number of electrons participating in each type can be arrived at from the data. The ϵ_{1g} MO represents the donation of ligand electrons to the metal. In these complexes a value of 0.4 ± 0.1 electron is donated by each Cp in the $\pi(\epsilon_{1g})$ MO to the metal 3dϵ. The ϵ_{2g} MO represents the back-acceptance of electrons from the Fe 3dδ into the ligand $\pi^*(\epsilon_{2g})$. A value of 0.5 ± 0.1 electron back-accepted by each Cp is obtained from the data. If we assume that all of the errors in the interpretation are cumulative, an error of ±0.1 electron can be placed on these numbers.

It cannot be said unequivocally at this point that Cb_2Co^- and Cp_2Co^+ are for practical purposes identical with the isoelectronic Cb_2Fe^{2-} and Cp_2Fe. However, it would appear from all available data that they are indeed very similar. Certainly Cb^{2-} and Cp^- are practically indistinguishable in their bonding to Co(III) and Fe(II), respectively.

Acknowledgment.—The $Cs(1,2\text{-}B_9C_2H_{11})Co$ salts were generously supplied by Professor M. F. Hawthorne, University of California, Riverside, Calif. This work was supported by the Inorganic Materials Research Division, Lawrence Radiation Laboratory, under the auspices of the United States Atomic Energy Commission.

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Five-Coordination with "Hybrid" Ligands. III.[1] High- and Low-Spin Five-Coordinate Nickel(II) Complexes with Ligands Containing Oxygen, Sulfur, Nitrogen, Phosphorus, and Arsenic Donor Atoms

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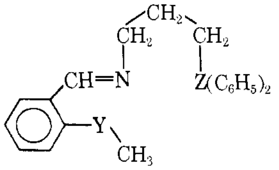
Tridentate Schiff bases formed from *ortho*-substituted benzaldehydes and 3-aminopropyldiphenylphosphine or 3-aminopropyldiphenylarsine (donor sets NNP, ONP, SNP, NNAs, ONAs, SNAs) form with nickel(II) bromide and iodide high- and low-spin complexes with the general formula $NiLX_2$. Their stereochemistry is assigned by spectrophotometric, molecular weight, conductometric, and magnetic susceptibility measurements. Results are discussed mainly in terms of the electronic properties of the donor atoms.

Introduction

Several five-coordinate complexes formed by nickel(II) salts, most often halides, with tridentate ligands, of the general formula $NiLX_2$, have been already described. The first complexes which were isolated were of the low-spin type where the ligands contained the sets of donor atoms AsAsAs, SPS, and PSP.[2-4] Since 1965 high-spin complexes obtained from tridentate ligands with NNN,[5,6] SNN,[7] ONN,[8] NON,[9] and NSN[10] donor sets have been also characterized. The stereochemistry of the complexes so far studied by X-ray analysis has been found to be intermediate between the square pyramid and the trigonal bipyramid. Ligands forming low-spin complexes always contain donor atoms of low electronegativity (P and/or As) and capable of back-bonding; ligands forming high-spin complexes invariably contain highly electronegative donor atoms such as O or N.

In order to study the donor atom influence on the stereochemistry and spin multiplicity of five-coordinate nickel(II) complexes, we have undertaken a thorough investigation systematically varying the donor atoms of tridentate ligands. In previous papers we have reported the results obtained with ligands formed by Schiff bases derived from *ortho*-substituted benzaldehydes and N,N-disubstituted ethylene- and trimethylenediamine (donor sets NNN, SNN, and ONN).[6-8] We wish now to report the results obtained with similar ligands, formed by the reaction of the same aldehydes and 3-aminopropyldiphenylphosphine or 3-aminopropyldiphenylarsine, of the general formula



I, Y = NH, O, S; Z = P, As

The trifunctional ligands formed contain donor atoms that are both high- and low-spin inducing. The

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sets of donor atoms obtained are NNP, ONP, SNP, NNAs, ONAs, and SNAs. These short symbols will also be used to represent the ligands. With nickel(II) bromide and iodide in anhydrous solvents such as 1-butanol, these ligands form crystalline compounds of the general formula $Ni(YNZ)X_2$. They have been characterized by means of spectrophotometric, magnetic, conductivity, and molecular weight measurements.

Experimental Section

Aromatic *ortho*-Substituted Aldehydes.—The aromatic aldehydes *o*-methylaminobenzaldehyde,[6] *o*-methylthiobenzaldehyde,[11] and *o*-methoxybenzaldehyde[12] were prepared by methods already described in the literature.

3-Aminopropyldiphenylphosphine.—It was prepared with a method essentially analogous to that described by Amundsen and Nelson[13] for the reduction of aliphatic nitriles to the corresponding amines with lithium aluminum hydride. To an ice-cold solution of 2.4 g (0.063 mol) of $LiAlH_4$ in 200 ml of anhydrous ethyl ether was slowly added 15 g (0.063 mol) of 2-cyanoethyldiphenylphosphine[14] dissolved in *ca.* 100 ml of anhydrous ether. To ensure complete dissolution a small amount of anhydrous THF was added. After stirring and refluxing for a few minutes, 2.5 ml of water, 1.9 ml of 20% NaOH, and 8.8 ml of water were cautiously added in succession. The solution was decanted from the white granular residue. The residue was washed twice with ether, after which all of the ether portions were combined and dried over anhydrous Na_2SO_4. The solvent was distilled off and the product was distilled at 150° (0.4 torr) to yield about 12 g (78%) of 3-aminopropyldiphenylphosphine as a dense yellow oil.

3-Aminopropyldiphenylarsine.—The method was the same as above except that 2-cyanoethyldiphenylarsine[15] was substituted for the corresponding phosphine. The product was distilled at 161–163° (0.8 torr); yield *ca.* 66%.

Synthesis of the Ligands.—All of the Schiff bases were prepared by the same general method. Stoichiometric amounts of the aldehyde and the aminophosphine or -arsine (about 0.03 mol) were mixed and warmed for 10 min on the steam bath. A few grams of finely crushed anhydrous $CaSO_4$ was then added. The mixture was allowed to stand overnight and then mixed with 10–15 ml of 1-butanol; the solution was filtered and stored at −20° until the Schiff base separated in a crystalline form. The ligands ONP and ONAs, which did not crystallize under the above conditions, were extracted with petroleum ether and recrystallized from the same solvent. All of the ligands are yellowish white, low-melting crystals, whose physical and analytical data follow. **NNP:** *Anal.* Calcd for $C_{23}H_{25}N_2P$: C, 76.64; H, 6.99; N, 7.77; P, 8.59. Found: C, 76.68; H, 7.17; N, 7.85; P, 8.66; mp 93–95°. **NNAs:** *Anal.* Calcd for $C_{23}H_{25}N_2As$: C, 68.31; H, 6.23; N, 6.92; As, 18.52. Found: C, 68.60; H, 6.51; N, 7.08; As, 18.26; mp 84–86°. **SNP:** *Anal.* Calcd for $C_{23}H_{24}NSP$: C, 73.18; H, 6.41; N, 3.71. Found: C, 72.00; H, 6.59; N, 3.63; mp 78–79°. **SNAs:** *Anal.* Calcd for $C_{23}H_{24}NSAs$: C, 65.55; H, 5.74; N, 3.32. Found: C, 65.53; H, 6.03; N, 3.18; mp 79–80°. **ONP:** *Anal.* Calcd for $C_{23}H_{24}NOP$: C, 76.44; H, 6.69; N, 3.87; P, 8.57. Found: C, 75.96; H, 6.73; N, 4.02; P, 8.38; mp 58–58.5°. **ONAs:** *Anal.* Calcd for $C_{23}H_{24}NOAs$: C, 68.15; H, 5.96; N, 3.45; As, 18.48. Found: C, 68.32; H, 6.16; N, 3.44; As, 18.28; mp 58–60°.

Preparation of the Complexes.—For all of the complexes except those of the SNP ligand the same general method was employed. A sample of 1 mmol of the ligand dissolved in 10 ml of 1-butanol was added to a hot solution of 1 mmol of the appropriate nickel salt in the same solvent. In some cases, for example $Ni(ONP)I_2$, a fine precipitate separated, which redissolved upon heating and stirring the solution. In these cases the solution was concentrated and cyclohexane was added dropwise to induce crystallization of the complex. In those cases when crystallization did not occur in the hot concentrated solution, it was allowed to cool in a desiccator and stored until the crystals separated. In the case of the SNP complexes, a black resinous solid separated on boiling the solution (possibly because of ligand decomposition), so they were prepared by mixing concentrated solutions of the ligand and the nickel salt at room temperature. All of the compounds were filtered using a sintered-glass funnel, washed with 1-butanol and petroleum ether, and then dried in a vacuum oven at 70°. They were recrystallized either from butanol–cyclohexane or butanol–chloroform mixtures.

Physical Measurements.—The absorption spectra were recorded with a Beckman DK 2 spectrophotometer using 1-cm silica cells. The absorption spectrum at various temperatures was recorded in *o*-dichlorobenzene solution. Allowance was made for the temperature variation of solution density when calculating extinction coefficients. The reflectance spectra were measured with the standard Beckman reflectance attachment using magnesium oxide as the reference.

The magnetic measurements were performed by the Gouy method with the apparatus and experimental technique described previously.[16] The sample tube was calibrated with $Hg[Co(NCS)_4]$ and freshly distilled water.[17]

The molar conductivity values were measured at 25° with a WTW Model LBR/B conductance bridge. The molecular weight measurements were performed using a Mechrolab Model 301 A vapor pressure osmometer calibrated with benzil.

Results and Discussion

All of the complexes are crystalline, deeply colored, and generally stable in dry air. With the exception of $Ni(NNP)I_2$ and $Ni(ONAs)Br_2$, the complexes are rather soluble in common polar organic solvents, such as nitro and chloro derivatives. Nitroethane solutions of the iodide compounds become turbid on standing. Analytical data and physical properties are reported in Table I. The complexes are all paramagnetic except $Ni(NNP)I_2$ and $Ni(SNP)I_2$ which are diamagnetic.

Paramagnetic Complexes.—These compounds show values of μ_{eff} ranging between 3.12 and 3.38 BM (Table I). The reflectance spectra, recorded between 5000 and 25,000 cm^{-1} (Table II, Figure 1), although poorly resolved, are not so different from the corresponding absorption spectra in 1,2-dichloroethane as to suggest a substantial change in the stereochemistry. All of the spectra show essentially the same features, but for a given donor atom or group Y (I) the frequencies of the bands shift on varying the type of other donor atoms. The shifts are in agreement with the positions of phosphorus, arsenic, and the halogens in the spectrochemical series ($P > As$, $Br > I$). This suggests that these atoms are in all cases coordinated to the metal. Upon varying Y, larger shifts are observed. In particular, the band at *ca.* 14,300–14,900 cm^{-1} shifts to 13,900–14,300 and to 11,600–12,900 cm^{-1} for Y = NH and O, respectively.

The features of all of the spectra seem to exclude an octahedral structure for these complexes. This geom-

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TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE COMPLEXES

Compound	Color	Mp or dec pt, °C	μ_{eff}, BM (°C)	Δ_M,[b] cm²/ohm M	% C		% H		% metal		% other	
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Ni(NNP)Br_2[a]	Mustard	212–218	3.12 (21)	0.87	47.71	47.80	4.35	4.70	10.14	9.93	4.84	4.59 (N)
Ni(NNP)I_2	Dark brown	210	diam (21)		41.04	40.92	3.74	3.73	8.72	8.76		
Ni(ONP)Br_2[a]	Brown	185–188	3.28 (22)	0.50	47.63	47.80	4.17	4.51	10.12	10.12	5.34	5.40 (P)
Ni(ONP)I_2	Brown	180	3.20 (25)	1.00	40.98	40.70	3.59	3.58	8.71	8.80	4.60	4.65 (P)
Ni(SNP)Br_2[a]	Mustard	214–218	3.36 (21)	0.40	46.35	46.20	4.06	3.85	9.85	10.08		
Ni(SNP)I_2	Dark brown	180	diam (25)	1.35	40.03	40.14	3.51	3.33	8.51	8.35		
Ni(NNAs)Br_2	Olive green	217	3.29 (21)	0.17	44.34	44.45	4.05	4.44	9.42	9.42	12.03	12.25 (As)
Ni(NNAs)I_2	Brown	220	3.38 (21)	0.58	38.47	38.07	3.85	3.66	8.18	8.31		
Ni(ONAs)Br_2	Dark purple	184–189	3.34 (25)		44.27	44.34	3.88	3.96	9.41	9.56		
Ni(ONAs)I_2	Brown	174–178	3.20 (25)	1.50	38.48	37.70	3.37	3.81	8.18	8.39		
Ni(SNAs)Br_2[a]	Mustard brown	202–205	3.14 (21)	0.40	43.16	43.45	3.78	4.15	9.17	9.18		
Ni(SNAs)I_2	Brown	190–193	3.17 (26)	0.32	37.63	37.46	3.30	3.46	7.98	8.07	4.37	4.26 (S)

[a] The ratio of the found to the theoretical molecular weight for *ca.* 10^{-2} M solution in 1,2-dichloroethane at 37° is respectively: Ni(NNP)Br_2, 0.99; Ni(ONP)Br_2, 0.96; Ni(SNP)Br_2, 0.96; Ni(SNAs)Br_2, 0.97. [b] For *ca.* 10^{-3} M solution in 1,2-dichloroethane at 25°. Reference value under the same conditions: $[(n\text{-}C_4H_9)_4N]Br$, 19.

TABLE II

THE MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA OF THE COMPLEXES

Compound		Absorption max, cm^{-1} (ϵ_{molar} for soln)
Ni(NNP)Br_2	DR[a]	6500, 9100 sh, 14,300, 18,500 sh, 23,800 sh
	$(CH_2Cl)_2$	7000 (9.2), 9260 (14.7), 15,150 (112), 23,800 sh
Ni(NNP)I_2	DR	12,500 sh, 17,900 sh, 26,300 sh
Ni(ONP)Br_2	DR	6000, 9260 sh, 12,100, 17,700 sh, 20,800
	$(CH_2Cl)_2$	7000 sh, 9340 (35), 12,900 (106), 17,900 (99), 21,500 sh
Ni(ONP)I_2	DR	6000, 8500 sh, 11,700, 14,900 sh, 20,800 sh, 23,500 sh
	$(CH_2Cl)_2$	6500 (13.8), 11,750 sh, 16,700 sh, 21,700 sh
Ni(SNP)Br_2	DR	8900, 9500 sh, 14,900, 19,400 sh, 23,500 sh, 27,800
	$(CH_2Cl)_2$	8850 (39), 11,800 sh, 14,700 (125), 20,000 sh, 23,800 sh
Ni(SNP)I_2	DR	11,800 sh, 15,100 sh, 18,200 sh, 22,400 sh, 28,500 sh
	$(CH_2Cl)_2$	11,800 sh, 14,700 (658), 18,200 sh, 22,400 sh
Ni(NNAs)Br_2	DR	6100, 9100 sh, 11,100 sh, 13,900, 18,500 sh, 23,800
	$C_2H_5NO_2$	8900 (22), 11,800 sh, 13,900 (78.5), 18,200 sh, 24,000 sh
Ni(NNAs)I_2	DR	5900, 8700 sh, 13,000 sh, 14,200, 21,300 sh, 24,500
	$(CH_2Cl)_2$	8700 sh, 14,500 (240), 22,400 sh, 24,500 (3030)
Ni(ONAs)Br_2	DR	5600, 9400 sh, 11,900, 17,400, 20,000, 25,000 sh
Ni(ONAs)I_2	DR	5700, 8900 sh, 11,600, 16,250 sh, 20,000
	$(CH_2Cl)_2$	8700 sh, 12,350 (145), 17,900 sh, 21,600 sh, 23,800 (2430)
Ni(SNAs)Br_2	DR	8800, 9500 sh, 14,300, 22,400 sh
	$(CH_2Cl)_2$	8700 (27.5), 13,700 (100), 22,700 sh, 27,800 (3750)
Ni(SNAs)I_2	DR	8500, 14,500, 18,500 sh, 22,400–23,800
	$(CH_2Cl)_2$	8100 sh, 14,100 (285), 21,600 sh, 23,800 (2820)

[a] Diffuse reflectance spectrum.

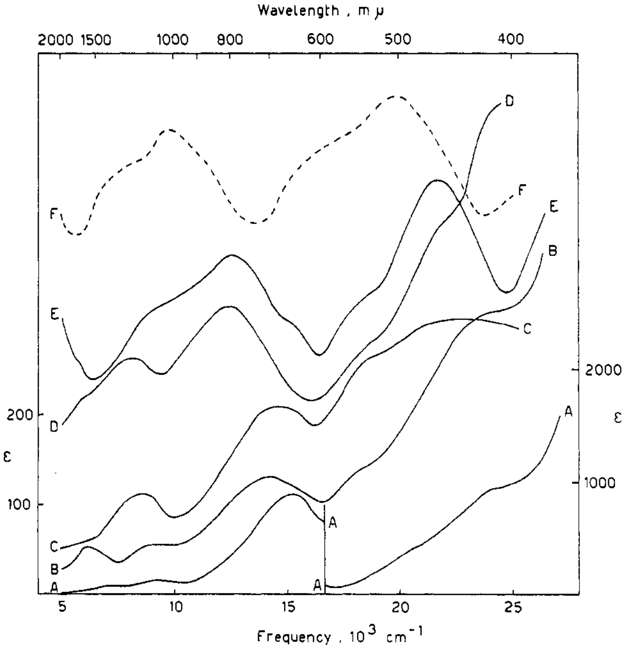

Figure 1.—Absorption spectrum of Ni(NNP)Br_2 in 1,2-dichloroethane solution (A) and diffuse reflectance spectra of Ni(NNP)Br_2 (B), Ni(SNAs)I_2 (C), Ni(MABen–NEt$_2$)Br_2 (D), Ni(Me$_5$dien)Br_2 (E), and Ni(Me$_4$en)Br_2 (F, dashed line).

etry is definitely discarded on the basis of the fact that the ligands are tridentate and the complexes are undissociated and monomeric in 1,2-dichloroethane solution (Table I). It is obvious that no more than five donor atoms can be coordinated to the nickel atom. For Y = NH or S, a pseudo-tetrahedral structure with the ligands acting as bidentate can be definitely excluded by comparing these complexes with the pseudo-tetrahedral Ni(Me$_4$en)Br_2 complex.[18] The spectra are different in the frequencies of the bands. In particular, a band at a frequency above 14,000 cm^{-1} is definitely too high if compared to those found for a ν_2 transition of a nickel(II) tetrahedral complex, regardless of the different set of donor atoms.[19] These complexes could thus be tentatively assigned a distorted five-coordinated configuration. Support of this is also given by the good agreement of their spectra and those of other complexes like Ni(Me$_5$dien)Br_2,[5a] Ni(MABen–NEt$_2$)Br_2[6] (Figure 1), and Ni(MSBen–N-

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$Et_2)Br_2$,[7] with the sets of donor atoms $NNNBr_2$ and $SNNBr_2$, whose five-coordinated structure has been already demonstrated. The ligands of the last two complexes are geometrically similar to the ligands NNP (As) and SNP(As). The shift toward higher frequencies of the bands of the complexes formed by NNP (As) and SNP(As) could be accounted for in terms of a greater ligand field strength.

Further support in favor of the five-coordination of these complexes is given by the reversible temperature-dependent equilibrium found for the $Ni(SNP)Br_2$ complex in solution in *o*-dichlorobenzene (Figure 2). When the temperature increases, the bands assigned to the five-coordinate species decrease in intensity and a new band at 11,600 cm^{-1} appears. This is typical of a five-coordinate $\rightleftharpoons$ tetrahedral equilibrium, as already found for structurally analogous complexes with sets of donor atoms $NNNX_2$, $SNNX_2$, and $ONNX_2$.[6-8]

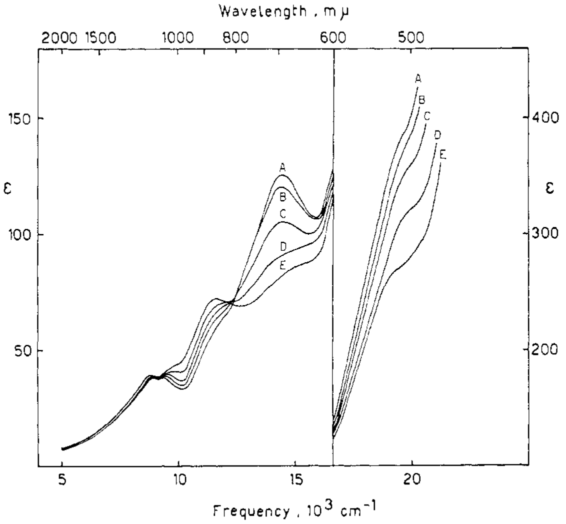


Figure 2.—Absorption spectra of $Ni(SNP)Br_2$ in *o*-dichlorobenzene solution at: (A) 26°, (B) 49°, (C) 68°, (D) 92°, and (E) 111°.

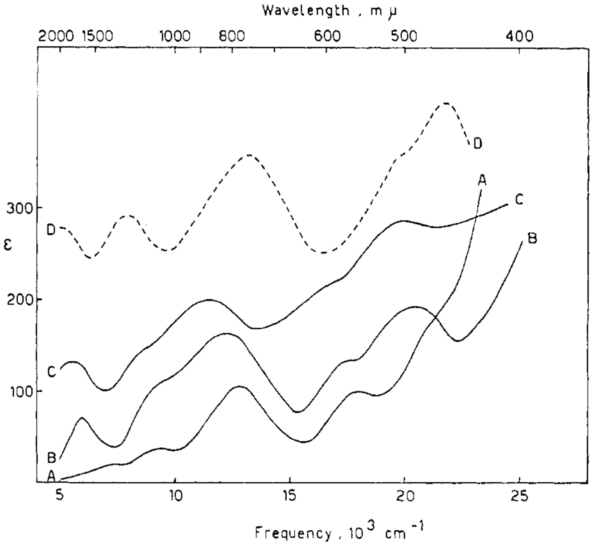
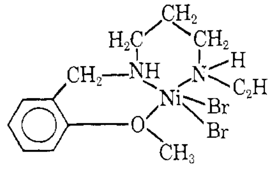


Figure 3.—Absorption spectrum of $Ni(ONP)Br_2$ in 1,2-dichloroethane solution (A) and diffuse reflectance spectra of $Ni(ONP)Br_2$ (B), $Ni(ONAs)I_2$ (C), and $Ni(MOBH_2tn\text{-}NHEt)Br_2$ (D, dashed line).

The spectra of the complexes with Y = O show ill-resolved absorption bands at 5600–6000, 8500–9400, 11,600–12,900, 16,250–17,900, and 20,000–20,700 cm^{-1} (Table II, Figure 3). These bands are shifted toward lower frequencies compared to the bands of the complexes with Y = NH or S. The bands at 8500–12,900 cm^{-1} are close to the range of those deriving from the ν_2 transition of the tetrahedral complexes. In order to attempt to make a plausible assignment of the configuration of these complexes, one can compare the spectra of the complexes with Y = O with that of a similar compound, deriving from a ligand with donor set ONN. This complex is $Ni(MOBH_2tn\text{-}NHEt)Br_2$ (II)[20] in which a complete structural investigation by X-rays has shown the coordination polyhedron about the nickel atom to be intermediate between the square pyramid and the trigonal bipyramid.[8,21] The spectrum of this complex, which shows bands at *ca.* 5000, 7880, 13,150, 20,000, and 21,800 cm^{-1}, is similar to those of some complexes deriving from ONP(As) ligands (Figure 3). This would suggest then a similar stereochemistry for these complexes. It must be noted that in the complex $Ni(MOBH_2tn\text{-}NHEt)Br_2$ the distance Ni–O has been found to be 2.32 Å and the four closer ligands are arranged at the apices of a very distorted tetrahedron.[21] This result could account for the fact that the ligand field splitting in the five-coordinate complexes derived from *o*-methoxybenzaldehyde is similar to that given by a set of donors with pseudo-tetrahedral symmetry.[8] For those complexes with Y = O that have bands closer to the range found for pseudo-tetrahedral complexes (*e.g.*, $Ni(ONAs)I_2$), the ethereal oxygen is still likely to interact, possibly very weakly, with the metal ion. This hypothesis is supported by the fact that X-ray powder patterns of the complexes $Ni(ONP)Br_2$, $Ni(ONAs)Br_2$, and $Ni(ONAs)I_2$ are strictly similar to those of the corresponding NNP(As) complexes discussed above.



II

It should be noted that the absorption frequencies for the complexes considered in the present research shift toward lower values as the set of donor atoms changes from SNP(As) to NNP(As) to ONP(As). This trend has been also observed in the analogous series of complexes with sets SNN, NNN, and ONN.[6-8]

Diamagnetic Complexes.—The complexes $Ni(NNP)I_2$ and $Ni(SNP)I_2$, in contrast to the bromo derivatives, are diamagnetic. The latter compound, which is the only one soluble, is essentially undissoci-

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(20) $MOBH_2tn\text{-}NHEt$ is the dihydrogenated Schiff base obtained from *o*-methoxybenzaldehyde and N-ethyltrimethylenediamine ($CH_3OC_6H_4CH_2NHCH_2CH_2CH_2NH(C_2H_5)$).

(21) P. L. Orioli and M. Di Vaira, to be submitted for publication.

ated in 1,2-dichloroethane, the slight conductivity being probably due to partial dissociation of the anion. The close similarity of the reflectance spectra of the two complexes, which show a large asymmetric band at 17,000–18,000 cm^{-1} with shoulders at 11,000–12,000 and 14,000–15,000 cm^{-1}, allow the same stereochemistry to be assigned to both of them. For the Ni(SNP)I$_2$ complex, the structure does not appear to change essentially in solution (Figure 4).

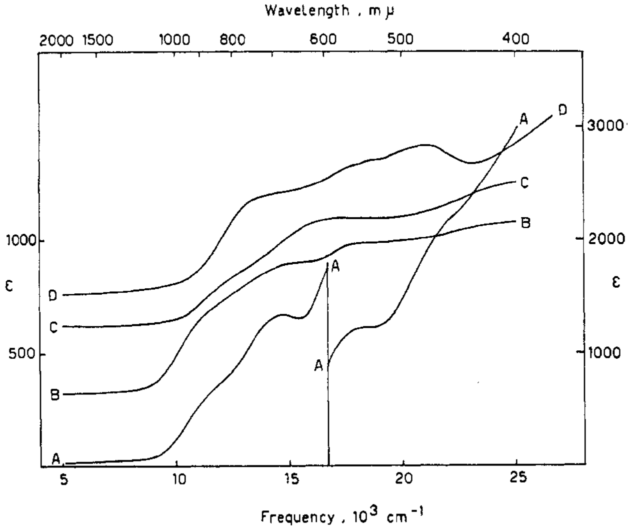

Figure 4.—Absorption spectrum of Ni(SNP)I$_2$ in 1,2-dichloroethane solution (A) and diffuse reflectance spectra of Ni(SNP)I$_2$ (B), Ni(NNP)I$_2$ (C), and Ni(TAS)Br$_2$ (D).

For both of these complexes a square-planar structure can be excluded on the basis of their electronic spectra. The spectra of the square-planar nickel(II) complexes, in fact, do not show appreciable absorption below 18,000–20,000 cm^{-1}. They can be roughly correlated, both for the shape and the frequencies of the bands, with the spectra of low-spin five-coordinate complexes, as for example Ni(TAS)Br$_2$[2] (Figure 4), after shifts in the band frequencies due to the different ligand field strengths of the donor atoms are discounted. The structure of Ni(TAS)Br$_2$ has been found by X-ray analysis to be intermediate between the square pyramid and the trigonal bipyramid.[22] A five-coordinate structure can then be attributed to the complexes Ni(NNP)I$_2$ and Ni(SNP)I$_2$.

Since all of the ligands considered in this work have a similar geometry, it is possible to draw partial conclusions about the influence of the donor atoms on the spin multiplicity of the ground state. When Y = O, Z = As, and X = Br, high-spin complexes are invariably obtained, whereas when Y = NH or S, Z = P, and X = I, the complexes are of the low-spin type. In other words, low-spin complexes are formed when Y, X, and Z are less electronegative atoms.

The spin multiplicity of nickel(II) in its ground state appears then in this case to be related to the electronegativity of the donor atoms. However, other factors such as steric effects and π-bonding ability are likely to exert a stronger influence. In fact, some five-coordinate complexes with the monodentate diphenylphosphine ligand (Ni(DPP)$_3$X$_2$) are found to be partially paramagnetic when X = I but diamagnetic when X = Br.[23]

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