although Ni(*ms*-1,2-diphenylethylenediamine)$_3^{2+}$ is formed much less readily than its analog with the racemic base. The band in the region 22,000–23,500 cm^{-1} for the diamagnetic complexes is probably due to the transition $d_{xy} \rightarrow d_{x^2-y^2}$.

Introduction

The relationship among the magnetic properties, colors, and structures of nickel(II) complexes with 1,2-diphenylethylenediamine[1] and related ligands has



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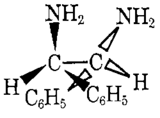

II

occasioned interest ever since they were first described by Lifschitz and his coworkers.[2-4] Although the main features of the unusual behavior of these compounds are now fairly well understood,[5] certain aspects merit further study. For example, whereas the "blue," fully paramagnetic complexes Ni(diamine)$_2X_2$ or their hydrates have distorted octahedral configurations with the anions or water molecules in axial positions,[6] the coordination numbers of the nickel(II) ions in the "yellow," diamagnetic complexes are less firmly established. The diamagnetism of a complex NiL_4X_2 does not necessarily differentiate between planar $[NiL_4]X_2$ and six-coordinate, tetragonal NiL_4X_2. In [Ni(*ms*-stien)$_2(CHCl_2CO_2)_2]_3\cdot 2C_2H_5OH\cdot 4H_2O$ one-third of the nickel(II) ions are present as planar, diamagnetic Ni(*ms*-stien)$_2^{2+}$ species,[6] but diamagnetic $Ni\{C_6H_4[As(CH_3)_2]_2\}_2I_2$ is pseudo-octahedral.[7] With anions as the potential axial ligands it is often difficult without an X-ray study to determine whether they are, in fact, coordinated.

Also there is, as yet, insufficient information concerning the extent to which steric and electronic factors contribute to produce either a spin-singlet or a spin-triplet ground state.

We have prepared some complexes of the type Ni(stien)$_2L_2(ClO_4)_2$ (where L is a monodentate, neutral ligand) with both *ms*- and *rac*-stien, to examine the effect on the magnetic properties of varying the steric requirements and donor strength of L. We report here the results of this work and also the preparation of Ni(*ms*-stien)$_3(ClO_4)_2$.

Experimental Section

Preparation of Compounds. Ni(*ms*-stien)$_3(ClO_4)_2$.—A concentrated ethanolic solution of $Ni(ClO_4)_2\cdot 6H_2O$ (0.73 g) was added dropwise to a mechanically stirred solution of *ms*-stien (2.54 g) in ethanol (20 ml). The resulting solution was immediately filtered, and after 2 hr the fine violet precipitate was filtered off and dried *in vacuo* (50% yield). *Anal.* Calcd for $C_{42}H_{48}Cl_2N_6NiO_8$: C, 56.39; H, 5.41; N, 9.40; Ni, 6.56. Found: C, 55.93; H, 5.51; N, 9.14; Ni, 6.58.

Ni(*rac*-stien)$_3(ClO_4)_2$.—This violet compound was obtained in 80% yield as for the *ms*-stien analog. The *rac*-stien complex precipitated immediately and was filtered off and dried to constant weight at 115°. *Anal.* Calcd for $C_{42}H_{48}Cl_2N_6NiO_8$: Cl, 7.93; N, 9.40; Ni, 6.56. Found: Cl, 7.71; N, 9.77; Ni, 6.59.

Ni(*ms*-stien)$_2[(C_6H_5)_3PO]_2(ClO_4)_2$.—A mixture of triphenylphosphine oxide (1.39 g) and finely powdered Ni(*ms*-stien)$_2(ClO_4)_2$[2] (1.36 g) in 1-butanol (150 ml) was boiled for 30 min and then filtered. On standing overnight, the deep yellow solution deposited bright yellow crystals (27% yield). *Anal.* Calcd for

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[1] Commonly called stilbenediamine (abbreviated here as stien) which can be obtained as *meso* and racemic forms (I and II, respectively).

[2] I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. Anorg. Allgem. Chem.*, **242**, 97 (1939).

[3] I. Lifschitz and J. G. Bos, *Rec. Trav. Chim.*, **59**, 407 (1940).

[4] I. Lifschitz and K. M. Dijkema, *ibid.*, **60**, 581 (1941).

[5] J. R. Miller, *Advan. Inorg. Chem. Radiochem.*, **4**, 172 (1962).

[6] S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3**, 468 (1964).

[7] N. C. Stephenson, *Acta Cryst.*, **17**, 592 (1964).

$C_{64}H_{62}Cl_2N_4NiO_{10}P_2$: C, 62.05; H, 5.04; N, 4.52. Found: C, 61.72; H, 5.00; N, 4.48.

Ni(stien)$_2$[(C$_6$H$_5$)$_3$AsO]$_2$(ClO$_4$)$_2$.—These yellow compounds were prepared in a manner similar to that described for the previous complex, but with ethanol as solvent. For the *ms*-stien complex there was 35% yield. *Anal.* Calcd for $C_{64}H_{62}As_2Cl_2N_4NiO_{10}$: C, 57.94; H, 4.71; N, 4.22; Ni, 4.42. Found: C, 58.16; H, 4.81; N, 4.30. For the *rac*-stien complex there was 90% yield. Found: C, 57.82; H, 4.77; N, 4.40; Ni, 4.42.

Ni(*rac*-stien)$_2$[(C$_6$H$_5$)$_3$PO]$_2$(ClO$_4$)$_2$.—Ni(*rac*-stien)$_2$(ClO$_4$)$_2$[8] (0.34 g) was boiled in ethyl acetate (20 ml) with triphenylphosphine oxide (0.7 g) for 5 min to give an orange precipitate of the desired complex in virtually quantitative yield. *Anal.* Found: C, 61.60; H, 4.96; N, 4.38.

Ni(*ms*-stien)$_2$(py)$_2$(ClO$_4$)$_2$.—Ni(*ms*-stien)$_2$(ClO$_4$)$_2$ (0.68 g) was dissolved in hot pyridine (3 ml). On standing for 12 hr blue crystals of the complex were formed in 50% yield. *Anal.* Calcd for $C_{38}H_{42}Cl_2N_6NiO_8$: C, 54.30; H, 5.04; N, 10.00. Found: C, 54.12; H, 4.99; N, 10.03. The complex loses pyridine on heating to 70° and reverts to Ni(*ms*-stien)$_2$(ClO$_4$)$_2$.

Ni(*ms*-stien)$_2$(*β*-picoline)$_2$(ClO$_4$)$_2$.—This violet compound was prepared in 45% yield by a method similar to that used for the pyridine analog. *Anal.* Calcd for $C_{40}H_{46}Cl_2N_6NiO_8$: C, 55.31; H, 5.34; N, 9.68. Found: C, 55.65; H, 5.47; N, 9.69.

Ni(*ms*-stien)$_2$(*α*-picoline)$_2$(ClO$_4$)$_2$.—Finely powdered Ni(*ms*-stien)$_2$(ClO$_4$)$_2$ (0.34 g) was dissolved in boiling *α*-picoline (35 ml). Yellow crystals of the adduct were obtained in 90% yield on addition of diethyl ether. *Anal.* Found: C, 55.17; H, 5.28; N, 9.66.

Ni(*rac*-stien)$_2$(*α*-picoline)$_2$(ClO$_4$)$_2$.—A pure sample of this compound could not be obtained. Bright blue crystals were formed from solutions of Ni(*rac*-stien)$_2$(ClO$_4$)$_2$ in *α*-picoline. However, these readily lost *α*-picoline after separation from the mother liquor, resulting in the presence of Ni(*rac*-stien)$_2$(ClO$_4$)$_2$ as impurity. Typical microanalytical results were: C, 53.88; H, 5.34.

Ni(stien)$_2$(ClO$_4$)$_2$[(CH$_3$)$_2$SO]$_4$.—The respective Ni(stien)$_2$(ClO$_4$)$_2$ was dissolved in ~3 ml of hot dimethyl sulfoxide and the resulting solution was left *in vacuo* over sulfuric acid until a solid formed. This was filtered off and dried *in vacuo* at 70° to constant weight. The *ms*-stien complex was yellow and was obtained in 90% yield. *Anal.* Calcd for $C_{36}H_{56}Cl_2N_4NiO_{12}S_4$: C, 43.47; H, 5.67; N, 5.63. Found: C, 43.45; H, 5.59; N, 5.51. The complex evolves DMSO and reverts to Ni(*ms*-stien)$_2$(ClO$_4$)$_2$ on heating at ~190°. The violet *rac*-stien complex was obtained in 76% yield. *Anal.* Found: C, 43.84; H, 5.83; N, 5.44.

Physical Measurements.—Magnetic measurements were made at room temperature using a conventional Gouy balance. Spectra were obtained as described previously.[8]

Results and Discussion

Ni(*ms*-stien)$_3$(ClO$_4$)$_2$.—Although *l*-stien forms the complex cations $M(\text{stien})_3^{n+}$ (M = Ni^{II}, Pt^{II}, or Co^{III}) quite readily,[3] attempts to prepare tris complexes with *ms*-stien have so far apparently been unsuccessful.[2,9] Moreover Basolo, Chen, and Murmann[10] found no evidence for the formation of Ni(*ms*-stien)$_3^{2+}$ in 1:1 dioxane–water. This difference in the coordination behavior of the two forms of the diamine has been attributed[6,9,10] to steric factors. In the complexes with *ms*-stien one of the phenyl groups of each diamine occupies an axial position, whereas in the compounds with the optically active forms of the ligand both groups may be equatorially directed, or both may be axially directed.[11] It has also been suggested[10] that internal strain in the chelate rings will be greater for coordinated *ms*-stien than for the active base, as with the former both phenyl groups are on the same side of the ring. However, we find that solid complexes [Ni(*ms*-stien)$_3$]X$_2$ can be isolated though, as expected, less readily than [Ni(*rac*-stien)$_3$]$^{2+}$.

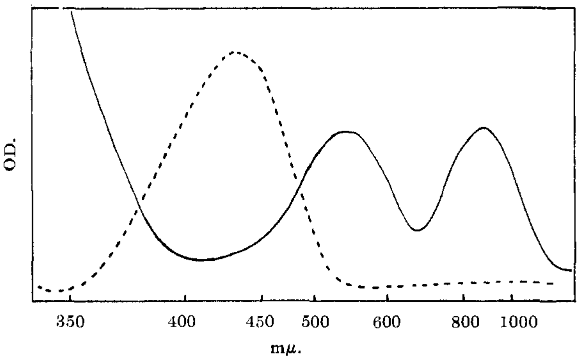

Figure 1.—Reflectance spectra of [Ni(*ms*-stien)$_2$(*β*-pic)$_2$](ClO$_4$)$_2$ (solid curve) and Ni(*ms*-stien)$_2$(ClO$_4$)$_2$·2(C$_6$H$_5$)$_3$AsO (dotted curve).

The violet compound Ni(*ms*-stien)$_3$(ClO$_4$)$_2$ was obtained by slow addition of an ethanolic solution of nickel perchlorate to an excess over a 3:1 molar ratio of *ms*-stien, also in ethanol. Excess *ms*-stien was necessary to avoid the formation of yellow Ni(*ms*-stien)$_2$(ClO$_4$)$_2$. Violet compounds were also obtained with nickel bromide or iodide, but these always contained traces of the corresponding 2:1 complexes.

The solid-state electronic spectra of both Ni(*ms*-stien)$_3$(ClO$_4$)$_2$ and its *rac*-stien analog (Table I) agree well with the Liehr and Ballhausen[12] energy level diagram for nickel(II) in ligand fields of O$_h$ symmetry, with $\Delta \simeq 11{,}000$ cm^{-1}. On this basis *ms*- and *rac*-stien lie between ammonia and ethylenediamine in the spectrochemical series, with the racemic form exerting a slightly stronger ligand field than the *meso* form.

Although stereospecific effects are possible in the synthesis of the tris and bis complexes using *rac*-stien, no experimental tests for these were carried out.

Complexes of the Type Ni(stien)$_2$(ClO$_4$)$_2$L$_n$.—The complexes Ni(stien)$_2$(ClO$_4$)$_2$ dissolved readily in coordinating solvents such as dimethyl sulfoxide (DMSO) or pyridine, and solid "adducts" were isolated from these solutions. With pyridine and *α*- or *β*-picoline the complexes had stoichiometry Ni(stien)$_2$(ClO$_4$)$_2$·2L, but with DMSO compounds of the type Ni(stien)$_2$(ClO$_4$)$_2$·4DMSO were obtained. The compound Ni(*rac*-stien)$_2$(ClO$_4$)$_2$ also dissolved in ethyl thiocyanate and ethyl isothiocyanate, to give violet and yellow solutions, respectively, but solid adducts could not be isolated, nor could solution be effected using thiophene.

Addition of triphenylphosphine oxide or triphenylarsine oxide much increases the solubility of Ni(stien)$_2$(ClO$_4$)$_2$ in organic solvents, and from these solutions compounds of the type Ni(stien)$_2$(ClO$_4$)$_2$·2L crystallize on cooling. Attempts to prepare analogous complexes

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(9) O. F. Williams and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 4464 (1959).

(10) F. Basolo, Y. T. Chen, and R. K. Murmann, *ibid.*, **76**, 956 (1954).

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(12) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

TABLE I

REFLECTANCE SPECTRA AND MAGNETIC MOMENTS OF THE COMPLEXES

Complex	μ_{eff},[a] BM	Band max,[b] cm^{-1}
Ni(*ms*-stien)$_3$(ClO$_4$)$_2$	3.15	10,930 (12,660), 17,700, (22,120), 28,090
Ni(*rac*-stien)$_3$(ClO$_4$)$_2$	3.24	11,110 ($\sim$12,700 sh), 18,080, ($\sim$22,200 sh), 29,240
N(*ms*-stien)$_2$[(C$_6$H$_5$)$_3$AsO]$_2$(ClO$_4$)$_2$	Diamag	23,100
Ni(*ms*-stien)$_2$[(C$_6$H$_5$)$_3$PO]$_2$(ClO$_4$)$_2$	Diamag	22,800
Ni(*ms*-stien)$_2$(ClO$_4$)$_2$·4(CH$_3$)$_2$SO	Diamag	23,400
Ni(*ms*-stien)$_2$(α-pic)$_2$(ClO$_4$)$_2$	Diamag	22,600
Ni(*ms*-stien)$_2$(ClO$_4$)$_2$	Diamag[c]	22,600
Ni(*ms*-stien)$_2$(py)$_2$(ClO$_4$)$_2$	3.05	10,530, 17,450, (21,750), 27,400
Ni(*ms*-stien)$_2$(β-pic)$_2$(ClO$_4$)$_2$	3.02	11,360, 18,420, *e*
Ni(*rac*-stien)$_2$[(C$_6$H$_5$)$_3$AsO]$_2$(ClO$_4$)$_2$	Diamag	22,320
Ni(*rac*-stien)$_2$[(C$_6$H$_5$)$_3$PO]$_2$(ClO$_4$)$_2$	Diamag	22,030
Ni(*rac*-stien)$_2$(ClO$_4$)$_2$	Diamag[d]	22,080
Ni(*rac*-stien)$_2$(α-pic)$_2$(ClO$_4$)$_2$[f]	3.12	9,525, 12,900 sh, 13,750 sh, 18,300, 22,080,[g] 29,600
Ni(*rac*-stien)$_2$(ClO$_4$)$_2$·4(CH$_3$)$_2$SO	3.10	11,330, ($\sim$12,700 sh), 18,150, (24,400), 30,120

[a] Calculated from Curie's law. [b] Spin-forbidden bands in parentheses. [c] From ref 2. [d] From ref 3. [e] Obscured by strong absorption edge from the uv region. [f] Impure sample. [g] Owing to Ni(*rac*-stien)$_2$(ClO$_4$)$_2$.

with triphenylphosphine or triphenylarsine were unsuccessful.

The magnetic moments (Table I) of the solid adducts depend on L and the form of stien used. Some had room-temperature moments (3.02–3.12 BM) within the range commonly found for six-coordinate nickel(II), while others were diamagnetic. None exhibited the anomalous moments sometimes observed[13] for tetragonal nickel(II) complexes.

The paramagnetism and electronic spectra (Table I) of Ni(*ms*-stien)$_2$(py)$_2$(ClO$_4$)$_2$, of its β-picoline analog, and of Ni(*rac*-stien)$_2$(α-pic)$_2$(ClO$_4$)$_2$ leave little doubt that in each case the heterocylic bases are coordinated giving a tetragonally distorted octahedral ligand field. Since Ni(*rac*-stien)$_2$(ClO$_4$)$_2$·4DMSO is also paramagnetic, it appears that two DMSO molecules occupy axial positions in this case also (coordination of all four DMSO molecules is ruled out by the electronic band energies—see below).

The diamagnetism of the other complexes does not necessarily imply that in these the metal ions are four-coordinate, as a strongly tetragonal six-coordinate nickel(II) compound may have a spin-singlet ground state. The infrared spectra of the diamagnetic complexes with (C$_6$H$_5$)$_3$PO, (C$_6$H$_5$)$_3$AsO, and DMSO were examined to obtain further information concerning the role of these ligands. Bands due to L in Ni(stien)$_2$(ClO$_4$)$_2$L$_n$ were identified by comparing the spectra with those of the corresponding complexes Ni(stien)$_2$(ClO$_4$)$_2$.

On coordination, the P–O stretching frequency of triphenylphosphine oxide is lowered,[14] usually by about 40–50 cm^{-1}, from the value of 1195 cm^{-1} in the free ligand. A shift in ν(P–O) of this magnitude was found for the complexes Ni(stien)$_2$(ClO$_4$)$_2$·2(C$_6$H$_5$)$_3$PO (see Table II), which suggests that in these compounds the phosphine oxide molecules are coordinated.

TABLE II

INFRARED DATA (CM^{-1}) FOR SOME OF THE COMPLEXES

Ni(*ms*-stien)$_2$(ClO$_4$)$_2$·2(C$_6$H$_5$)$_3$PO	1152 ms[a]
Ni(*rac*-stien)$_2$(ClO$_4$)$_2$·2(C$_6$H$_5$)$_3$PO	1153 ms[a]
Ni(*ms*-stien)$_2$(ClO$_4$)$_2$·2(C$_6$H$_5$)$_3$AsO	876 s,[b] 861 m[b]
Ni(*rac*-stien)$_2$(ClO$_4$)$_2$·2(C$_6$H$_5$)$_3$AsO	877 s[b]
Ni(*ms*-stien)$_2$(ClO$_4$)$_2$·4DMSO	1019 s, 1011 s, 950 s
Ni(*rac*-stien)$_2$(ClO$_4$)$_2$·4DMSO	1000 s, 951 s, 944 s

[a] ν(P–O). [b] ν(As–O).

With triphenylarsine oxide and DMSO clear detection of coordination from infrared spectra is more difficult. In the case of triphenylarsine oxide the decrease in ν(As–O), because of the lowering of the As–O bond stretching force constant, appears to be comparable with the kinematic raising of ν(As–O) due to the coupling of ν(As–O) and ν(M–O).[15] This results in the ν(As–O) values for triphenylarsine oxide complexes differing little from that (880 cm^{-1}) observed[16] for the free ligand. Consequently, despite the close similarity of the ν(As–O) values in Table II to those found[15] for, *e.g.*, Fe[(C$_6$H$_5$)$_3$AsO]$_2$Cl$_2$ (874 cm^{-1}) and Zn[(C$_6$H$_5$)$_3$AsO]$_2$Br$_2$ (874 cm^{-1}), these results alone cannot differentiate between coordinated and noncoordinated (C$_6$H$_5$)$_3$AsO. The splitting of ν(As–O) observed for the *ms*-stien complex is also found[15,17] for some other triphenylarsine oxide complexes.

With the complexes involving DMSO the situation is complicated on two counts. First, there is disagreement[18,19] concerning the assignment of the S–O stretch in coordinated DMSO. Second, in the compounds Ni(stien)$_2$(ClO$_4$)$_2$·4DMSO two of the DMSO molecules will be noncoordinated even if the others are bonded to the metal atom. In solution DMSO shows[18] a ν(S–O) band at 1055 cm^{-1}, but the very strong, broad ν_3 band of the perchlorate ion dominates the spectra of these stien complexes in this region and prevents the detection of noncoordinated DMSO by this means. In both compounds strong bands were observed in the regions $\sim$1000 and $\sim$950 cm^{-1} (Table II). However, as both free and coordinated DMSO also give bands in these regions,[18,19] these results do not show whether any of the DMSO molecules in the *ms*-stien complex are coordinated, although from the magnetic and electronic

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spectral data this is clearly the case for the *rac*-stien compound.

The electronic spectra of the diamagnetic complexes studied here all consist of a single band in the region 22,000–23,500 cm^{-1}. For spin-paired Ni^{II} in a ligand field of approximately D_{4h} symmetry three bands are to be expected, owing to the transitions $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{z^2} \rightarrow d_{x^2-y^2}$, and d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$. The transitions d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ and, in particular, $d_{z^2} \rightarrow d_{x^2-y^2}$ are expected to shift to lower energy on going from a square-planar complex to one with weak axial coordination. A bathochromic shift of ~3000 cm^{-1} in two of the three bands observed for cupric acetylacetonate on going from chloroform solution to solutions in coordinating solvents such as propanol and pyridine has been used[20] as a criterion for the assignment of the energy levels in this compound. If, as seems likely, the diamagnetic adducts Ni(*ms*-stien)$_2$(ClO$_4$)$_2$L$_n$ contain molecules weakly coordinated to the nickel ions along the z axis, then the close similarity of the band positions in these complexes to that in Ni(*ms*-stien)$_2$(ClO$_4$)$_2$ suggests that the band at ~22,500 cm^{-1} is due to the transition $d_{xy} \rightarrow d_{x^2-y^2}$, with the other transitions either being masked under the intense parity-allowed absorption above ~30,000 cm^{-1} or being too weak to be observed. This assignment receives some confirmation from the lack of any significant change in the electronic spectrum in the visible region on dissolving diamagnetic stilbenediaminenickel complexes in water or ethanol.[21] It is also consistent with the energy-level ordering $d_{x^2-y^2} \gg d_{xy} > d_{z^2} > d_{xz} \sim d_{yz}$ predicted[22] for some square-planar situations. A band at 20,800 cm^{-1} for diamagnetic Ni(ethylenebisbiguanide)$_2$ has been assigned[23] as $d_{xy} \rightarrow d_{x^2-y^2}$, while the other transitions were thought to lie above 33,000 cm^{-1}.

The paramagnetic compounds Ni(stien)$_2$(ClO$_4$)$_2$L$_2$ may be assumed, for steric reasons, to have *trans*-octahedral structure. Pronounced differences between the in-plane and axial ligand fields should lead to a splitting of the $^3T_{2g}$ and $^3T_{1g}$ states.[24] The only complex described here to show any marked departure from O_h symmetry, in terms of band splittings, was the impure compound thought to be Ni(*rac*-stien)$_2$(ClO$_4$)$_2$(α-pic)$_2$ (see Experimental Section). Spectra of samples soon after isolation showed pronounced splitting of the transitions to the $^3T_{2g}$ and $^3T_{1g}$ levels (in O_h) (see Table I). However, the compound readily lost α-picoline and reverted to the parent compound Ni(*rac*-stien)$_2$(ClO$_4$)$_2$. This easy loss of the picoline is consistent with a weak nickel–picoline bond in the adduct and hence the large tetragonal component to the ligand field is understandable.

The electronic spectrum of the complex [Ni(*rac*-stien)$_2$(DMSO)$_2$](ClO$_4$)$_2$·2DMSO is somewhat surprising. As *Dq* for DMSO in Ni(DMSO)$_6^{2+}$ is known[25] to be only 775 cm^{-1}, the electronic transitions for Ni(*rac*-stien)$_2$(DMSO)$_2^{2+}$ would be expected at lower energy (~10,000 cm^{-1} for the first spin-allowed band) than those for Ni(*rac*-stien)$_3^{2+}$ and there should be a significant splitting of some, or all, of the orbital triplet levels. In fact the bands in the DMSO adduct are at slightly higher energies than those in Ni(*rac*-stien)$_3^{2+}$, and no band splittings were observed. The reasons for this are not clear. A similar lack of band splittings has been found[26] for [Ni(en)$_2$(DMSO)$_2$](BF$_4$)$_2$ at room temperature, although for this compound band components were resolved at ~80°K.[26] The higher band energies in the DMSO adduct presumably reflect the failure of the average ligand field strength approximation owing to changes in ligand–ligand repulsions on passing from Ni(stien)$_3^{2+}$ and Ni(DMSO)$_6^{2+}$ to the mixed-ligand complex. A similar effect has been observed for the nickel complexes of the chelating amine di-2-pyridylamine.[27]

In conclusion, although the paramagnetic complexes Ni(stien)$_2$(ClO$_4$)$_2$L$_2$ clearly contain coordinated L molecules, X-ray studies are required to show whether this is also the case for the diamagnetic compounds (where L = (C$_6$H$_5$)$_3$PO, (C$_6$H$_5$)$_3$AsO, or DMSO). The infrared evidence for the phosphine oxide complexes suggests that these may well be six-coordinate, and, in view of the method of preparation, it seems more likely that in the arsine oxide compounds the (C$_6$H$_5$)$_3$AsO molecules are also coordinated, if only weakly, rather than being present as molecules of "solvation." The bond energy of the two axial metal–ligand bonds is likely to be relatively low in diamagnetic, six-coordinate complexes of nickel(II), and their formation may well be strongly influenced by such factors as hydrogen-bonding and crystal-packing considerations.

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