lysine monohydrochloride)nickel(II). *Anal.* Calcd for Ni(C$_{12}$-H$_{15}$N$_2$O$_3$)$_2$: C, 54.46; H, 5.71; N, 10.59. Found: C, 54.46; H, 5.69; N, 10.45.

2,4-Diaminobutyric Acid System.—Typically, 2 g (0.01 mole) of 2,4-diaminobutyric acid dihydrochloride was dissolved in 50 ml of water, the resulting solution added to a slurry of 0.6 g (0.005 mole) of NiCO$_3$ in 10 ml water, and the mixture stirred with heating until CO$_2$ evolution stopped. The violet solution was filtered to remove insoluble materials, and the filtrate was evaporated to dryness. The pink-violet product was extracted with methanol in a Soxhlet extractor overnight. The soluble fraction was evaporated to dryness in a stream of air. The insoluble fraction was dried *in vacuo* over P$_4$O$_{10}$. Consistent analyses could not be obtained.

Visible Spectral Studies.—Solutions were prepared by pipeting 15 ml of a 0.283 *M* nickel(II) chloride solution into a 50-ml volumetric flask, to which was added either a solution of neutralized ligand or a solution of the diamino acid dihydrochloride followed by neutralization with standard 0.248 *N* sodium hydroxide. The ionic strength was adjusted to 0.5 with sodium chloride and the solutions were diluted to the mark. The final concentrations were 0.0851 *M* in nickel. Spectra were obtained from solutions containing ligand to metal ratios varying between 1:5 and 6:1.

All electronic spectra were obtained with a Cary Model 14 recording spectrophotometer at 20.0 ± 0.5°. Matched quartz 10- and 50-mm cells were used. The observed absorption maxima and molar extinction coefficients include uncertainties of not more than 4% introduced by ligand absorption above 850 mμ and below 450 mμ.

Infrared Absorption Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 137B Infracord spectrophotometer. The samples were dispersed in potassium bromide disks.

Analysis.—Carbon, hydrogen, and chloride analyses were performed by Galbraith Microanalytical Laboratories and by Schwarzkopf Microanalytical Laboratories. Nitrogen analyses were performed in these laboratories using a Coleman Model 29 nitrogen analyzer.

Axial Distortion and Electronic Structure in the Macrocyclic Complexes, Diacido-S,S'-*o*-xylyl-2,3-pentanedionebis(mercaptoethylimine)nickel(II)

BY GEORGE R. BRUBAKER AND DARYLE H. BUSCH

A series of diacido derivatives of a tetradentate macrocyclic complex has been prepared. These are Ni(PEX)Y$_2$, where PEX is S,S'-*o*-xylyl-2,3-pentanedionebis(mercaptoethylimine). Three distinct structural types are found: diamagnetic, presumably square-planar, nickel(II) for Y$^-$ = ClO$_4^-$ or I$^-$; pseudo-tetragonal six-coordinate paramagnetic nickel(II) for Y$^-$ = N$_3^-$, NCS$^-$, or Cl$^-$; and a more complex paramagnetic behavior in the case of Y$^-$ = Br$^-$. From extensive determination over a 200° temperature range it has been found that all the paramagnetic materials obey the Curie–Weiss law and values of μ_{eff} and θ are reported. The spectra of the unambiguous pseudo-tetragonal complexes conform closely to an adaptation of the Piper–Wentworth model. Values of the empirical tetragonal splitting parameter Dt' have been calculated. It has also been possible to estimate the octahedral field strengths Dq of the acido groups. The spectrochemical series observed *within* the composition Ni(PEX)Y$_2$ is ClO$_4^-$, I$^-$ < Br$^-$ < Cl$^-$ < N$_3^-$ < PEX < NCS$^-$. The unit cell of the crystalline complex Ni(PEX)Br$_2$ probably contains one six-coordinate paramagnetic nickel ion for every three diamagnetic nickel(II) ions. The species absorbs 0.5 mole of water and changes into a strictly spin-paired material without recrystallization but with an anisotropic change in spectral properties.

Introduction

The incremental variations in the coordinating abilities of ligands along a fourfold axis, by means of which square-planar complexes may ultimately be derived from octahedral ones, are of particular interest, for the theoretical description of this class of distortion is substantially in advance of the experimental facts.[1–7] It is common in such treatments to assume first that a six-coordinate molecule or ion is octahedral and then treat deviations from cubic structure as perturbations. Applications to the cases of cobalt(III) and chromium(III) have dominated the subject because of the relatively great number of appropriate examples available. The development of a number of tetradentate macrocyclic ligands[8] which fix the spatial arrangement and ligand field strengths of four coplanar donor sites simplifies the study of tetragonally distorted six-coordinate nickel(II). The present study is concerned with derivatives[9] of S,S'-*o*-xylyl-2,3-pentanedionebis(mercaptoethylimine)nickel(II) cation (abbreviated Ni(PEX)$^{2+}$, structure I). The closed tetradentate ligand

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(2) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162, 1129 (1958).

(3) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709, 1524 (1965).

(4) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 101.
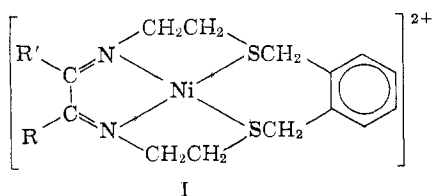
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(6) W. E. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956).

(7) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

(8) D. H. Busch, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **25**, 107 (1964).

(9) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964).

I

encircles the nickel(II) ion presenting it with two imine nitrogen and two thioether sulfur donor atoms. Thompson reported the synthesis of the bromide, thiocyanate, and perchlorate derivatives, $Ni(PEX)Y_2$, and suggested that the crossover between the singlet and triplet ground states occurs for an axial ligand field strength intermediate between those of the bromide and thiocyanate anions.[9] The effects of variations in the extraplanar ligands on the electronic properties of $Ni(PEX)^{2+}$ are reported here. Extraplanar ligands were selected from the spectrochemical series to give a range of axial ligand field strengths which embraces both singlet and triplet ground states. Electronic spectra and magnetic moments were measured using solid samples. The magnetic susceptibilities were determined as a function of temperature over a range of some $200°$. The observed properties are correlated with theoretical expectations.

Experimental Section

Materials.—The nickel acetate tetrahydrate, all alkali metal salts, and all solvents were of reagent grade or equivalent. N,N-Dimethylformamide and dimethyl sulfoxide were dried by storing over 5-A molecular sieves for 24 hr or more. 1,2-Dichloroethane was dried by passing the solvent through a column of neutral Brockman grade 1 alumina about 20 mm in diameter and 30 cm in length. Practical grade 2,3-pentanedione and 2,5-hexanedione (Aldrich Chemical Co., Inc., Milwaukee, Wis.) were used without further purification except as noted. 2-Aminoethanethiol hydrochloride (Evans Chemetics, Inc., New York, N. Y., 97–99% purity) was dried under high vacuum (pressure of 0.5 mm or less) at room temperature prior to use.

Preparation of 2,3-Pentanedionebis(mercaptoethylimino)-nickel(II), Ni(PE).[10]—Nickel acetate tetrahydrate (24.7 g, 0.10 mole) was dissolved in 225 ml of absolute ethanol by stirring rapidly at room temperature for 1 hr. 2-Aminoethanethiol hydrochloride (22.7 g, 0.20 mole) was dissolved in 200 ml of absolute ethanol containing 4.2 g. (0.2 g-atom) of sodium, and the sodium chloride produced was removed by filtering. The resulting solution of 2-aminoethanethiol was heated to its boiling point and 10 g (0.10 mole) of 2,3-pentanedione was added, yielding a pale yellow solution. This solution was stirred at its boiling point for about 10 min. The nickel acetate solution was then added and the resulting solution stirred at the boiling point for an additional 20 min, then placed in the freezer for 8 hr. A dark green crystalline product was isolated by filtration, washed with two 50-ml portions of absolute methanol, and washed through the filter with a minimum of boiling chloroform (as much as 1 l. of solvent may be required, depending on the yield of the crude product; washing is continued until the solvent is pale pink). The dark red chloroform solution was evaporated to dryness at room temperature, yielding dark green crystals which were dried *in vacuo* over P_4O_{10} at room temperature. The infrared spectrum was identical with that reported by Thompson.[10] *Anal.* Calcd for $Ni(C_9H_{16}N_2S_2)$: N, 9.8. Found: N, 9.2.

Preparation of S,S'-o-Xylyl-2,3-pentanedionebis(mercapto-ethylimine)nickel(II) Bromide, Ni(PEX)Br₂.—The procedure of Thompson and Busch[9] was followed with the following modifications: 2,3-pentanedionebis(mercaptoethylimino)nickel(II) (5.05

g, 0.02 mole) was dissolved in 300 ml of 1,2-dichloroethane, and 5.28 g (0.92 mole) of α,α'-dibromo-o-xylene was added to the solution. The solution was stirred for 8 hr at room temperature, followed by evaporation to dryness with a rotary film evaporator. The gray solid was dissolved in 1 l. of boiling ethanol and filtered. On cooling under reduced pressure, a dark green crystalline product separated from the dark red solution. This was isolated by filtering under dry air and dried *in vacuo* over P_4O_{10} at room temperature. *Anal.* Calcd for $Ni(C_{17}H_{24}N_2S_2)Br_2$: C, 37.87; H, 4.49; N, 5.20; S, 11.90; Br, 29.65. Found: C, 37.95; H, 4.79; N, 5.20; S, 11.74; Br, 29.65.

Preparation of S,S'-o-Xylyl-2,3-pentanedionebis(mercapto-ethylimine)nickel(II) Iodide, Ni(PEX)I₂.—Two grams (0.003 mole) of $Ni(PEX)Br_2$ was dissolved in 300 ml of hot absolute methanol containing 10 g (0.072 mole) of sodium iodide. On cooling, the black crystalline solid precipitated. It was filtered and dried *in vacuo* at room temperature using P_4O_{10}. *Anal.* Calcd for $Ni(C_{17}H_{24}N_2S_2)I_2$: C, 32.23; H, 3.82; N, 4.43; S, 10.14; I, 40.12. Found: C, 32.06; H, 4.15; N, 4.47; S, 9.93; I, 40.02.

Preparation of Diazido-S,S'-o-xylyl-2,3-pentanedionebismer-captoethylimine)nickel(II), Ni(PEX)(N₃)₂.—Five grams (0.007 mole) of sodium azide was dissolved in 200 ml of water, and acetone was added until the sodium azide started to precipitate. Two grams (0.003 mole) of $Ni(PEX)Br_2$ was added slowly, and the resulting mixture was stirred at room temperature for 30 min. The red-brown solution was filtered and the excess acetone was removed by evaporation under reduced pressure. The bronze crystals were filtered under dry air and dried *in vacuo* at room temperature over P_4O_{10}, whereupon they became pink. *Anal.* Calcd for $Ni(C_{17}H_{24}N_2S_2)(N_3)_2 \cdot H_2O$: C, 42.43; H, 5.25; N, 23.28; S, 13.32. Found: C, 42.91; H, 5.25; N, 22.76; S, 13.22.

Preparation of Diisothiocyanato-S,S'-o-xylyl-2,3-pentanedione-bis(mercaptoethylimine)nickel(II), Ni(PEX)(NCS)₂.[9]—A solution of 2.0 g (0.0037 mole) of $Ni(PEX)Br_2$ in 100 ml of absolute methanol was added to a solution of 5.0 g (0.052 mole) of potassium thiocyanate in absolute methanol. A pink solid was formed almost immediately. The product was filtered and dried *in vacuo* at room temperature over P_4O_{10}. *Anal.* Calcd for $Ni(C_{19}H_{24}N_4S_4)$: C, 46.07; H, 4.88; N, 11.31; S, 25.90. Found: C, 45.75; H, 4.88; N, 11.39; S, 25.75

Preparation of S,S'-o-Xylyl-2,3-pentanedionebis(mercapto-ethylimine)nickel(II) Perchlorate, Ni(PEX)(ClO₄)₂.[9]—The preparation was identical with that of the diisothiocyanate complex except for the substitution of 5.0 g of sodium perchlorate in place of the potassium thiocyanate. An orange solid was obtained, washed three times with ethyl acetate to remove the excess perchlorate, and dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $Ni(C_{17}H_{24}N_2S_2)(ClO_4)_2$: C, 35.32; H, 4.18; N, 4.85; S, 11.09; Cl, 12.27. Found: C 34.72; H, 4.34; N, 4.67; S, 11.48; Cl, 12.30.

Preparation of Dichloro-S,S'-o-xylyl-2,3-pentanedionebis(mer-captoethylimine)nickel(II), Ni(PEX)Cl₂.—To a cold solution containing 30 g of sodium chloride and 5.0 ml of 12 N HCl in 100 ml of water was added 2.00 g (0.0037 mole) of $Ni(PEX)Br_2$. The resulting solution was stirred for 10 min in an ice bath, transferred to a 1000-ml separatory funnel, and repeatedly extracted with chloroform until the organic phase showed no color. The green chloroform solution was dried with anhydrous sodium sulfate and then concentrated to 50 ml. A tenfold excess of anhydrous ether was added and the solution was warmed for 1 hr to increase the particle size of the solid. The product was filtered under dry air. The procedure was repeated starting with the crude $Ni(PEX)Cl_2$ in place of $Ni(PEX)Br_2$, and the solid obtained was dried under high vacuum over P_4O_{10}. *Anal.* Calcd for $Ni(C_{17}H_{24}N_2S_2)Cl_2$: C, 45.33; H, 5.39; N, 6.22; S, 14.27; Cl, 15.78. Found: C, 45.21; H, 5.61; N, 6.11; S, 14.06; Cl, 16.03.

Physical Measurements.—Magnetic measurements were made by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. Measurements of the variation of the magnetic susceptibility

(10) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 213 (1964).

with temperature were made using an apparatus constructed by Burke,[11] based on that of Figgis and Nyholm,[12] but modified as recommended by Stoufer.[13] The magnetic susceptibilities were calculated, and the least-squares refinement and regression analyses performed on an IBM 7094 computer using a SCATRAN program written by F. L. Urbach.

Infrared spectra were obtained using a Perkin-Elmer Model 337 recording spectrophotometer. Hexachlorobutadiene mull and potassium bromide disk techniques were employed.

Electronic spectra were obtained using a Cary Model 14 recording spectrophotometer and diffuse reflectance accessory. Reflectance spectra were obtained from pressed disks containing the complex dispersed in the sodium salt of the anion.

The X-ray powder patterns were obtained using a Norelco X-ray diffractometer fitted with an 11.5-cm Debye–Scherrer powder diffraction camera. The samples were loaded into 0.5-mm capillaries which were sealed with a small flame. The exposure time was 12 hr under Cu Kα radiation at 32 kv and 12 ma. Analyses were performed by Schwarzkopf Microanalytical Laboratories and Galbraith Microanalytical Laboratories. Most of the nitrogen analyses were obtained in these laboratories using a Coleman Model 29 nitrogen analyzer.

Results and Discussion

Magnetic Properties.—By a series of metathetical reactions, the compounds $Ni(PEX)Y_2$ were prepared for $Y = ClO_4$, I, Br, Cl, N_3, and NCS. The magnetic susceptibilities of these substances were first measured at room temperature and then those compounds exhibiting significant moments were subjected to study over a temperature range of some 200°.

The series of compounds may be conveniently divided into groups exhibiting either the singlet or triplet ground states as solids on the basis of their magnetic moments (Table I). The iodide and perchlorate complexes belong to the former group, and the dichloro, diazido, and diisothiocyanato complexes belong to the latter. The peculiar magnetic moment observed for the bromide sets it apart from either group.

Table I

Observed Magnetic Moments of Some Diacido-S,S'-*o*-xylyl-2 3-pentanedionebis-(mercaptoethylimine)nickel(II) Complexes

Compound	$10^6\chi_M$	μ_{eff}	θ, °K
$Ni(PEX)(C O_4)_2$	51	0.35	...
$Ni(PEX)I_2$	153	0.61	...
$Ni(PEX)Br_2$	...	1.57[a]	1.8
$Ni(PEX)Cl_2$	...	3.12[a]	0.1 ± 1.8
$Ni(PEX)(N_3)_2$	...	3.23[a]	7.2 ± 2.6
$Ni(PEX)(NCS)_2$	...	2.99[a]	1.1 ± 2.2

[a] Calculated from the slopes of the Curie–Weiss plots.

The magnetic susceptibilities of the paramagnetic complexes were found to obey the Curie–Weiss law

$$1/\chi_M = (3k/N\mu^2)T + (3k/N\mu^2)\theta$$

Plots of $1/\chi_M$ against temperature afforded straight lines in all cases. The reported values of the Curie–Weiss law parameters were calculated from the linear function by the method of least squares and, except for the bromide, are given at the 95% confidence level. The results represent the compilation of data from 70

or more determinations of the magnetic susceptibility for each compound. The small paramagnetism of the bromide, with the resultant reduction in the weight changes, limited the precision to a low confidence level. Nevertheless, the magnetic susceptibility could be reproduced from sample to sample.

The ground state for octahedral nickel(II) is a $^3A_{2g}$ state. It is a spin triplet, and the absence of orbital degeneracy suggests that it will not be split by fields of lower symmetry. The lowest excited state, however, is an orbital triplet (T) state which is susceptible to Stark splitting on descent from O_h to lower symmetry. The descent in symmetry is assumed, for convenience, to involve the superposition of an axial component on the octahedral structure. Following Ballhausen,[14] under the influence of spin–orbit coupling, the spin–orbit components of the orbitally degenerate excited states interact with the spin components of the ground state. This results in a splitting of the ground state by an interval, D, the zero field splitting. In the region where D is comparable to the thermal energy, kT, there will be a distribution between the various spin components so that the susceptibility is given by[15]

$$\chi_M = \frac{2Ng^2\mu^2}{kT}\left[\frac{1}{2 + e^{D/kT}}\right]$$

If, however, kT is much larger than D, the preceding equation reduces to the Curie–Weiss form for which $D = 3\theta$.

Under the assumption that spin–orbit coupling is largely responsible for the zero field splitting, the relationship between the zero field splitting and the splitting of the first excited state (on descent from octahedral symmetry) is given by

$$D \sim \frac{9k_1\lambda^2}{\Delta^2}$$

where Δ is the difference in energy between the ground state and the first excited state $(10Dq)$, λ is the spin–orbit coupling constant, and k_1 is the splitting of the first excited state.

Assuming that the complex is only slightly perturbed from octahedral symmetry, the observed magnetic moment is related to the spin-only moment by

$$\mu = \mu_0(1 - \alpha\lambda/\Delta)$$

where μ is the observed magnetic moment, μ_0 is the spin-only magnetic moment (2.83 for high-spin d^8 ions), and α is a constant (4 for high-spin nickel(II) complexes). The latter expressions may be combined to eliminate the necessity for evaluating Δ or λ

$$D = 9k_1/\alpha^2[(\mu/\mu_0)^2 - 2(\mu/\mu_0) + 1]$$

Values of the zero field splitting have been calculated using k_1 from the spectra (see below) and the magnetic moments given in Table I. The values of D calculated

(11) J. A. Burke, Ph.D. Dissertation, The Ohio State University, 1963.
(12) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1958).
(13) R. C. Stoufer, private communication, 1960.
(14) Reference 4, p 142.
(15) Although similar to the equation given by Ballhausen for the susceptibility parallel to the magnetic field, this equation is derived directly from the Van Vleck equation for magnetic susceptibility. Consequently, it applies to the anisotropic case.

TABLE II

ESTIMATES OF THE ZERO FIELD SPLITTING OF
THE COMPLEXES Ni(PEX)Y$_2$

Y	μ_{eff}	D,[a] cm^{-1}	D,[b] cm^{-1}
NCS	2.99	1.5	2.4
Br	(3.14)[c]	6.7	3.8
Cl	3.12	8.0	0.2
N$_3$	3.23	14.7	15.4

[a] Calculated from k_1 and μ_{eff}. [b] Calculated from θ. [c] Estimated by assuming one out of four Ni^{2+} to be paramagnetic.

in this way are compared with values obtained directly from the Weiss constant in Table II. The values are not accurately determined by either route, yet a general qualitative agreement is found among the values. Since D is expected to depend strongly both on the relative ligand field strength of Y $vs.$ the in-plane donors and on the nephelauxetic effect of Y, the observed variation of D with the nature of Y is not surprising. The vicissitudes of the Weiss constant are well illustrated by attempting to estimate spin–orbit coupling constants on that basis and comparing the result with values calculated from carefully determined magnetic moments. For the compounds given, the latter source gives for λ (cm^{-1}): Br$^-$, −294; Cl$^-$, −292; N$_3^-$, −302; NCS$^-$, −281, whereas the first method gives values varying over a range that spans an order of magnitude.

Electronic Spectra.—The electronic spectra of the compounds with the triplet ground state exhibit four broad bands (Table III). The lowest in energy occurs at about 10,000 cm^{-1}, as is common for paramagnetic six-coordinate nickel(II) complexes. In this series, the appearance of an absorption maximum in this low-energy region is always accompanied by the triplet ground state.

TABLE III

REFLECTANCE SPECTRA[a] OF COMPOUNDS WITH THE TRIPLET
GROUND STATE

Compound	ν_1	ν_2	ν_3	ν_4
Ni(PEX)Cl$_2$	9,280	10,700	18,400	24,800
Ni(PEX)(N$_3$)$_2$	9,900	10,800	19,900	26,800
Ni(PEX)(NCS)$_2$	10,800	11,700	18,400	24,000

[a] All values in cm^{-1}.

In the crystal field model, the perturbing potential for an octahedral field can be written as the sum of three contributions, each containing a sum of axial charges. As a result, only the sum of the axial charges determines the electronic structure when all of the internuclear distances are equal.[4] It is therefore possible to treat the electronic properties of S,S'-o-xylyl-2,3-pentanedionebis(mercaptoethylimine)nickel(II) complexes as if the symmetry is D$_{4h}$, though the true symmetry approximates C$_{2v}$.

Proceeding on this basis, the treatment of Ballhausen[4] can be adapted in order to use the interpretations applied to cobalt(III) by Wentworth and Piper.[3] This scheme is particularly useful and its application to the nickel(II) case should prove most helpful.

From the energy level diagram, the order and energy values for the transitions between the energy levels derived from the ^{3}F term in D$_{4h}$ symmetry are

$$\nu_1 = E(^3E_g{}^a) - E(^3B_{1g}) = 10Dq - {}^{35}/_4Dt$$

$$\nu_2 = E(^3B_{2g}) - E(^3B_{1g}) = 10Dq$$

$$\nu_3 = E(^3A_{2g}) - E(^3B_{1g}) = 18Dq - 4Ds - 5Dt$$

$$\nu_4 = E(^3E_g{}^b) - E(^3B_{1g}) = 18Dq - 2Ds - {}^{25}/_4Dt$$

The lowest excited state is ^{3}T$_{2g}$ and this state is split in a manner that reveals the tetragonal character of the complexes. In D$_{4h}$ this splitting is $\Delta E(^3T_{2g}) = {}^{35}/_4Dt$.

The direction of the tetragonal distortion determines which of the states derived from ^{3}T$_{2g}$(O$_h$) lies lowest. If the axial ligands are the weaker, $^3E_g{}^a$ lies lowest. In any case, it is the transition $^3B_{1g} \rightarrow {}^3E_g{}^a$ which measures the tetragonal character of the complexes, for the transition to ^{3}B$_{2g}$ is independent of both Ds and Dt and may be used to determine the in-plane ligand field splitting parameter Dq^{xy}. It is a prediction of this model that this band will occur at the same energy for all of the complexes, Ni(PEX)Y$_2$. Reference to Table III shows that the reflectance spectra of the three complexes having unambiguous triplet ground states have an absorption band at 10,700–10,800 cm^{-1}. This band is assigned to the transition $^3B_{1g} \rightarrow {}^3B_{2g}$ and is denoted as ν_B. The remaining low-energy band must correspond to the transition $^3B_{1g} \rightarrow {}^3E_g{}^a$ and is abbreviated as ν_E.

Piper and Wentworth[3] point out the generality of the expression

$$Dt(D_{4h}) = {}^4/_7(Dq^{xy} - Dq^z)$$

which indicates that a determination of Dt and Dq^{xy} permits the calculation of a parameter measuring the ligand field strength of the axial groups (Dq^z). In the original work with cobalt(III), Dq^{xy} was not determined from the spectra of mixed ligand complexes but rather taken as equal to Dq for the corresponding octahedral complex; for example, for Dq^{NH_3}, the value for Co(NH$_3$)$_6^{3+}$ was used. It is helpful to find the value of Dq^{xy} directly measurable in the present case. Under these circumstances a very simple relationship may be used to calculate the ligand field splitting parameter for the axial ligands

$$Dq^z = \frac{2\nu_E - \nu_B}{10}$$

The results are summarized in Table IV, where Ni(PEX)Br$_2$ is included, even though the spectrum had to be measured in solution in that case. In order to minimize the effect of uncertainties in the data, an average value for ν_B ($10Dq^{xy}$) was used (10,620 cm^{-1}). The tetragonal splitting parameter is labeled Dt' in Table IV because it is derived from the average Dq^{xy} value.

Recalling that the perchlorate and iodide are spin paired, the observed spectrochemical series within the formulation Ni(PEX)Y$_2$ is ClO$_4^-$, I$^-$ < Br$^-$ < Cl$^-$ <

Table IV

Spectral Assignments and Crystal Field Parameters for
the Pseudo-Tetragonal Complexes Ni(PEX)Y₂

Complex	ν_E, cm^{-1}	ν_B, cm^{-1}	Dt', cm^{-1}	Dq^z, cm^{-1}
Ni(PEX)Br₂[a]	9,010	10,200	187	740
Ni(PEX)Cl₂	9,280	10,700	153	794
Ni(PEX)(N₃)₂	9,900	10,800	82.3	918
Ni(PEX)(NCS)₂	11,700	10,800	−124	1280

[a] Measured in dichloroethane by Thompson.[9]

$N_3 <$ PEX $<$ NCS. The series is typical for nickel(II), although azide is not comparably placed in the cobalt-(III) case.[3] On the other hand, the ratios Dq_{Co}/Dq_{Ni} agree rather well for the remaining anions. Proceeding from an average ratio of 1.76, iodide is estimated to have a Dq_{Ni} value of about 550 cm^{-1} in Ni(PEX)I₂. Since this complex exists in the singlet state, the critical axial ligand field for the occurrence of spin pairing for these macrocyclic complexes occurs somewhere in the range 550 cm$^{-1} < Dq^z < 740$ cm^{-1}. Failure to observe spin-state isomerism suggests that the critical range is toward the center of the interval. The treatment described here should have broad applicability among nickel(II) complexes.

Although the calculation of B essentially involves the dubious assumption that the tetragonal splitting is small, the nephelauxetic series appears to be Br$^- <$ NCS$^- <$ Cl$^- <$ N₃$^-$.

The first electronic transition observed in the reflectance spectra of the singlet compounds (Table V) occurs at about 16,000 cm^{-1}, as expected for four-coordinate square-planar nickel(II) complexes. The lowest energy band, ν_1, may be assigned to the transition $^1A_{1g} \rightarrow {}^1B_{1g}$ in pseudo D_{4h} symmetry. The remaining transitions, in the order of increasing energy are: ν_2, $^1A_{1g} \rightarrow {}^1E_g$; ν_3, $^1A_{1g} \rightarrow {}^1B_{2g}$. In the true C_{2v} symmetry, the transitions may be assigned: ν_1, $^1A_1 \rightarrow {}^1B_1$; ν_2, $^1A_1 \rightarrow {}^1A_2$; and ν_3, $^1A_1 \rightarrow {}^1B_2$, in the order of increasing energy, following the assignments of Maki.[11]

Table V

Reflectance Spectra[a] of Compounds with the Singlet
Ground State

Compound	ν_1	ν_2	ν_3
Ni(PEX)(ClO₄)₂	16,200	20,000	24,900
Ni(PEX)I₂	15,700	16,900	23,800

[a] All values given in cm^{-1}.

Crystalline Ni(PEX)Br₂.—Referring to Table I, it will be noted that the magnetic moment of the bromide complex, Ni(PEX)Br₂, was found to be intermediate between the values expected for singlet and triplet ground states.

Clearly the possibility of spin-state isomerism required investigation in this case. The full temperature range of magnetic measurements was applied to a sample of the compound having a room-temperature moment of about 1.5 BM. The magnetic susceptibility obeys the Curie–Weiss law and is independent of the field strength, precluding the possibilities of spin-state isomerism and of cooperative interactions in the

crystal. It was also observed that the magnetic moment may reflect the history of the sample. If the sample is handled exclusively in a drybox, the magnetic moment approaches the maximum obtained from the slope of the Curie–Weiss graph. When, on the other hand, the sample is exposed to air, the observed moment tends to fall around 1.2 BM. If the sample is exposed to a humid atmosphere for 1 hr, about 0.5 mole of water is absorbed and the color turns from green to red-brown. Simultaneously, the moment decreases and approaches the small residual value typical of spin-paired nickel(II) complexes. It has not been possible to remove the absorbed water completely even on heating at 80° overnight *in vacuo*.

The presence of water in the brown compound was confirmed by sharp absorption bands at 3750 and 3460 cm^{-1} in the infrared spectrum of the compound in a hexachlorobutadiene mull. The absence of these absorptions from the spectrum of the green form suggests that water is not present in that case. It was not possible to diminish the intensity of these absorptions even on prolonged heating under high vacuum.

Under a microscope, both the brown and green forms appear as needlelike crystals. They are yellow-brown when viewed parallel to one of the short axes. The green form is green when viewed parallel to the long axis, but the brown form is yellow-brown. If the crystals are exposed to a moist atmosphere while under the microscope, the intensity of the green form decreases without destruction of the crystal. The X-ray powder patterns of the two forms reveal no changes in the crystal spacings, though some of the intensities are diminished in the powder pattern of the brown form.

The reflectance spectrum was obtained from the hydrated form. Available equipment did not permit measurement of reflectance spectra under a highly protective atmosphere. The spectrum of the hydrated form corresponds to the singlet ground state, as do the magnetic properties, for both are closely similar to those of the iodide and perchlorate complexes.

The behavior of the bromide in the solid state suggests that more than one stereochemical modification may coexist in the crystal. Nyburg and Wood[16] have determined the crystal structure of a yellow form of bis-(C,C'-diphenylethylenediamine)nickel(II) dichloroacetate and found that the unit cell contains both octahedral nickel ions and square-planar nickel ion in the ratio of 2:1. The crystal has an electronic spectrum which is dominated by the features of the diamagnetic metal ions and a magnetic moment of about 2.5 BM. A related example is found for bis(diphenylmethylphosphine)nickel(II) bromide.[17] In this crystal two paramagnetic tetrahedral molecules coexist with one diamagnetic square-planar molecule. The electronic spectrum shows features of both stereochemistries, and the magnetic moment is reported to be 2.8 BM.

In the Ni(PEX)Br₂ crystal, octahedral dibromo molecules may coexist with either the square-pyra-

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(17) B. T. Kilbourn, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 207 (1963).