

Figure 2.—The packing of molecules in the $[\pi\text{-CH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{NiBr}]_2$ crystal, viewed along c .

observed for $[\pi\text{-C}_3\text{H}_5\text{PdCl}]_2^{2d}$ and is in the range predicted by the overlap calculations of Kettle and Mason.¹⁹

TABLE V

$[\pi\text{-CH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{NiBr}]_2$:

BOND ANGLES WITH ESTIMATED STANDARD DEVIATIONS^a

| Atoms | Angle, deg | Atoms | Angle, deg |
|-----------------------------------|------------------|--|-----------------|
| Ni-Br-Ni* | 87.05 ± 0.19 | C ₁ -C ₂ -C ₃ | 119.6 ± 1.3 |
| Br-Ni-Br* | 92.95 ± 0.19 | C ₁ -C ₂ -C ₄ | 121.6 ± 1.8 |
| Br-Ni-C ₁ | 95.09 ± 0.67 | C ₃ -C ₂ -C ₄ | 118.6 ± 1.4 |
| Br*-Ni-C ₃ | 95.45 ± 0.57 | C ₂ -C ₄ -O ₁ | 119.1 ± 1.7 |
| C ₁ -Ni-C ₂ | 43.3 ± 0.80 | C ₂ -C ₄ -O ₂ | 110.6 ± 1.4 |
| C ₂ -Ni-C ₃ | 42.9 ± 0.81 | O ₁ -C ₄ -O ₂ | 130.3 ± 1.4 |
| C ₁ -Ni-C ₃ | 75.6 ± 0.88 | C ₄ -O ₂ -C ₅ | 114.0 ± 1.3 |
| | | O ₂ -C ₅ -C ₆ | 107.1 ± 1.4 |

^a Estimated standard deviations are obtained from the full correlation matrix, using ORFFE

TABLE VI

$[\pi\text{-CH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{NiBr}]_2$: LEAST-SQUARES PLANE THROUGH THE π -ALLYL AND CARBOXYLATE GROUPS (ATOMS WEIGHTED EQUALLY)

Plane:^a $0.4335X + 0.5919Y + 0.6622Z = 3.1818$

| Atom | Deviation from plane | Atom | Deviation from Plane |
|----------------|----------------------|----------------|----------------------|
| C ₁ | -0.027 | C ₄ | +0.006 |
| C ₂ | +0.033 | O ₁ | -0.023 |
| C ₃ | +0.001 | O ₂ | +0.010 |

^a Orthogonal coordinates; see ref 31.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, QUEEN'S UNIVERSITY, BELFAST, NORTHERN IRELAND

High-Spin Five-Coordinate Complexes of Nickel(II) with Di(2-pyridyl- β -ethyl)amine and Di(2-pyridyl- β -ethyl) Sulfide

BY S. M. NELSON AND J. RODGERS

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The tridentate ligands di(2-pyridyl- β -ethyl)amine (DPEA) and di(2-pyridyl- β -ethyl) sulfide (DPES) form stable, crystalline complexes with nickel(II) of general formula NiLX_2 , where $\text{L} = \text{DPEA}$ or DPES and $\text{X}^- = \text{Cl}^-$, Br^- , I^- , or NCS^- . Magnetic, electronic spectral, conductivity, and molecular weight data indicate that the halide complexes have high-spin five-coordinate configurations both in the solid state and in solution in solvents of low polarity. The stereochemistries of the thiocyanato complexes are not certain. In the case of $\text{Ni}(\text{DPEA})(\text{NCS})_2$ the available evidence supports a binuclear, six-coordinate structure containing both bridging and terminal NCS groups. The results are discussed in relation to steric and possible π -bonding effects.

Five-coordination in nickel(II) complexes is now well known.¹ Almost all such complexes are, however, low-spin and usually contain ligand atoms such as P, As, S, or Se capable of forming strong covalent bonds with the metal ion. They also possess vacant d orbitals so

(1) See, for example: G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965); G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398, (1965); D. W. Meek, G. Dyer, M. Workman, and G. S. Benner, Abstracts, 9th International Conference on Coordination Chemistry, St. Moritz, Switzerland, 1966.

there is also the possibility that π bonding may play a part in promoting spin pairing in these compounds. Recently, however, a few high-spin five-coordinate complexes of nickel(II) have been reported. These have contained N-substituted salicylaldimines,² ali-

(2) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965); L. Sacconi, P. Nannelli, N. Nardi, and V. Campigli, *Inorg. Chem.*, **4**, 943 (1965).

phatic polyamines with bulky terminal groups,^{3,4} or the monodentate ligand diphenylmethylarsine oxide.⁵ In all three cases the donor ligand atoms are the electronegative oxygen or nitrogen. This paper describes two series of new high-spin five-coordinate complexes of nickel(II) with the tridentate ligands di(2-pyridyl- β -ethyl)amine (DPEA) and di(2-pyridyl- β -ethyl) sulfide (DPES). The former ligand bears a formal structural similarity to bis(2-dimethylaminoethyl)methylamine which also forms high-spin five-coordinate complexes.⁴ It does, however, incorporate two new features: (i) the chelate rings which it forms are six-membered and (ii) two of the donor atoms (the pyridine ring nitrogens) have available π -acceptor orbitals. The second tridentate ligand studied here (DPES) is the first example of a sulfur-containing ligand to form high-spin five-coordinate nickel(II) complexes.

Experimental Section

Materials.—All materials were of reagent grade quality. Nitromethane was dried over Drierite and fractionally distilled, the fraction with bp 101–101.5° being collected. 1,2-Dichloroethane was dried over Drierite and fractionated (bp 83–84°).

Synthesis of DPEA.—The method and proportions of reactants used by Brady⁶ were employed. On vacuum distilling the crude product, the first fraction consisted of a small amount (7.3% yield) of 2-pyridyl- β -ethylamine, a colorless oil (bp 88–89° (8 mm)). The main product was di(2-pyridyl- β -ethyl)amine (47.1% yield), a pale yellow viscous oil (bp 122–124° (0.05 mm), n_D^{25} 1.5572). It was redistilled before use. *Anal.* Calcd for $C_{14}H_{17}N_3$: C, 73.97; H, 7.54. Found: C, 74.01; H, 7.64. Di(2-pyridyl- β -ethyl)amine proved to be thermally unstable. In several preparations, when the crude product was heated strongly during the distillation, infrared spectra of the distillate showed a peak of moderate intensity in the region for C=CH₂ deformation indicating the presence of substantial quantities of 2-vinylpyridine. However, an infrared spectrum prior to distillation showed no trace of this peak. The pure amine was obtained by employing as high a vacuum as possible and not heating above about 150°.

Synthesis of DPES.—The method of Uhlig⁷ was employed. A 150-ml aliquot of absolute ethanol was saturated with a stream of hydrogen sulfide. Several drops of piperidine was added as catalyst. A solution of 30.0 g of freshly distilled 2-vinylpyridine in 50 ml of ethanol was slowly added with vigorous stirring. During this operation and for a further 30 min a steady stream of hydrogen sulfide was passed through the solution. The ethanol was removed under vacuum, and the residual oil was vacuum distilled. The first fraction consisted of 13.8 g (34.7% yield) of 2-pyridyl- β -ethyl mercaptan (bp 62–64° (0.1 mm)). The second fraction consisted of 20.4 g (58.5% yield) of di(2-pyridyl- β -ethyl) sulfide (bp 146–148° (0.05 mm), n_D^{25} 1.5808). It was redistilled before use. *Anal.* Calcd for $C_{14}H_{16}N_2S$: C, 68.82; H, 6.60. Found: C, 68.63; H, 6.57.

Preparation of Complexes.—The halide complexes were all prepared by the same method. A hot solution of the appropriate hydrated nickel salt in absolute ethanol was added with stirring to a solution of the ligand (same molar proportion) in ethanol. The bromide and iodide complexes separated almost immediately as crystalline solids. The chloride complexes were obtained by adding ether to promote crystallization, followed by cooling. On mixing the solutions of nickel chloride and DPES there was initially a slight dark brown precipitate, which was removed before treatment with ether.

The thiocyanate complexes were obtained by mixing ethanolic solutions of 2:1 molar quantities of potassium thiocyanate and hydrated nickel nitrate, filtering the precipitated potassium nitrate, and slowly adding the resulting solution to an equimolar solution of the ligand. The products separated immediately.

Spectra.—Electronic absorption spectra of solutions were recorded in the range 30,000–5000 cm^{-1} at room temperature using a Unicam SP700 spectrophotometer with 1-cm Infrasil cells. Diffuse-reflectance spectra were measured in the range 30,000–12,500 cm^{-1} using the Unicam SP735 diffuse-reflectance accessory and magnesium oxide as reference. Nujol mulls were mounted on filter paper and measured in the same range as solution spectra using an appropriate blank. Infrared spectra were recorded on a Perkin-Elmer Model 21 with LiF optics, in potassium bromide disks.

Conductivity Measurements.—Electrical conductances were measured at 25° on an ac resistance-capacitance bridge circuit using a magic eye detector.

Molecular Weights.—These were determined in purified 1,2-dichloroethane at 37° (and in dichloromethane at 25°) with a Mechrolab Model 301A vapor pressure osmometer. Calibration was carried out in the range 0.003–0.010 *M* using benzil. Balance readings were taken 2 min after 1 drop of the solution was placed on the thermistor. The solutions were approximately 0.005 *M*. Reproducibility of the balance reading was $\pm 5\%$ at this concentration. Reported values (Table III) are the means of not less than three determinations.

Magnetic Measurements.—Magnetic susceptibility measurements were made at room temperature using the Gouy method. The calibrant was $Hg[Co(SCN)_4]$.

Results and Discussion

The complexes to be described all have the stoichiometry $NiLX_2$ where L is the tridentate ligand DPEA or DPES, and X is a halide or NCS. Colors and analytical data are given in Table I. With the exception of $Ni(DPES)Cl_2$, none of the complexes is appreciably hygroscopic. Table II gives the magnetic moments determined at room temperature. The values 3.1–3.3 BM fall within the range expected for spin-free nickel(II).

The Halide Complexes.—It is believed that the chloride, bromide, and iodide complexes with both tridentate ligands contain five-coordinate nickel(II) atoms. The evidence for five-coordination comes from the stoichiometry, molecular weight, electrical conductance, and electronic spectral measurements. That all but one of the complexes have nonionic structures in nitromethane is demonstrated by the conductivity data (Table III). With one exception, $Ni(DPES)I_2$, the observed conductances in nitromethane do not exceed about 30% of the value expected for typical univalent electrolytes. The relatively small conductances that are observed may be attributed to a partial displacement of coordinated halide by solvent molecules. The fact that with both series of complexes the conductivity increases from chloride to bromide to iodide is consistent with this view since the coordinating power of the halide ions usually decreases in this same sequence, at least with predominantly class A acceptors such as nickel(II). In the case of $Ni(DPES)I_2$, there is clearly extensive solvolysis in nitromethane solution and this conclusion is supported by the spectral data to be considered below.

The monomeric nature of the complexes in nonpolar

(3) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

(4) M. Ciampolini and G. P. Sponeri, *ibid.*, **5**, 45 (1966).

(5) J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, **207**, 72 (1965).

(6) L. E. Brady, *J. Org. Chem.*, **26**, 4757 (1961).

(7) E. Uhlig and G. Heinrich, *Z. Anorg. Allgem. Chem.*, **330**, 45 (1964).

TABLE I
 COLORS AND ANALYTICAL DATA FOR THE NICKEL(II) COMPLEXES

| Compound | Color | % Ni | | % C | | % H | | % N | |
|--------------------------------------|--------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| Ni(DPEA)Cl ₂ | Green | 16.44 | 16.26 | 47.11 | 46.77 | 4.80 | 4.86 | 11.77 | 11.90 |
| Ni(DPEA)Br ₂ | Green | 13.16 | 13.20 | 37.71 | 38.06 | 3.84 | 3.72 | ... | ... |
| Ni(DPEA)I ₂ | Dark green | 10.87 | 10.92 | 31.16 | 31.58 | 3.18 | 3.58 | ... | ... |
| Ni(DPEA)(SCN) ₂ | Blue | 14.60 | 14.55 | 47.78 | 48.16 | 4.27 | 4.52 | ... | ... |
| Ni(DPES)Cl ₂ | Green | 15.70 | 15.51 | 44.96 | 44.74 | 4.31 | 4.31 | 7.49 | 7.62 |
| Ni(DPES)Br ₂ ^a | Yellow-green | 12.69 | 12.71 | 36.34 | 36.14 | 3.49 | 3.54 | 6.05 | 5.95 |
| Ni(DPES)I ₂ | Brown | 10.54 | 10.54 | 30.21 | 30.56 | 2.90 | 2.85 | ... | ... |
| Ni(DPES)(SCN) ₂ | Pale green | 14.01 | 13.87 | 45.83 | 45.88 | 3.85 | 4.14 | ... | ... |

^a Anal. Calcd for Ni(DPES)Br₂: S, 6.93; Br, 34.53. Found: S, 7.05; Br, 34.47.

 TABLE II
 MAGNETIC DATA FOR THE NiLX₂ COMPLEXES

| Compound | Temp, °C | 10 ⁵ χ _g | 10 ⁵ χ _M ^{cor a} | μ _{eff} , BM |
|----------------------------|----------|--------------------------------|---|-----------------------|
| Ni(DPEA)Cl ₂ | 18.3 | 12.03 | 4497 | 3.25 |
| Ni(DPEA)Br ₂ | 20.4 | 9.68 | 4541 | 3.28 |
| Ni(DPEA)I ₂ | 17.7 | 7.35 | 4225 | 3.15 |
| Ni(DPEA)(SCN) ₂ | 18.5 | 10.11 | 4282 | 3.17 |
| Ni(DPES)Cl ₂ | 18.3 | 11.12 | 4357 | 3.20 |
| Ni(DPES)Br ₂ | 18.5 | 9.49 | 4613 | 3.29 |
| Ni(DPES)I ₂ | 18.4 | 7.21 | 4265 | 3.17 |
| Ni(DPES)(SCN) ₂ | 18.6 | 9.41 | 4158 | 3.13 |

^a Diamagnetic corrections were calculated from Pascal's constants.

TABLE III

| Compound | Molar conductance, ΔM, ^a ohm ⁻¹ cm ² | | Mol wt ^b | | |
|-------------------------|--|------------------|---------------------|-------|-----|
| | CH ₃ NO ₂ | H ₂ O | Calcd | Found | |
| Ni(DPEA)Cl ₂ | 7.4 | 236 | 357 | 366 | ... |
| Ni(DPEA)Br ₂ | 8.6 | 244 | 446 | 471 | 439 |
| Ni(DPEA)I ₂ | 33.2 | 240 | 540 | 553 | 528 |
| Ni(DPES)Cl ₂ | 20.6 | ... | ... | ... | ... |
| Ni(DPES)Br ₂ | 25.9 | ... | 463 | 479 | ... |
| Ni(DPES)I ₂ | 70.1 | ... | 557 | 543 | ... |

^a 10⁻³ M solutions at 25°. ^b 5 × 10⁻³ M solutions.

solvents is shown by the molecular weight data (Table III) in 1,2-dichloroethane (or in dichloromethane also, in two cases). In spite of the rather low solubility of the compounds (*ca.* 5 × 10⁻³ M), agreement between observed values and those calculated for the NiLX₂ monomer is good, even in the case of Ni(DPES)I₂, for which conductivity measurements in the much more polar solvent nitromethane indicate extensive solvolysis.

Electronic spectra were measured both in the solid state and in solution in dichloroethane, nitromethane, and water. Band maxima and molar extinction coefficients are reported in Table IV. For the solution spectra and Nujol mull transmittance spectra the range covered was 30,000–5000 cm⁻¹. However, for the diffuse-reflectance spectra, measurements were restricted to energies higher than 12,500 cm⁻¹. Solution spectra in dichloroethane (and also in nitromethane in most cases) are in good agreement with the diffuse-reflectance spectra, not only with regard to band position but also, qualitatively, with respect to relative intensities of the bands. Agreement with the solid transmittance spectra is also good except in a few cases at energies below about 10,000 cm⁻¹. The quality of the latter spectra in this low-energy region, however,

 TABLE IV
 MAXIMA AND EXTINCTION COEFFICIENTS
 FOR THE SPECTRA OF THE COMPLEXES

| Compound | State | Absorption max, cm ⁻¹ (ε _M for soln) |
|----------------------------|---|--|
| Ni(DPEA)Cl ₂ | DR ^a | 24,400, 19,800 sh, 15,000 |
| | C ₂ H ₄ Cl ₂ | 24,500 (129), 19,600 sh, 15,100 (49), 11,500 sh, 8700 (21) |
| | H ₂ O | 26,800 (14.5), 16,300 (7.8), 13,300 sh, 10,400 (7.3) |
| Ni(DPEA)Br ₂ | DR | 24,500, 19,500 sh, 15,300 |
| | C ₂ H ₄ Cl ₂ | 24,400 (240), 19,500 sh, 15,200 (81), 8800 (25) |
| | H ₂ O | 26,800 (12.7), 16,300 (7.7), 13,300 sh, 10,400 (7.2) |
| Ni(DPEA)I ₂ | DR | ≈24,700, 15,300 |
| | Nujol mull | ≈24,200, 15,400, 8700 |
| | C ₂ H ₄ Cl ₂ | 31,600 (6040), ^b 27,500 (2870), ^b 24,700 (4300), 15,300 (148), 8700 (33) |
| Ni(DPEA)(SCN) ₂ | H ₂ O | 26,800 (11.8), 16,300 (7.2), 13,300 sh, 10,400 (6.8) |
| | DR | 26,500 sh, 16,600 |
| | Nujol mull | 26,300 sh, 16,600, 12,700 sh, 11,400, 8400 |
| Ni(DPES)Cl ₂ | DR | 24,600, 20,500 sh, 18,700 sh, 14,900 |
| | C ₂ H ₄ Cl ₂ | 23,100 (122), 18,800 sh, 14,100 (44), 8500 (18) |
| | DR | 22,300, 18,800 sh, 13,700 |
| Ni(DPES)Br ₂ | Nujol mull | 22,400, 18,700 sh, 13,800, 8700 |
| | C ₂ H ₄ Cl ₂ | 22,600 (272), 18,600 sh, 14,000 (79), 8300 (19) |
| | DR | ≈23,100, ≈21,100, 14,900 sh, 13,700 |
| Ni(DPES)I ₂ | C ₂ H ₄ Cl ₂ | 34,600 (7840), ^b 28,600 (5460), ^b 22,900 (1650), 14,500 (124), 8200 (20) |
| | CH ₃ NO ₂ | 15,100 (99), 13,900 sh, 8600 (17) |
| | DR | ≈28,400, 19,700 sh, 16,400 |
| Ni(DPES)(SCN) ₂ | Nujol mull | 20,000 sh, 16,400, 8600 |

^a Diffuse reflectance spectrum. ^b Charge-transfer absorption.

was poor and it was sometimes difficult to locate the positions of the weak bands occurring in this region precisely. In spite of this, there can be little doubt that the complexes dissolve in nonpolar solvents without appreciable decomposition or configurational rearrangement. A special case is Ni(DPES)I₂ in nitromethane. The high conductance of nitromethane solutions of this complex has already been mentioned. Here, in contrast to the other complexes, the spectrum of the nitromethane solution is distinctly different from that of the solid or of the solution in dichloroethane. There

are two differences: (i) molar extinction coefficients are smaller than in dichloroethane and (ii) the absorption maximum at $13,700\text{ cm}^{-1}$ in the solid has fallen in intensity relative to the shoulder at $\sim 14,900\text{ cm}^{-1}$ which, in nitromethane, has become the point of maximum absorption in this region. It seems clear from both the spectral and the conductance data that partial decomposition of this complex into ionic species occurs in this solvent. It is not possible, however, to identify the nature of the product(s) of decomposition on the information available. There are also slight band shifts in the dichloroethane solution spectra, relative to the solid, suggesting that here also there may be some decomposition; however, the molecular weight data indicate that the effect must be very small.

The electronic spectra (in the solid state or in dichloroethane solution) consist of three main bands: (i) at $8200\text{--}8800\text{ cm}^{-1}$ (ϵ_M 18–33), (ii) at $14,000\text{--}15,300\text{ cm}^{-1}$ (ϵ_M 44–148), and (iii) at $22,300\text{--}24,700\text{ cm}^{-1}$ (ϵ_M 122 to *ca.* >1000). Estimation of ϵ_M for the third band for the iodo complexes is difficult since it is overlapped by strong charge-transfer absorptions. The similarity in the spectra of all six complexes is striking. Change in band position with change in coordinated halide is small, particularly for the DPEA series. There are, however, marked increases in the intensities of the bands with increase in the polarizability of the halide, particularly in the case of the highest energy transition. The band maxima of the DPES complexes are shifted to lower energies, with respect to the DPEA compounds, indicating the lower field strength of the thioether ligand (Figure 1). Although there is a resemblance of the spectra, with regard to band position, to those of octahedral nickel(II) complexes, this stereochemistry is ruled out by the high extinction coefficients of the two higher energy bands and also by the relative intensities of the bands. Ciampolini has recently published⁸ the splitting of the free-ion terms of nickel(II) for five equivalent point dipoles (at 2.00 Å from the metal atom) in square-pyramidal and trigonal-bipyramidal fields. Table V compares the observed positions of the band maxima with those obtained by interpolation from Ciampolini's energy level diagram for a trigonal-bipyramidal field with $\mu \approx 6.0\text{ D.}$, for Ni(DPEA)Br₂ and Ni(DPES)Br₂. Having regard for the assumptions of the model and the fact that the complexes have a symmetry lower than D_{3h}, the agreement seems fair.

While five spin-allowed transitions are predicted, only three major bands are observed. However, two of the levels derived from the ³F term lie close together and transitions to them are not expected to be resolved. Also the highest energy transition corresponds to a two-electron jump in the strong-field limit; it should therefore be weak and in any case might well be masked by the stronger ligand absorption or halide charge-transfer bands occurring in this region. A weak absorption at $\sim 19,000\text{ cm}^{-1}$, which shows good correspondence to a spin-forbidden transition to the singlet

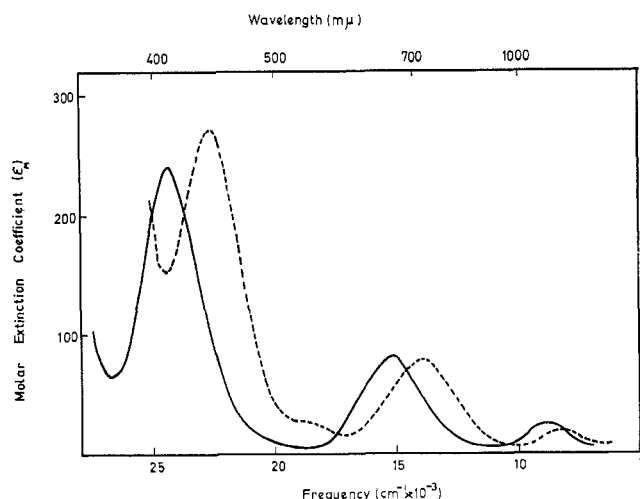


Figure 1.—Electronic spectra of Ni(DPEA)Br₂ (continuous line) and Ni(DPES)Br₂ (dotted line) in 1,2-dichloroethane.

TABLE V
COMPARISON OF OBSERVED SPECTRA WITH THOSE
PREDICTED FOR TRIGONAL-BIPYRAMIDAL NICKEL(II)

| Transition | Band max, cm ⁻¹ | | |
|--|---|--|-------------------------------------|
| | Calcd ^a for $\mu = 6.0\text{ D.}$ | Obsd ^b for Ni(DPEA)Br ₂ | Obsd for Ni(DPES)Br ₂ |
| ³ E' → ³ E''(F) | 7,600 | 8,800 | 8,300 |
| $\left\{ \begin{array}{l} {}^3A_1'' \\ {}^3A_2'' \end{array} \right\}$ | 16,700 | 15,200 | 14,000 |
| ¹ E'' | 19,000 | 19,500 | 18,700 |
| ³ E''(P) | 24,300 | 24,400 | 22,600 |

^a Reference 8. ^b C₂H₄Cl₂ solution.

¹E'' level, is also observed in the spectra of both complexes.

Agreement of the observed spectra with those predicted⁸ and observed² for a square-pyramidal field is less satisfactory. For this configuration a total of six spin-allowed transitions is expected. Until complete X-ray structure determinations⁹ are carried out, the precise arrangement of the ligands must remain uncertain. In view of the nonequivalence of the ligand atoms, a completely regular structure is not possible. However, the electronic spectral evidence suggests that the complexes have configurations closer to the trigonal-pyramidal extreme.

The combined results presented above provide positive evidence for high-spin five-coordinate structures for all of the halide complexes in the solid state and for the predominant species in dichloroethane solution. The evidence also specifically excludes alternative structures involving other coordination numbers, such as a dimeric six-coordinate complex with halide bridging, or planar or tetrahedral [NiLX]⁺X⁻ salt structures. One of the complexes, Ni(DPES)Cl₂, has been prepared previously by Uhlig and Heinrich,⁷ who proposed a dimeric octahedral structure with bridging chlorides on the basis of the magnetism and low conductance in acetonitrile. In the light of the present evidence, this is clearly not correct.

(9) A preliminary single-crystal X-ray study reveals that Ni(DPEA)Br₂ is monoclinic, with the cell parameters: $a = 13.88 \pm 0.1\text{ Å}$, $b = 14.51 \pm 0.1\text{ Å}$, $c = 7.98 \pm 0.1\text{ Å}$, $\beta = 100^\circ 24' \pm 1^\circ$. The crystals are twinned with the *c* axis common to the components of the twin.

(8) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

When the chloro, bromo, and iodo complexes of DPEA were dissolved in water, the resulting blue solutions showed identical electronic spectra (Table IV) and almost identical extinction coefficients. The spectrum is typical of octahedral nickel(II) and does not show the strong absorption in the near-ultraviolet region which would be expected for coordinated halide (at least in the case of the bromide and iodide). Taken in conjunction with the fact that all three complexes behave as uni-bivalent electrolytes in water (Table III), the spectral evidence indicates the formation of $[\text{Ni}(\text{DPEA})(\text{H}_2\text{O})_3]^{2+}$. When a gross excess of DPEA was added to these solutions, no significant change in the spectrum was found and thus there was no evidence to support the formation of $[\text{Ni}(\text{DPEA})_2]^{2+}$ in solution. Attempts to isolate BF_4^- and ClO_4^- salts of this complex ion were unsuccessful.

The Thiocyanate Complexes.—Both $\text{Ni}(\text{DPEA})(\text{NCS})_2$ and $\text{Ni}(\text{DPES})(\text{NCS})_2$ are very poorly soluble in nonpolar solvents and even in nitromethane. Data for these complexes are therefore limited to the solid-state electronic and vibrational spectra. The former are shown in Figure 2. The spectrum of $\text{Ni}(\text{DPEA})(\text{NCS})_2$ is distinctly different in band position and in profile from the spectra of the halide complexes discussed above. It is, rather, typical of the spectra of distorted octahedral complexes. The two higher energy bands at 26,300 and 16,600 cm^{-1} are tentatively assigned to the transitions from the ${}^3\text{A}_{2g}$ ground state (in O_h symmetry) to the levels ${}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{T}_{1g}(\text{F})$, respectively, and the two low-energy bands at 11,400 and 8400 cm^{-1} to the split components of the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ transition. The infrared spectrum shows two well-resolved bands of nearly equal intensity (at 2094 and 2128 cm^{-1}) in the region expected for the NCS anti-symmetric stretching vibration. Splitting of this order has previously been shown¹⁰ to occur when two different kinds of NCS group occur in the same molecule. The 2128- cm^{-1} band falls in the region expected for bridging NCS and the 2094- cm^{-1} band, in the region expected for terminal NCS.¹¹ Two absorption bands (at 476 and 457 cm^{-1}) also occur in the NCS bending vibration region; the corresponding halide complexes do not absorb between 450 and 500 cm^{-1} . The symmetric stretching vibrations of coordinated NCS could not be assigned because of overlapping ligand absorption between 750 and 820 cm^{-1} . However, the region 650–750 cm^{-1} is completely free of absorption so it seems very unlikely that terminal sulfur-bonded NCS groups are present. On the basis of the evidence of both the electronic and the vibrational spectra, therefore, a binuclear structure such as shown in Figure 3 is suggested for this complex. The adoption of the higher coordination may be due to the smaller size of the NCS group compared to the halide ions. In addition, electronic effects may be of some importance. In a study of the relative stabilities of tetrahedral and octahedral cobalt(II) and nickel(II) com-

(10) J. Chatt and L. A. Duncaison, *Nature*, **178**, 997 (1956).

(11) S. M. Nelson and T. M. Shepherd, *J. Inorg. Nucl. Chem.*, **27**, 2123 (1965).

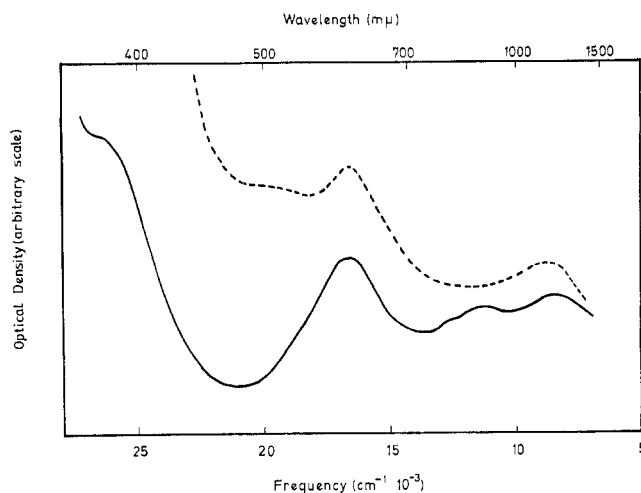


Figure 2.—Transmittance spectra of Nujol mulls of $\text{Ni}(\text{DPEA})(\text{NCS})_2$ (continuous line) and $\text{Ni}(\text{DPES})(\text{NCS})_2$ (dotted line).

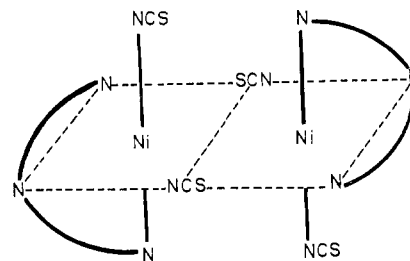


Figure 3.—Suggested structure for $\text{Ni}(\text{DPEA})(\text{NCS})_2$.

plexes, it has been observed that NCS consistently stabilizes the higher coordination number.¹²

Figure 2 also shows the electronic spectrum of solid $\text{Ni}(\text{DPES})(\text{NCS})_2$. This shows similarity both to that of $\text{Ni}(\text{DPEA})(\text{NCS})_2$ and to those of the five-coordinate halide complexes. The infrared spectrum shows single bands only at 2094 and 474 cm^{-1} in the NCS anti-symmetric stretching and in the NCS bending regions, respectively. As with $\text{Ni}(\text{DPEA})(\text{NCS})_2$, no absorption occurs in the 650–750- cm^{-1} region. In the absence of other evidence the structure must remain uncertain.

It seems highly probable that the fivefold coordination and the high-spin electronic configuration for complexes of DPEA and DPES arise from (i) the weak nature of the average ligand field, which ensures that the ground state is a triplet, and (ii) a steric limitation to the attainment of the more usual higher coordination number of six. Thus, as pointed out above, no evidence for the formation of the bis-tridentate cation $[\text{Ni}(\text{DPEA})_2]^{2+}$ was found. Molecular models support the idea of severe steric hindrance in this complex ion; the hydrogen atoms on the carbons of the aliphatic side chain of the tridentate ligand molecule prevent the close approach of the pyridine nitrogens of a second molecule to the metal ion. Steric effects are even greater for DPES and it may be that the greater solvolysis in nitromethane of the DPES complexes arises from a greater steric interaction even when the coordination number is five.

(12) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963); 4832 (1964); S. M. Nelson and T. M. Shepherd, *ibid.*, 3284 (1965).

It is of interest to compare the electronic spectra of the DPEA series of complexes with those of the structurally similar tridentate, $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2$, studied by Ciampolini and Speroni⁴ to which five-coordinate structures have been attributed. The spectra of the two series of complexes are similar. However, the absorption bands in the spectra of the DPEA series occur at positions about 3000 cm^{-1} higher in energy. Assuming the same stereochemistry, this represents a very substantial increase in effective ligand field strength. There are two possible interpretations of this effect. Either there is greater steric hindrance (which is not apparent from an examination of molecular models) in the aliphatic triamine complex causing reduced metal-ligand interaction or there is a measure of metal-pyridine π overlap in the DPEA (and DPES) complexes. The latter explanation seems the more likely. Evidence for nickel-to-pyridine π bonding in (six-coordinate) nickel(II) complexes has been presented previously.^{12,13}

(13) S. M. Nelson and T. M. Shepherd, *Inorg. Chem.*, **4**, 813 (1965).

Finally, it is of interest to note that, in the aliphatic polyamine complexes studied by Ciampolini and co-workers,^{3,4} the chelate rings are five membered. In both ligands reported in the present work, the chelate rings have six member atoms. When the ring size is reduced to five as in chelates of di(2-pyridylmethyl)amine (DPMA), stable six-coordinate complex ions containing two ligand molecules are formed,¹⁴ e.g., $[\text{Ni}(\text{DPMA})_2]^{2+}$. Solutions containing this complex ion have spectra typical of nickel(II) complexes of O_h symmetry with $Dq = 1255\text{ cm}^{-1}$, a value only 10 cm^{-1} lower than that observed for the very stable tris(dipyridyl)nickel(II) cation.

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(14) S. M. Nelson and J. Rodgers, Proceedings of the 9th International Symposium on Coordination Chemistry, St. Moritz, Switzerland, 1966.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Five-Coordination. IV. Nickel(II) Complexes of Diphenyl(*o*-diphenylarsinophenyl)phosphine¹⁻³

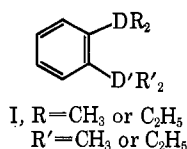
BY THOMAS D. DUBOIS AND DEVON W. MEEK

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Diphenyl(*o*-diphenylarsinophenyl)phosphine forms four-coordinate, diamagnetic $[\text{Ni}(\text{ligand})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) complexes, five-coordinate, diamagnetic $[\text{Ni}(\text{ligand})_2\text{X}]\text{ClO}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{NCS}, \text{NCSe}$) complexes, and the six-coordinate, paramagnetic $[\text{Ni}(\text{ligand})_2(\text{NCS})_2]$ complex. These compounds have been characterized by magnetic and conductivity measurements, electronic and infrared spectra, and elemental analyses. The electronic spectra of the five-coordinate complexes differ significantly from those of trigonal-bipyramidal nickel(II) complexes with ligands containing similar donor atoms and may be interpreted in terms of a square-pyramidal structure.

Introduction

Several *o*-phenylene compounds (I) in which D and D' are phosphorus, arsenic, or nitrogen or any com-



ination of them have been prepared and the properties of selected coordination compounds investigated.^{4,5}

(1) The authors gratefully acknowledge the financial support of this research by the National Science Foundation (Grant No. GP-5729).

(2) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; Abstracts, No. H-64.

(3) Part III: G. Dyer and D. W. Meek, *Inorg. Chem.*, **6**, 140 (1967).

(4) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 560 (1958), and references therein; *ibid.*, 564, 567, 572 (1958); J. E. Fergusson and R. S. Nyholm, *Chem. Ind. (London)*, 1555 (1958); N. F. Curtis, J. E. Fergusson, and R. S. Nyholm, *ibid.*, 625 (1958); H. L. Nigam and R. S. Nyholm, *Proc. Chem. Soc.*, 321 (1957); J. Chatt and F. A. Hart, *Chem. Ind. (London)*, 1474 (1958).

For example, the ligand *o*-phenylenebisdimethylarsine ($\text{D} = \text{D}' = \text{As}$ and $\text{R} = \text{R}' = \text{CH}_3$) forms the tetragonal, six-coordinate complexes $[\text{M}(\text{diarsine})_2\text{I}_2]$ (where $\text{M} = \text{Ni}, \text{Pd},$ and Pt) in the solid state,^{6,7} however, these compounds are uni-univalent electrolytes and five-coordinate in solution.⁸ This ligand also forms $[\text{Ni}(\text{diarsine})_3](\text{ClO}_4)_2$, which is thought to be the only regular octahedral, diamagnetic nickel(II) complex.⁹ In contrast to the diarsine ligand, only planar $[\text{Ni}(\text{diphos-}$

(5) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 1269 (1955); E. R. H. Jones and F. G. Mann, *ibid.*, 4472 (1955); W. Cochran, F. A. Hart, and F. G. Mann, *ibid.*, 2816 (1957); F. A. Hart and F. G. Mann, *Chem. Ind. (London)*, 574 (1956); *J. Chem. Soc.*, 3939 (1957); F. G. Mann and H. R. Watson, *ibid.*, 3945, 3950 (1957).

(6) N. C. Stephenson and G. A. Jeffrey, *Proc. Chem. Soc.*, 173 (1963).

(7) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 791, 797 (1962).

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(9) B. Bosnich, R. Bramley, R. S. Nyholm, and M. L. Tobe, *J. Am. Chem. Soc.*, **88**, 3926 (1966).