

netic moment of Co(II) in $[(\text{CH}_3)_4\text{N}]_2\text{-}[\text{Co}(\text{NCS})_4]$ was measured in a tube carefully calibrated with $\text{HgCo}(\text{NCS})_4$ using the susceptibility reported by Figgis and Nyholm^{7a,20} for the latter. Thus the difference in the moments of Co(II) in the two compounds is measured with maximal accuracy. It is seen that both the spectral data and the magnetic moments support the conclusion that in these compounds, as in those studied by Schäffer, attachment of the sulfur atoms enhances the ligand field at the ion to which the nitrogen atoms are coordinated.

Finally, we have prepared the complex $\text{Co}[(\text{C}_6\text{H}_5)_3\text{PO}]_2(\text{NCS})_2$, that is, the triphenylphosphine oxide analog of the triphenylphosphine complex discussed above, and studied its spectrum and magnetic moment. We have also measured the spectra and treated the spectral data along with previously reported magnetic data^{4,6} in the manner outlined in ref. 5. All of these data and derived quantities are reported in Table IV. It is evident from the comparisons exhibited there that in the phosphine oxide complex the thiocyanate ion is coordinated

(20) See the Experimental section for more detailed discussion of the accuracy of calibrations and comparisons of moments.

TABLE IV
SOME PARAMETERS OF THE SPECTRA AND ELECTRONIC STRUCTURE OF Co(II) IN $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{PO}\}_2\text{X}_2]$, X = $-\text{NCS}^-$, Co^- , Br^-

	$-\text{NCS}^-$	Cl^-	Br^-
ν_1 , cm.^{-1}	6900 ± 400	5710 ± 200	5560 ± 400
ν_2 , cm.^{-1}	16,000	15,500	15,300
Δ , cm.^{-1}	4030 ± 300	3270 ± 150	3180 ± 300
B' , cm.^{-1}	725	760	754
β ($= B'/B$) ^a	0.75	0.79	0.78
Magnetic moment, B.M.	4.46 ^b	4.63 ^c	4.69 ^c
λ' , cm.^{-1}	148	156	164

^a B (free ion) = 967 cm.^{-1} . ^b Measured by present authors. ^c Cf. ref. 4b and 6.

through nitrogen since both the spectra and the magnetic moments show that it is here providing a contribution to the ligand field which is far greater than that given by either Cl^- or Br^- rather than one intermediate between those due to these two ions.

Acknowledgments.—We are grateful to the United States Atomic Energy Commission for financial support under contract No. AT(30-1)-1965. We also thank Claus Schäffer and C. Klix-büll-Jørgensen for private discussions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Electronic Spectra of Some Tetrahedral Nickel(II) Complexes

By D. M. L. GOODGAME, M. GOODGAME AND F. A. COTTON¹

RECEIVED APRIL 24, 1961

The electronic spectra of eight tetrahedral complexes of nickel(II), *viz.*, $[\text{NiCl}_4]^{2-}$, $[\text{NiBr}_4]^{2-}$, $[\text{NiI}_4]^{2-}$, $[\text{Ni}(\text{Ph}_3\text{PO})_2\text{Cl}_2]$, $[\text{Ni}(\text{Ph}_3\text{PO})_2\text{Br}_2]$, $[\text{Ni}(\text{Ph}_3\text{PO})_2\text{I}_2]$, $[\text{Ni}(\text{Ph}_3\text{AsO})_2\text{Cl}_2]$ and $[\text{Ni}(\text{Ph}_3\text{AsO})_2\text{Br}_2]$, have been carefully studied in the region of the two highest energy, spin-allowed bands, ν_3 and ν_2 . It is shown that the tetrahalo ions are very sensitive to solvolysis, even by nitromethane and acetonitrile, and that the spectra of the solvolyzed species, most probably $[\text{NiX}_3\text{solvent}]^-$, especially in the region of ν_3 , are quite different from the true spectra of the $[\text{NiX}_4]^{2-}$ ions. The true spectra can be obtained by measuring solid compounds either by reflectance (ν_3 only) or using mulls. It is then found that if excess X^- , in the form of soluble salts of R_4P^+ or R_4N^+ cations, is added to the solutions the bands of the solvolyzed species can be completely, or almost completely, suppressed and the true $[\text{NiX}_4]^{2-}$ spectra obtained. From these spectra the values of Δ and B have been calculated using Liehr and Ballhausen's complete theory. The order of Δ values is $[\text{NiI}_4]^{2-} \sim [\text{NiBr}_4]^{2-} < [\text{NiCl}_4]^{2-}$. The five mixed ligand complexes are not so readily subject to solvolysis. Their spectra in the ν_3 and ν_2 regions are also reported and analyzed to yield Δ and B values. The oscillator strengths of the bands are reported and discussed. Some remarks on the relatively low magnetic moment of $[\text{NiI}_4]^{2-}$ are also given.

Introduction

It has been established conclusively during the last few years that tetrahedral complexes of nickel(II) do exist. It has been shown by Nyholm and Gill² and others^{3,4,5} that the tetrahedral tetrahalonickel(II) complex anions can exist in crystalline compounds provided the cations are large and also in solvents of only moderate dielectric constant and coordinating power. It is now also known that certain mixed ligand complexes are tetrahedral. The most numerous class of these have the general formula $[\text{NiL}_2\text{X}_2]$; they include three types: (1) those in which L is triphenylphosphine and X is Cl, Br or I^{6,7}; (2) those in which L is triphenylphosphine oxide and X is Cl, Br or

I⁸; and (3) those in which L is triphenylarsine oxide and X is Cl or Br.⁹ The second established class of mixed ligand complexes are those of the stoichiometry $[\text{NiLX}_3]^-$, and the known members of this class include some well-characterized compounds in which L is triphenylphosphine and X is Br or I⁷ as well as, probably, some similar ones which are not so well characterized.⁷

A study of the spectra of the mixed ligand complexes containing triphenylphosphine was published recently. It was shown that the ligands present in these species differ so much in their positions in the spectrochemical series that there are strong low symmetry components in the ligand fields which have quite pronounced effects on the spectra. For the complexes containing triphenylphosphine oxide and triphenylarsine oxide the low symmetry components are evidently rather small since no effects clearly attributable to them were found in the spectra^{8,9} nor did the magnetic moments of the

(1) Alfred P. Sloan Foundation Fellow.
(2) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
(3) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).
(4) F. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).
(5) F. Cotton and R. Francis, *J. Inorg. Nuclear Chem.*, **17**, 62 (1961).
(6) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).
(7) F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

(8) F. A. Cotton and D. M. L. Goodgame, *ibid.*, **82**, 5771 (1960).

(9) D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960).

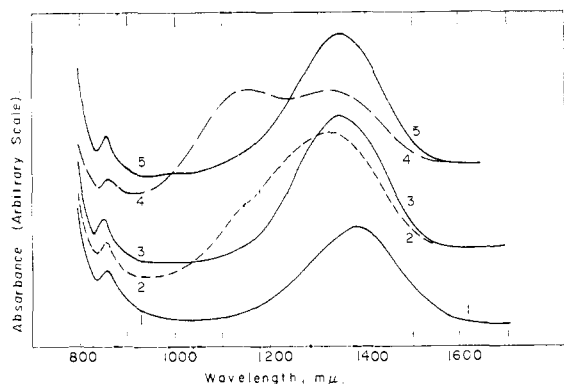


Fig. 1.—Spectra of $((\text{C}_6\text{H}_5)_3\text{MeP})_2[\text{NiCl}_4]$ in the ν_2 region: (1) mull in hexachlorobutadiene; (2) 0.0104 M solution in acetonitrile; (3) 0.01 M solution plus 0.1 M $((\text{C}_6\text{H}_5)_3\text{MeP})\text{Cl}$ in acetonitrile; (4) 0.01 M solution in nitromethane; (5) 0.01 M solution plus 0.1 M $((\text{C}_6\text{H}_5)_3\text{MeP})\text{Cl}$ in nitromethane.

compounds, which are rather sensitive in this respect, show any evidence of the existence of strong deviations from tetrahedral symmetry.^{8,9}

Before proceeding further with chemical studies of tetrahedral nickel(II) complexes, it seemed desirable to carry out a fairly thorough study of the spectra of those complexes which are truly tetrahedral, that is, the $[\text{NiX}_4]^{2-}$ species, and those which appeared, as noted above, to approximate very closely to being truly tetrahedral, that is, the $[\text{Ni}(\text{Ph}_3\text{PO})_2\text{X}_2]$ and $[\text{Ni}(\text{Ph}_3\text{AsO})_2\text{X}_2]$ compounds. For truly tetrahedral complexes, theoretical treatment is feasible and, indeed, the necessary calculations for the analysis of the spectra have been made by Liehr and Ballhausen.¹⁰

Experimental

Preparation of Compounds. Cesium Tetrachloronickelate(II).—A solid solution of cesium tetrachloronickelate(II) in cesium tetrachlorozincate(II), (~ 24 mole % Ni(II)), was prepared by the method of Gruen and McBeth.³ We are indebted to Dr. Antony Blake for this sample.

Methyltriphenylphosphonium Tetrachloronickelate(II).—On addition of ethyl acetate (20 ml.) to a hot solution of nickel chloride hexahydrate (1.58 g., 0.0067 mole) and methyltriphenylphosphonium chloride (4.18 g., 0.0132 mole) in anhydrous ethanol (12 ml.) blue crystals began to separate. After the mixture had cooled, these blue crystals were filtered off, washed with a 1:1 mixture of ethyl acetate and anhydrous ethanol (9 ml.) and dried *in vacuo* over sulfuric acid. The yield was 1.19 g. (24%). The compound melted at 198°.

Anal. Calcd. for $\text{C}_{38}\text{H}_{38}\text{Cl}_4\text{NiP}_2$: C, 60.44; H, 4.81; Cl, 18.78; P, 8.20. Found: C, 60.55; H, 5.16; Cl, 18.76; P, 8.10.

Tetraphenylphosphonium Tetrabromonickelate(II).—The preparation of this compound has been reported previously.⁷

Tetra-*n*-butylammonium Tetraiodonickelate(II).—A solution of nickel iodide (2.08 g., 0.0067 mole) and tetra-*n*-butylammonium iodide (4.92 g., 0.0133 mole) in anhydrous ethanol (20 ml.) was evaporated to very small volume on a water bath. A deep red solid separated, which was dried *in vacuo* over sulfuric acid. The compound melted at 115°. It was hygroscopic.

Anal. Calcd. for $\text{C}_{32}\text{H}_{72}\text{I}_4\text{NiN}_2$: C, 36.56; H, 6.90; N, 2.67. Found: C, 36.67; H, 6.96; N, 2.91.

The compound was soluble in the cold to give red solutions in acetone, methylene chloride, chloroform and nitromethane. It was decomposed by alcohols, with the formation of

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

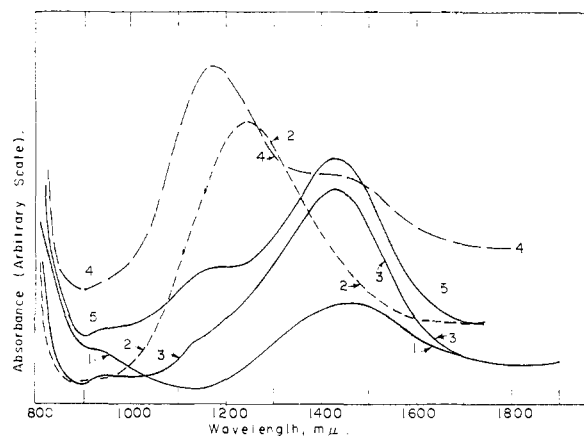


Fig. 2.—Spectra of $((\text{C}_6\text{H}_5)_4\text{P})_2[\text{NiBr}_4]$ in the ν_2 region: (1) mull in hexachlorobutadiene; (2) 0.01 M solution in acetonitrile; (3) 0.01 M solution in acetonitrile plus 0.1 M $((\text{C}_6\text{H}_5)_3\text{-}n\text{-BuP})\text{Br}$; (4) 0.01 M solution in nitromethane; (5) 0.01 M solution in nitromethane plus 0.1 M $((\text{C}_6\text{H}_5)_3\text{-}n\text{-BuP})\text{Br}$.

yellow-green solutions, and was insoluble in benzene, chlorobenzene, ligroin, cyclohexane, dioxane and ethyl acetate.

Electrolytic Conductance Measurements.—Electrolytic conductance measurements were carried out using a Serfass bridge and a conventional cell, previously calibrated with an aqueous solution of potassium chloride.

Results:	Molar conductance, $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, $10^{-3}M$ in CH_3NO_2	Temp., °C.
$[\text{Me}(\text{C}_6\text{H}_5)_3\text{P}]_2[\text{NiCl}_4]$	158	26.3
$[n\text{-Bu}_4\text{N}]_2[\text{NiI}_4]$	168	25.6

The molar conductance of a $10^{-3} M$ solution of tetraphenylphosphonium tetrabromonickelate in nitrobenzene at 26.9° previously has been reported to be 61.7 ohm^{-1} .⁷

Magnetic Measurements.—Measurements of the magnetic susceptibility of tetra-*n*-butylammonium tetraiodonickelate(II) were made using the Gouy method as previously described.¹¹

Results:	χ_m corr. $\times 10^5$ c.g.s.u.	Dia-magnetic corr. $\times 10^5$	μ_{eff} B.M.
$[n\text{-Bu}_4\text{N}]_2[\text{NiI}_4]$	300.0	4970	3.47 ± 0.04
	73.7	17820	3.25 ± 0.04

Spectral Measurements.—The reflectance spectrum of tetra-*n*-butylammonium tetraiodonickelate(II) was measured with a Beckman DU spectrophotometer, using a standard reflectance attachment and magnesium carbonate as the reference. A Cary Model 14 recording spectrophotometer was used for all other spectra. The results are shown in Table I and Figs. 1-3.

Discussion

In this discussion, the reader's familiarity with or access to the theoretical treatment of tetrahedrally coordinated Ni(II) given by Liehr and Ballhausen¹⁰ will be assumed. We have found quite generally that the data reported here cannot be interpreted satisfactorily with any less rigorous treatment. In particular, the use of the relatively simple Tanabe and Sugano¹² matrices, in which spin-orbit coupling is ignored, leads to internal inconsistencies and unlikely Δ values. In these complexes, the λ values are larger relative to the orbital level separations than for any other metal

(11) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959).

(12) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

ion of the first transition series excepting only Cu(II).

Table I summarizes numerically all of our experimental observations. The strong, multi-component bands observed in the visible spectra are designated ν_3 since they are assigned to the highest of the three expected spin-allowed bands. The distinctly weaker but still relatively strong bands found between 6500 and 10,000 cm^{-1} are assigned to the second highest of the three expected spin-allowed transitions and are therefore listed in the column headed ν_2 .

The position of ν_1 for all of the complexes can be calculated to be below our range of observation (~ 4500 – $25,000 \text{ cm}^{-1}$), namely, in the region of 3000 to 4000 cm^{-1} . Unambiguous recognition of these ν_1 bands would be a difficult matter in any event, since this same region will include vibrational bands due to C-H fundamentals in the complex organic cations and solvents, as well as O-H bands due to any moisture present. Therefore, no attempts were made to study the region of ν_1 for these complexes. In the columns of Table I headed 1G and 1D are listed weak bands which we assign as spin-forbidden transitions from the 3T_1 ground state to certain states arising from the 1G or 1D states of the free ion.

Spectra of the Tetrahalo Ions.—An important qualitative observation to be made concerning the spectra of these complex ions is their marked sensitivity, especially for the ν_2 bands, to the environment of the complex species. In Figs. 1–3 the spectra of the three $[\text{NiX}_4]^{2-}$ species in the region of the ν_2 bands are plotted so as to show the effects of changes in the environment of the ions. The same general features are found in all three cases, but the details differ from one to another. Our general interpretation is as follows. The spectra of the crystalline compounds in the form of hexachlorobutadiene mulls are assumed to be spectra of the true $[\text{NiX}_4]^{2-}$ anions. Since the upper state for ν_2 is not orbitally degenerate, the additional complexity of the absorption in the ν_2 region for the solutions cannot be attributed to splitting of the upper state in solvated species. Instead, it must be ascribed to the presence of tetrahedral species other than the undistorted $[\text{NiX}_4]^{2-}$ ones in the solutions. It seems likely that these other species would be $[\text{NiX}_3(\text{solvent})]^-$ or similar ones in which halide ions have been displaced by solvent molecules. Since the halide ions lie at the weak end of the spectrochemical series, it might then also be expected that the ν_2 bands due to solvent-containing species would be at higher energies than those due to the $[\text{NiX}_4]^{2-}$ ions.

The $[\text{NiCl}_4]^{2-}$ Ion.—The mull spectrum of the methyltriphenylphosphonium salt of this ion shows only one rather symmetrical band at 7272 cm^{-1} . In acetonitrile solution the band maximum is displaced somewhat, to 7550 cm^{-1} , and shows a definite asymmetry indicative of an unresolved weak band on the high energy side. In nitromethane there is a band at 7520 cm^{-1} and a second one of about the same intensity at 8620 cm^{-1} . If, as suggested above, the higher frequency absorptions are properly attributed to solvolyzed

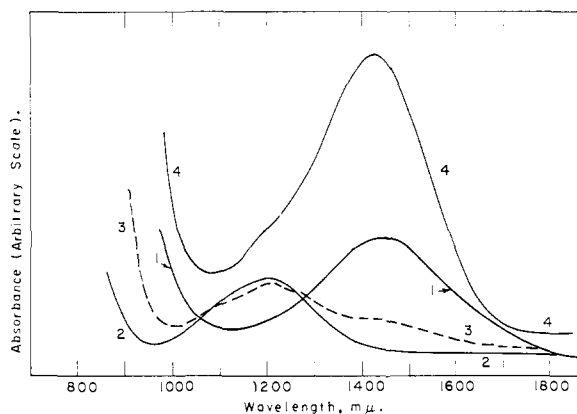


Fig. 3.—Spectra of $(n\text{-Bu}_4\text{N})_2[\text{NiCl}_4]$ in the ν_2 region: (1) mull in hexachlorobutadiene; (2) 0.002 M solution in nitromethane; (3) 0.002 M solution in nitromethane plus 0.1 M $(n\text{-Bu}_4\text{N})\text{I}$; (4) 0.01 M solution in nitromethane plus 0.5 M $(n\text{-Bu}_4\text{N})\text{I}$.

species, it should be possible to suppress them by introducing excess halide ion into the solutions.¹³ In each of these cases, use of solvent containing 0.1 mole/l. of $((\text{C}_6\text{H}_5)_3\text{MeP})\text{Cl}$ instead of pure solvent completely suppresses the high energy absorption as seen in Fig. 1. The addition of the excess phosphonium chloride also modifies the ν_3 absorption, though less dramatically.

Now that the "true" ν_2 bands of $[\text{NiCl}_4]^{2-}$ are identified in the various media, it is of some interest to note the variability in their frequencies, *viz.*, from 7272 cm^{-1} for crystalline $((\text{C}_6\text{H}_5)_3\text{MeP})_2\text{NiCl}_4$ to 7750 cm^{-1} for $\text{Cs}_2[(\text{Zn}_{0.76}\text{Ni}_{0.24})\text{Cl}_4]$, with the frequencies for the solutions lying between these extremes. It should first be noted³ that the energy of the 3A_2 state (the upper state for ν_2) is a very steep function of Δ ; indeed, the entire range of ν_2 values, from 7270 to 7750 cm^{-1} , covers a range in Δ of only 190 cm^{-1} . The much smaller variability in the energy of ν_3 is expected theoretically, since a change of $\sim 200 \text{ cm}^{-1}$ in Δ alters the energy of the ${}^3T_1(\text{P})$ levels by only $\sim 125 \text{ cm}^{-1}$, a magnitude barely outside the range of experimental uncertainties. We believe that these variations in the position of ν_2 must be due mainly to variations in the compressive force to which the $[\text{NiCl}_4]^{2-}$ complex ion is subjected in the various environments and perhaps also to varying degrees of polarization of the coordinated anions by the cations present. In particular, it seems quite reasonable that in the host Cs_2ZnCl_4 lattice the compression would be greater than in the $((\text{C}_6\text{H}_5)_3\text{MeP})_2\text{NiCl}_4$ lattice because of the smaller size of Cs^+ compared to $((\text{C}_6\text{H}_5)_3\text{MeP})^+$ and especially because of the smaller size of Zn^{2+} which will tend to cause a contraction of the whole array compared to the dimensions it would assume if these were dictated entirely by Ni^{2+} ions. In this connection the interesting high pressure studies on $((\text{C}_6\text{H}_5)_4\text{As})_2\text{NiCl}_4$ by Stephens and Drickamer¹⁴ may be noted. They find that the frequency of ν_2 changes

(13) This technique of adding excess halide salt already has been used by Gill and Nyholm² in studying the ν_3 bands of several complexes.

(14) D. R. Stephens and H. G. Drickamer, *J. Chem. Phys.*, **35**, 429 (1961).

TABLE I
VISIBLE ABSORPTION SPECTRA OF SOME TETRAHEDRAL NICKEL(II) COMPLEXES

Compound	State ^a	CTB ^b	^c G	^r 3	^r 4	^r 5	^r 6				
Cs ₂ NiCl ₄ 24 mole % in Cs ₂ ZnCl ₄	Solid, C ₄ Cl ₆ mull		~20620 sh		~16400 sh,	15150,	14200	~11400 sh	7750		
	Solid, C ₄ Cl ₆ mull		~19800 sh		~16000 sh,	15110, 14080,	~13040 sh	11600	7272		
(Me(C ₆ H ₅) ₂ P) ₂ (NiCl ₂)	MeCN (0.0104 M)				~15950 sh,	15240(160),	14250(160)	11630(6.2)	~8700 sh, 7549(21)		
	0.1 M (Me(C ₆ H ₅) ₂ P)Cl in MeCN (0.01 M)				~16000 sh,	15220(196),	14180(202)	11630(8.4)	7407(22)		
	MeNO ₂ (0.01 M)			~17570 sh,	~16080 sh,	15200(140),	14220(134)	11630(5.6)	8621(18), 7519(18)		
	0.1 (Me(C ₆ H ₅) ₂ P)Cl in MeNO ₂ (0.01 M)					15150(190),	14080(197)	11630(7.5)	7407(22)		
(C ₆ H ₅) ₄ P ₂ (NiBr ₄)	Solid, reflectance		21000	18000	~14810 sh,	13800,	12900	10400			
	Solid, C ₄ Cl ₆ mull			18260	~15060 sh,	14100,	12900	~10500 sh	7040		
	MeCN (0.01 M)		20000(13.6),	19230 sh	~16300 sh,	15380(189),	14180(155),	~13500 sh	~8620 sh, 8098(40) ^d		
	0.1 M ((C ₆ H ₅) ₂ - <i>n</i> -Bu ₄)Br in MeCN (0.01 M)				~16700 sh	~15200 sh,	14140(250),	13230(241)	6995(30)		
	MeNO ₂ (0.01 M)				~16500 sh,	15380(159),	14290(163),	13300(124)	8475(38), 6993 sh		
0.1 M (C ₆ H ₅) ₂ - <i>n</i> -Bu ₄)Br in MeNO ₂ (0.01 M)			21190(5.4)		~16700 sh,	~15200 sh,	14120(237),	13210(225)	~10720(5.7)	8450 sh	6995(30)
<i>n</i> -(Bu ₄ N) ₂ (NiI ₄)	Solid, reflectance		19420	14880,	13330	~11900 sh,	11300				
	C ₄ Cl ₆ mull		19230	14810,	~13640	12050,	11250		6954		
	MeNO ₂ (0.002 M)		18870(1106)			14180(275) ^b			8300(78)		
	0.1 M (<i>n</i> -Bu ₄ N) ₂ I in MeNO ₂ (0.002 M)					14530 sh,	14030(242),	12800 sh,	11480 sh	8300(65)	6940 sh
0.5 M (<i>n</i> -Bu ₄ N) ₂ I in MeNO ₂ (0.01 M)					14530 sh,	14030(242),	12800 sh,	11480 sh	8330 sh	7042(55)	
Ni{(C ₆ H ₅) ₂ PO} ₂ Cl ₂	Solid, reflectance		22470			16260,	14290	~12120 sh			
	Solid, C ₄ Cl ₆ mull		22420			16310,	14470	~12120 sh	7288		
Ni{(C ₆ H ₅) ₂ PO} ₂ Br ₂	Solid, reflectance		20530			15750,	14290	~11980 sh			
	Solid, C ₄ Cl ₆ mull		20410			15720	14370	~11930 sh	7143		
	Acetone (0.01 M)		20490(21.7)			15580(101.),	~14290 sh		7250(19)		
Ni{(C ₆ H ₅) ₂ PO} ₂ I ₂	Solid, reflectance		18350			14880,	13330				
	Solid, C ₄ Cl ₆ mull		18690			14900,	~13500 sh		7124		
	C ₆ H ₅ Cl (0.005 M)		~18620 sh			15100(137),	~13680 sh		7078(18.2)		
	Acetone (0.01 M)					14010(136),	~12500 sh		7255(19.2)		
Ni{(C ₆ H ₅) ₂ AsO} ₂ Cl ₂	Solid reflectance		~22220 sh			16530,	14560	11950			
	Solid, C ₄ Cl ₆ mull		~21370 sh			16670,	14780	12176	7974		
	C ₆ H ₅ Cl (0.005 M)				~17390 sh,	16470(79),	15020(76.5)	12350(6.5)	7861(15)		
Ni{(C ₆ H ₅) ₂ AsO} ₂ Br ₂	Solid, reflectance		20410			15630	~14710 sh	11700			
	Solid, C ₄ Cl ₆ mull		~20600 sh			15720	14750	11920	7692		
	C ₆ H ₅ Cl (0.005 M)					15920(184),	14600(164)	~11960 sh	7654(27)		

^a Figures in parentheses are the molar concentrations of the nickel complexes. ^b CTB = charge transfer band. ^c Center of broad band. ^d Broad asymmetric band with a long low-energy "tail," probably concealing a band at lower energy; sh = shoulder.

by about $+20 \text{ cm.}^{-1}$ per kilobar, while that of ν_3 changes by only about 4 cm.^{-1} per kilobar. Our result for ν_2 compares well with that of Stephens and Drickamer at 1 bar, *viz.*, 7500 cm.^{-1} , and with the recent report¹⁵ of a broad band with a maximum between 7500 and 7600 cm.^{-1} for a mull of an unspecified $[\text{NiCl}_4]^{2-}$ salt.

The $[\text{NiBr}_4]^{2-}$ Ion.—For the $((\text{C}_6\text{H}_5)_4\text{P})^-$ salt of this ion, the mull spectrum shows the ν_2 band to be at 7040 cm.^{-1} . In pure acetonitrile, there is only one band in this region which has its maximum at 8048 cm.^{-1} with a rather long low-energy tail, which might be due to the presence of a weak broad band around 7000 cm.^{-1} . When acetonitrile containing 0.1 mole/l. of $((\text{C}_6\text{H}_5)_3\text{-}n\text{-BuP})\text{Br}$ is used instead of the pure solvent, a remarkable transformation (Fig. 2) takes place, the spectrum now consisting of only one symmetrical band with a maximum at 6995 cm.^{-1} . In pure nitromethane, the strongest absorption is a band centered at 8475 cm.^{-1} , but there is a distinct band at 6993 cm.^{-1} . On using a $0.1 M$ solution of $((\text{C}_6\text{H}_5)_3\text{-}n\text{-BuP})\text{Br}$ in nitromethane instead of the pure solvent, the high-energy band is reduced to a mere shoulder and the major absorption has a maximum at 6990 cm.^{-1} . We therefore conclude that ν_2 for $[\text{NiBr}_4]^{2-}$ has a frequency of $6990\text{--}7040 \text{ cm.}^{-1}$.

The $[\text{NiI}_4]^{2-}$ Ion.—The mull spectrum of $[\text{n-Bu}_4\text{N}]_2[\text{NiI}_4]$ shows a symmetrical ν_2 band at 6954 cm.^{-1} . In nitromethane solution this band is not discernible at all, being replaced by one at 8300 cm.^{-1} . However, with progressive increase in the concentration of $(\text{n-Bu}_4\text{N})\text{I}$ the true ν_2 band at $\sim 7000 \text{ cm.}^{-1}$ grows in with concomitant decrease in the intensity of the spurious band. It was found that acetonitrile attacked this compound so severely as to give a turbid solution, so no attempt was made to study it in this solvent.

Electronic Structure Parameters.—These computations were made using the results of Liehr and Ballhausen¹⁰ in which λ is assigned the value -275 cm.^{-1} and F_2 is taken as $14F_4$ (equivalent to $C/B = 3.9$). The parameters Δ ($= 10 Dq$) and B were adjusted to give an exact fit for ν_3 (the energy being estimated as the center of gravity of all components of the absorption in the visible) and ν_2 . Table II gives the values of Δ and B along with a comparison of the observed and calculated positions of some small bands which may be assigned as spin-forbidden transitions to upper states arising from the 1D and 1G states of the free ion. These acquire intensity by mixing, *via* spin-orbit coupling of the upper "singlet" states with nearby "triplet" states of the same symmetry.

The Δ values lead to the following order of the halide ions in the spectrochemical series: $\text{I}^- \sim \text{Br}^- < \text{Cl}^-$. The closeness of I^- and Br^- here is noteworthy. They are close (*e.g.*, in $[\text{CoBr}_4]^{2-}$ and $[\text{CoI}_4]^{2-}$) but more often with $\text{I}^- < \text{Br}^-$. It is interesting to compare the values of Δ in these tetrahedral nickel(II) complexes (Δ_t) with those reported by Asmussen and Bostrup¹⁶ for octahedrally coordinated nickel(II), (Δ_o). For octahedral chloro species, they report Δ_o to be

(15) S. Buffagni and T. M. Dunn, *Nature*, **188**, 937 (1960).

(16) R. W. Asmussen and O. Bostrup, *Acta Chem. Scand.*, **11**, 745 (1957).

about 7100 cm.^{-1} which makes the ratio Δ_t/Δ_o about 0.51 , while for the octahedral bromo species they give Δ_o values of about 6900 cm.^{-1} , making Δ_t/Δ_o about 0.49 . These ratios are in reasonable agreement with the theoretical ratio of $4/9 = 0.444$ for pure electrostatic complexes.¹⁷

The β values show that the order of the halide ions in the nephelauxetic series is $\text{Cl} < \text{Br} < \text{I}$, in order of increasing cloud-expanding effect.

Our results are in satisfactory agreement with those of Weakliem,¹⁸ who finds for Ni^{2+} in $\text{Cs}_2\text{-ZnCl}_4$ $\Delta = 3850$, $B = 725 \text{ cm.}^{-1}$ and for Ni^{2+} in $\text{Cs}_2\text{-ZnBr}_2$ $\Delta = 3300$ and $B = 695 \text{ cm.}^{-1}$.

The Magnetic Moment of $[\text{NiI}_4]^{2-}$.—In their original report of the preparation of the $[\text{NiI}_4]^{2-}$ ion, as the methyltriphenylarsonium salt, Gill and Nyholm² gave for μ_{eff} at room temperature 3.49 B. M., a value well below those found for other tetrahedral nickel(II) complexes in which the four ligand atoms are identical or differ little in their positions in the spectrochemical series ($3.7\text{--}4.0$ B.M.^{2,8,9}). They suggested that this might be due to mixing of the 3T_1 ground state with the 3A_2 excited state, thus diminishing the orbital angular momentum in the former. Our analysis¹⁹ indicates that there are no matrix elements between the T_1 and A_2 states; moreover, the results given in Table II show that there is no sharp decrease in Δ for $[\text{NiI}_4]^{2-}$ as compared to its value in $[\text{NiCl}_4]^{2-}$ and $[\text{NiBr}_4]^{2-}$ such as would be necessary to explain the appreciably lower value of μ_{eff} by this or any other mechanism depending on a mixing of states inversely proportional to the first power of Δ . Two other explanations for the low value of μ_{eff} in $[\text{NiI}_4]^{2-}$ have been considered here.

First, if it be assumed that the effective value of λ , the spin-orbit coupling constant, is $20\text{--}25\%$ higher in $[\text{NiI}_4]^{2-}$ than in the other complexes (which is equivalent to assuming that the iodide ions cause less of a decrease in λ from the free ion value than do Cl^- or Br^-) the value of μ_{eff} at room temperature would be ~ 3.5 B.M. according to the theoretical results given by Figgis.²⁰ There is, fortunately, a direct test of this hypothesis, which consists in measuring μ_{eff} at a much lower temperature. The theory²⁰ shows that at liquid nitrogen temperature the moment should be ~ 1.8 B.M. We find for the tetra-*n*-butylammonium salt of $[\text{NiI}_4]^{2-}$, however, a drop to only 3.25 B.M. at 74°K . so that this explanation is also untenable. Since the $[\text{NiI}_4]^{2-}$ ion seems the least stable one, and also the most deformable, we believe that the most likely explanation of the low moment for Ni(II) in $[\text{NiI}_4]^{2-}$ is that distortion of the complex in the crystal causes considerable splitting and separation of the ground state multiplet (3T_1 , 3T_3 , 3T_4 and 3T_5 of $^3T_1(F)$). It has already been shown for the $[\text{Ni}((\text{C}_6\text{H}_5)_3\text{P})_2\text{X}_2]$ compounds that the introduction of low-symmetry components into the tetrahedral fields about

(17) C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd.*, **29**, No. 4 (1954).

(18) H. A. Weakliem, R.C.A. Laboratories, private communication.

(19) In the group T_d , $L \cdot S$ transforms as T_1 and the direct product $A_1 \times T_1 \times T_1 = A_1 + E + T_1 + T_2$. Hence, matrix elements of the sort $(A_1 | L \cdot S | T_1)$ are identically zero.

(20) B. N. Figgis, *Nature*, **182**, 1568 (1958).

TABLE II
LIGAND FIELD STRENGTHS, RACAH PARAMETERS AND SOME CALCULATED SPIN-FORBIDDEN TRANSITIONS FOR THE $[\text{NiX}_4]^{2-}$ IONS

Compound	Medium	Δ^a cm. ⁻¹	B'^a cm. ⁻¹	β^b (= B'/B)	Upper states of spin-forbidden transitions			
					${}^1D(\Gamma_6)$		1G	
					Obsd.	Calcd.	Obsd.	Calcd.
$\text{Cs}_2[\text{NiCl}_4]$	Cs_2ZnCl_4	3770	750	0.728	11400	11340	~20620	20220(Γ_3)
$(\text{CH}_3(\text{C}_6\text{H}_5)_2\text{P})_2[\text{NiCl}_4]$	Mull	3580	746	.724	11600	11270	~19800	19780(Γ_3)
	0.1 M $[\text{MePh}_2\text{P}]\text{Cl}$ in CH_3CN	3610	765	.742	11630	11490	Not obsd.
	0.1 M $[\text{MePh}_2\text{P}]\text{Cl}$ in CH_3NO_2	3610	765	.742	11630	11490	Not obsd.
$((\text{C}_6\text{H}_5)_2\text{P})_2[\text{NiBr}_4]$	Mull	3380	691	.671	~10500	10600	18200	18360(Γ_3)
	0.1 M $[\text{Ph}_2\text{-}n\text{-BuP}]\text{Br}$ in CH_3CN	3380	713	.692	10680	10820	Not obsd.
	0.1 M $(\text{Ph}_2\text{-}n\text{-BuP})\text{Br}$ in CH_3NO_2	3380	713	.692	10720	10820	Not obsd.
$(n\text{-Bu}_4\text{N})_2[\text{NiI}_4]$	Mull	3350	572	.555	Not obsd.	...	~13640	13280(Γ_3)
	0.5 M $[n\text{-Bu}_4\text{N}]\text{I}$ in CH_3NO_2	3380	^c	^c	Not obsd.	...	14810	14890(Γ_4)

^a Δ and B' were calculated from the energies of ν_2 and ν_3 and the calculated energies of these transitions therefore match the experimental values exactly. ^b B for the free $\text{Ni}(\text{II})$ ion equals 1030 cm.⁻¹. ^c B' was not determined since the ν_3 band is too strong to measure under these conditions.

TABLE III
LIGAND FIELD STRENGTHS, RACAH PARAMETERS AND SOME CALCULATED SPIN-FORBIDDEN TRANSITIONS FOR THE $[\text{Ni}((\text{C}_6\text{H}_5)_3\text{MO})_2\text{X}_2]$ COMPLEXES ($M = \text{P, As}$; $X = \text{Cl, Br, I}$)

Compound	Medium	Δ^a	B'^a	β^b (= B'/B)	Upper states of spin-forbidden transitions			
					${}^1D(\Gamma_3)$		1G	
					Obsd.	Calcd.	Obsd.	Calcd.
$\text{Ni}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Cl}_2$	Mull	3580	800	0.777	12120	11860	22420	20900(Γ_3)
$\text{Ni}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Br}_2$	Mull	3460	780	.757	11930	11640	20410	20370(Γ_3)
	Acetone	3500	790	.767	Not obsd.	11790	20490	20600(Γ_3)
$\text{Ni}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{I}_2$	Mull	3440	736	.715	Not obsd.	11120	18690	18430(Γ_4)
	$\text{C}_6\text{H}_5\text{Cl}$	3420	770	.747	Not obsd.	11570	18620	18880(Γ_4)
	Acetone	3500	696	.676	Not obsd.	10630	Not obsd.
$\text{Ni}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Cl}_2$	Mull	3920	790	.767	12170	11870	21370	21270(Γ_3)
	$\text{C}_6\text{H}_5\text{Cl}$	3850	847	.822	~12350 sh	12450	Not obsd.
$\text{Ni}((\text{C}_6\text{H}_5)_3\text{AsO})_2\text{Br}_2$	Mull	3750	778	.755	11920	11680	~20660 sh	20750(Γ_3)
	$\text{C}_6\text{H}_5\text{Cl}$	3730	810	.786	~11960 sh	12050	Not obsd.

^a Δ and B' were calculated from the energies of ν_2 and ν_3 and the calculated energies of these transitions therefore match the experimental values exactly. ^b B for the free $\text{Ni}(\text{II})$ ion equals 1030 cm.⁻¹.

$\text{Ni}(\text{II})$ causes marked reductions in the magnetic moments.⁷ In regard to the susceptibility of the $[\text{NiI}_4]^{2-}$ ion to deformation by its surroundings, results obtained in This Laboratory for $[\text{CoI}_4]^{2-}$, which must surely be rather similar in this respect, show that it also exhibits marked sensitivity to its environment.²¹

The Neutral Complexes.—In none of these compounds were any major medium effects noted, the media used being the pure crystalline compounds, acetone and chlorobenzene. Hence the interpretation of the data proceeds straightforwardly. The Δ and B' values, estimated from the energies of the ν_2 and ν_3 bands, using Liehr and Ballhausen's equations,¹⁰ are given in Table III along with a comparison of the calculated and observed band positions for some spin-forbidden bands.

This series of compounds is the most extensive one of its type so far studied in this way and several definite conclusions about the ligands can be drawn. First, intercomparison of the Δ and B' values for the three triphenylphosphine oxide complexes and for the two triphenylarsine oxide complexes demonstrates quite clearly that in the

spectrochemical series the order of the halide ions is $\text{I} \approx \text{Br} < \text{Cl}$ and, a little less neatly, due to the small variations from one medium to another, that in the nephelauxetic series the order is $\text{Cl} < \text{Br} < \text{I}$. These results are in agreement with the accepted orders. Furthermore, comparison of the results for the two analogous pairs of phosphine oxide and arsine oxide complexes shows that the order of these two ligands in the spectrochemical series is, decidedly, $(\text{C}_6\text{H}_5)_3\text{PO} < \text{Ph}_3\text{AsO}$, while in the nephelauxetic series there is no difference outside experimental uncertainties. Finally, comparison of the data for the $[\text{Ni}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{X}_2]$ compounds with data for the $[\text{NiX}_4]^{2-}$ complexes shows that $(\text{C}_6\text{H}_5)_3\text{PO}$ is at about the same position as Cl^- in the spectrochemical series, and weaker than Cl^- (*i.e.*, $(\text{C}_6\text{H}_5)_3\text{PO} < \text{Cl}^- < \text{Br}^- < \text{I}^-$) in the nephelauxetic series. Insofar as comparisons can be made with analogous or related complexes of $\text{Co}(\text{II})$,²¹ these conclusions are substantiated by the $\text{Co}(\text{II})$ work.

Band Intensities.—For most of the complexes studied we have made graphical estimates, which should be accurate to within $\pm 10\%$, and probably less, of the oscillator strengths of the observed bands. This was not done for $[\text{Ni}((\text{C}_6\text{H}_5)_3\text{PO})_2\text{Cl}_2]$, since only reflectance and null spectra are available for this complex, nor for $[\text{NiI}_4]^{2-}$ because

(21) F. A. Cotton, M. Goodgame and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, in press.

TABLE IV
 OSCILLATOR STRENGTHS OF THE ABSORPTION BANDS^a

Compound	Solvent	$f\nu_3$	$f\nu_2$	$f\nu_3/f\nu_2$
((C ₆ H ₅) ₃ MeP) ₂ [NiCl ₄]	CH ₃ CN	2.30×10^{-3}	2.01×10^{-4}	11.4
	CH ₃ NO ₂	2.21×10^{-3}	2.35×10^{-4}	9.40
	0.1 M ((C ₆ H ₅) ₃ MeP)Cl in CH ₃ NO ₂	2.24×10^{-3}	1.42×10^{-4}	15.8
((C ₆ H ₅) ₄ P) ₂ [NiBr ₄]	CH ₃ NO ₂	3.12×10^{-3}	4.85×10^{-4}	6.44
	CH ₃ CN	2.97×10^{-3}	4.28×10^{-4}	6.94
	0.1 M ((C ₆ H ₅) ₃ - <i>n</i> -BuP)Br in CH ₃ CN	3.15×10^{-3}	2.61×10^{-4}	12.1
[Ni((C ₆ H ₅) ₃ PO) ₂ Br ₂]	Acetone	1.59×10^{-3}	1.63×10^{-4}	9.75
[Ni((C ₆ H ₅) ₃ PO) ₂ I ₂]	C ₆ H ₅ Cl	2.06×10^{-3}	1.08×10^{-4}	19.1
[Ni((C ₆ H ₅) ₃ AsO) ₂ Cl ₂]	C ₆ H ₅ Cl	1.52×10^{-3}	1.21×10^{-4}	12.6
[Ni((C ₆ H ₅) ₃ AsO) ₂ Br ₂]	C ₆ H ₅ Cl	2.92×10^{-3}	1.79×10^{-4}	16.3

^a The estimates include all absorption in the region of the ν_3 concerned. Thus, for the ν_2 bands, the intensity of the absorption known to be due to solvolyzed species is included.

heavy ultraviolet absorption trailing off into the region of ν_3 makes accurate intensity assessment difficult.

The most striking aspect of the intensity data is the relatively high intensity of the bands of the tetrahedral nickel(II) complexes as compared to the band intensities for octahedral complexes of nickel(II). The ratio is about 10². This effect is quite general, having been found for Co(II),^{21,22} Mn(II),^{23,24} and Cu(II),¹⁷ and Ballhausen and Liehr have discussed the possible reasons for it.²⁵ The intensity ratios show that

(22) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961).

(23) D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, Aug. (1961).

(24) F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, in press.

(25) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spect.*, **2**, 342 (1958); **4**, 190 (1960).

ν_3 is generally 10 to 20 times stronger than ν_2 . This is in agreement with the fact that in the strong field limit ν_3 remains a one-electron transition while ν_2 becomes a two-electron transition.

It is also noteworthy that the intensity of ν_3 is relatively insensitive to solvolysis effects, whereas for ν_2 the solvolyzed species are more strongly absorbing than are the [NiX₄]²⁻ ions.

Acknowledgments.—The generous financial support of the United States Atomic Energy Commission (Contract No. AT(30-1)-1965) is gratefully acknowledged. We thank Professor H. G. Drickamer and Dr. Herbert Weakliem for informing us of some of their results in advance of publication and Dr. A. D. Liehr for sending us some numerical results of the Liehr and Ballhausen calculations.

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK, AND THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

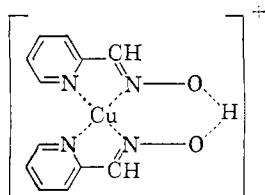
Hetero-binuclear Chelates of Copper(II) and Silver(I)

BY C. H. LIU AND CHUI FAN LIU

RECEIVED MAY 4, 1961

Interaction between silver(I) ion and bis-(pyridine-2-aldoxime)-copper(II) ion has been investigated by potentiometric measurements. The hetero-binuclear chelate involved has also been isolated as the perchlorate and examined by infrared spectroscopy.

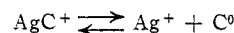
In a previous investigation,¹ it has been shown that monohydrogen bis-(pyridine-2-aldoxime)-copper(II) ion has the structure



The acidic hydrogen is intramolecularly bonded in a six-membered ring. From this structure, it would appear that the complex itself might form chelates with other metal ions through the oximate

(1) C. H. Liu and Chui-Fan Liu, work presented at the 138th National Meeting of the American Chemical Society, New York, 1960.

groups. The present work is concerned with the interaction between the complex ion and silver(I) ion. This interaction has been studied by measuring the two competing equilibria



where HC⁺ is the monohydrogen bis-(pyridine-2-aldoxime)-copper(II) ion, AgC⁺ is the analogous silver complex, and C⁰ is the basic form of the complex. For the second equilibrium, neglecting activity coefficients

$$K_d = \frac{[\text{Ag}^+][\text{C}^0]}{[\text{AgC}^+]} \quad (1)$$

and

$$[\text{Ag}^+] = \frac{K_d[\text{AgC}^+]}{[\text{C}^0]} \quad (2)$$