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New Tetrahedral Complexes of Nickel(II)

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The Ni(II) complexes $[(C_6H_5)_3PO]_2NiX_2$ where X = Cl, Br and I have been prepared. Their physical properties, especially their electronic spectra and high magnetic moments, leave little doubt that the nickel ion is in each case surrounded by two oxygen atoms and two halogen ions in an essentially tetrahedral array.

Introduction

The occurrence of tetrahedrally coördinated nickel(II) ions evidently is rather rare, considerably rarer than was believed only a few years ago. It is now well established that, contrary to the presumption long made on the basis of valence bond theory, but in accord with the suggestion early made by Ballhausen,[1] paramagnetic nickel(II) complexes may be planar.[2-4] Thus it cannot now be certain, and is perhaps even unlikely, that many of the complexes formerly assumed to be tetrahedral simply because they are paramagnetic are, actually, tetrahedral.

Moreover, calculations by the methods of ligand field theory have provided criteria by which tetrahedral complexes may be identified with fair certainty. Liehr and Ballhausen[5] have provided definitive calculations of the energy levels of a Ni (II) ion in fields of T_d symmetry which provide a basis for ascertaining by spectral studies whether the ion is tetrahedrally coördinated. Figgis[6] has established the range in which the magnetic moments of nickel ions in fields of T_d symmetry may be expected to lie at room temperature and also has shown what the intrinsic temperature dependence of the moment should be.

Within the past few years a few authentic examples of tetrahedrally coördinated Ni(II) ions have been reported. Tetrahalo nickel(II) ions have been shown to exist in certain molten salt mixtures[7,8] and in salts with very large cations,[9,10] and Ni(II) ions have been trapped in tetrahedral interstices in oxides[11,12] and glasses.[13] In all these cases, the coördination is "truly" tetrahedral, in the sense that all four ligand atoms are identical. It has been suggested[14,15] that even in such cases the geometry could not remain exactly tetrahedral because of a Jahn–Teller distortion expected for a T_2 electronic ground state. However, Liehr[16] has pointed out that when the effects of spin-orbit coupling are considered, the ground state is not degenerate (it has A_1 symmetry) and Jahn–Teller forces are inoperative. Moreover, since the closest electronic state, which under nuclear displacements might perturb the ground state conformational regularity, is $\sim$300 cm.$^{-1}$ distant,[5] there should not be any large pseudo Jahn–Teller distortions either, and the regular tetrahedral configuration should be stable. The only certain

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"pseudotetrahedral" nickel(II) complexes to be reported heretofore are compounds $(C_6H_5P)_2NiX_2$ (X = Cl, Br, I). We use the prefix pseudo in those cases where the nickel(II) ion is surrounded by several different kinds of ligand atoms, either two of one kind and two of another or three of one kind and one of another kind, which stand exactly or approximately at the apices of a tetrahedron with the nickel(II) ion at its center. Such complexes cannot have T_d symmetry of the ligand field but only C_{2v} (in the 2, 2, case) or C_{3v} (in the 3, 1 case). Venanzi and Powell[14] have demonstrated the pseudotetrahedral character of these molecules, which is in marked contrast to the *cis*-planar or dimeric nature of all other $(R_3P)_2NiX_2$ compounds so far investigated[17–22] with the possible exception of $[(C_2H_5)_3P]_2Ni(NO_3)_2$.[14,18,19,22]

In this paper we report the preparation and thorough characterization of the new pseudotetrahedral nickel(II) complexes $[(C_6H_5)_3PO]_2NiX_2$, where X = Cl, Br and I. Attempts to obtain corresponding compounds with acetate and thiocyanate as anions gave yellow materials which have not as yet been characterized further. They are presumably planar as is $Ni(OPC_6H_5)_2(NO_3)_2$ which has already been reported.[23]

Experimental

Preparation. Bis-(triphenylphosphine oxide)-dichloronickel.—This compound has not been prepared in a completely pure state. A solution of triphenylphosphine oxide (4.40 g., 0.0158 mole) and hexa-aquo nickel chloride (1.78 g., 0.0075 mole) in absolute ethanol (10 ml.), was placed in an evacuated desiccator over sulfuric acid for several days. The dark green residue was heated on a steam-bath to remove the last traces of ethanol, when a blue solid contaminated with some yellow product was obtained. Excess triphenylphosphine oxide was removed by treating the solid with two portions of 25 ml. of hot cyclohexane. The pale blue product was filtered, washed with 25 ml. of cold cyclohexane and dried *in vacuo*. The yield was practically quantitative. The compound melted at 190°.

Anal. Calcd. for $C_{36}H_{30}Cl_2NiO_2P_2$: C, 63.01; H, 4.41; Cl, 10.33; Ni, 8.55. Found: C, 61.16; H, 4.57; Cl, 9.68; Ni, 8.20.

The compound is soluble in alcohols to give green solutions. It is very soluble in dimethylformamide to give solutions which are blue when hot but green when cold. A blue solution also is formed on heating with acetonitrile, but a yellow solid is formed in cooling this solution. The compound is insoluble in but not decomposed by ligroin, *n*-hexane or cyclohexane. All other solvents (fourteen were tried) decomposed the compound with the formation of mainly yellow solids. The compound could not therefore be recrystallized and no stable blue solution could be obtained.

Bis-(triphenylphosphine oxide)-dibromonickel.—A solution of triphenylphosphine oxide (4.70 g., 0.0169 mole) and nickel bromide (2.05 g., 0.0075 mole) in absolute ethanol (45 ml.) was evaporated on a steam-bath until blue crystals began to separate out from the deep blue-green solution. The mixture then was kept overnight in an evacuated desiccator over sulfuric acid. The resulting mixture of blue crystals and viscous blue-green solution was treated with about 50 ml. of hot diethyl ether to remove excess triphenylphosphine oxide. The deep blue crystalline solid was filtered off, washed with cold ether and dried *in vacuo*. The compound melted at 208°.

Anal. Calcd. for $C_{36}H_{30}Br_2NiO_2P_2$: C, 55.78; H, 3.90; Br, 20.62; Ni, 7.57; P, 7.99. Found: C, 55.60; H, 3.87; Br, 20.57; Ni, 7.72; P, 7.79.

The compound is slightly soluble in nitrobenzene but readily soluble in cold acetone to give a blue solution. It is decomposed by nitromethane and yields orange-yellow solids on treatment with benzene or chloroform.

Bis-(triphenylphosphine oxide)-di-iodonickel.—A solution of triphenylphosphine oxide (4.69 g., 0.0169 mole) and nickel iodide (2.35 g., 0.0075 mole) in absolute ethanol (37.5 ml.) was heated to boiling and then cooled and placed in an evacuated desiccator over sulfuric acid. After a week a dark red viscous product remained. On treating this with hot ethyl acetate (40 ml.) and filtering, a dark olive-green crystalline solid was obtained. The solid product was washed at the pump with cold ethyl acetate (25 ml.) and dried *in vacuo*. The yield was 2.66 g. (41%). The compound melted at 209.5°.

Anal. Calcd. for $C_{36}H_{30}I_2NiO_2P_2$: C, 49.75; H, 3.48; I, 29.21; Ni, 6.75; P, 7.13. Found: C, 49.49; H, 3.40; I, 28.85; Ni, 6.77; P, 6.92.

The compound is insoluble in carbon tetrachloride, cyclohexane and ligroin. It is decomposed by nitrobenzene, dioxane and chloroform. On treatment with cold acetonitrile the compound becomes dark red and then readily dissolves to give a very pale green solution. Dark green solutions are formed in benzene, chlorobenzene, toluene and hot ethyl acetate. Red-brown solutions are given by acetone, methyl ethyl ketone, nitromethane and 2-nitropropane.

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

Bis-(triphenylphosphine oxide)-dibromonickel was found to be a non-electrolyte in nitrobenzene solution. Bis-(triphenylphosphine oxide)-di-iodonickel had a molar conductance of 33.9 mhos at 23.8° for a 10^{-3} molar solution in nitromethane.

Magnetic Measurements.—Bulk susceptibility measurements were made at room temperature using a Gouy method as previously described.[24] Mohr's salt and copper sulfate pentahydrate were used to calibrate the Gouy tubes. Duplicate determinations were carried out.

	T, °K.	$\chi^M_{corr.} \times 10^6$	Diamagnetic corr. $\times 10^6$	μ (B.M.)
$[Ni((C_6H_5)_3PO)_2Cl_2]$	298.5	5694	−406	3.7 ± 0.1
$[Ni((C_6H_5)_3PO)_2Br_2]$	297.3	6615	−427	3.98 ± .05
$[Ni((C_6H_5)_3PO)_2I_2]$	296.5	6171	−455	3.84 ± .05

The diamagnetic corrections were calculated using the measured value for the susceptibility of triphenylphosphine oxide given by Foex.[25]

Infrared Absorption Spectra.—Infrared absorption spectra were taken on a Perkin-Elmer 21 spectrophotometer, fitted with a rock-salt prism. Nujol mulls were used. The positions of the peaks due to the P=O stretching vibration of the coördinated phosphine oxide ligands are shown below together with the P=O frequency of triphenylphosphine oxide itself.

	P=O stretching freq., cm.$^{-1}$	Shift, cm.$^{-1}$
$(C_6H_5)_3PO$	1195	..
$[Ni((C_6H_5)_3PO)_2Cl_2]$	1160	−35
$[Ni((C_6H_5)_3PO)_2Br_2]$	1154	−41
$[Ni((C_6H_5)_3PO)_2I_2]$	1151	−44

These results are in good agreement with those previously reported for other complexes of triphenylphosphine oxide.[26]

Electronic Spectra.—The reflectance spectra of the solid compounds were measured using a Beckman DU spectro-

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TABLE I

ELECTRONIC ABSORPTION SPECTRA OF THE COMPLEXES

Compound	Medium	Color	Position of absorption bands, mμ Molar extinction coefficients, for solns.; sh = shoulder				
$((C_6H_5)_3PO)_2NiCl_2$	Solid	Blue	440		615	700	>1200
$((C_6H_5)_3PO)_2NiBr_2$	Solid	Blue	487		635	700	>1200
	0.01 *M* in acetone	Blue	487(21.5)		645(101)	750(sh)	1370(19)
$((C_6H_5)_3PO)_2NiI_2$	Solid	Green	∼400(broad)	545	670	750(sh)	>1200
	0.005 *M* in PhCl	Green	440(470)	∼540(sh)	662(137)	730(sh)	1415(18.2)
	0.01 *M* in acetone	Red	515(535)	∼590(sh)	715(136)	775(sh)	1365(19.2)

photometer with the standard Beckman reflectance accessory and magnesium carbonate as the reference sample. The solution spectra were measured with a Beckman DK2 recording spectrophotometer. The results are shown in Table I and Fig. 1.

Discussion

The data quoted in Table I and in the Experimental section and the spectra given in Fig. 1 suffice to show that each of the compounds reported here is a true pseudotetrahedral nickel(II) complex, and, moreover, that the C_{2v} component necessarily superimposed on the main cubic hemihedral symmetry of the ligand field is, in these cases, of no major importance insofar as the spectra and magnetic moments at room temperature are concerned.

The evidence for these conclusions is essentially perfect in the case of $((C_6H_5)_3PO)_2NiBr_2$ and we shall discuss this case first. The compound is a non-electrolyte in nitrobenzene, which rules out any possibility of its being ionic in nature, *e.g.*, $[((C_6H_5)_3PO)_4Ni][NiBr_4]$, although this kind of ionic structure is common among dimethyl sulfoxide complexes[10] and the $[((C_6H_5)_3PO)_4Ni]^{+2}$ cation is known.[27] Thus evidence of the presence of tetrahedrally coördinated nickel(II) must also show that it is the molecular species $[Ni(OP(C_6H_5)_3)_2Br_2]$ which is tetrahedral. There are three principal lines of evidence for the presence of this tetrahedral molecule. (1) The energies of the bands in the electronic spectrum (Fig. 1 and Table I) agree very well with the energy level scheme calculated by Liehr and Ballhausen,[5] using $B = 810$ cm.$^{-1}$, $\lambda = -275$ cm.$^{-1}$ and $Dq \approx 250$ cm.$^{-1}$. We assign the doublet at 635–700 mμ to the $T_1(^3T_{1g}) \rightarrow {}^3P$ transition and the symmetrical band at 1370 mμ to the $\Gamma_1(^3T_{1g}) \rightarrow {}^3\Gamma_5(^3F)$ transition. From the Liehr–Ballhausen nomograph, it seems reasonable to assign the weak band at 487 mμ to the $T_1(^3T_{1g}) \rightarrow {}^1\Gamma_3(^1G)$ transition. (2) The intensity of the $\Gamma_1(^3T_{1g}) \rightarrow {}^3P$ absorption is so high that from this datum alone it is fairly certain that we must be dealing with a tetrahedral complex. Our spectra also may be compared with spectra previously reported for nickel(II) known or believed to be tetrahedrally coördinated.[7-12] (3) The very high magnetic moment, 3.98 B.M. at 297°K., of the nickel (II) ion in this compound is also by itself strong evidence for the presence of tetrahedrally coördinated nickel(II), when compared with the theoretical predictions of Figgis.[6] Again, on a purely empirical basis, our moment may be compared with those reported for other known or presumed tetrahedral nickel(II) complexes.[9,10]

It also appears that the C_{2v} component of the ligand field is sufficiently small that it does not appreciably alter the level pattern expected to subsist in a truly tetrahedral ligand field which is, in the sense of Figgis,[6] weak. This is credible since oxygen and bromide are not much separated in the spectrochemical series. Were the C_{2v} component of the ligand field very large, we should expect to see splitting in the electronic absorption bands and we should expect the magnetic moment to be substantially lower than that found. Such effects of a really strong C_{2v} perturbation have been observed in $((C_6H_5)_3P)_3CoX_2$ and $((C_6H_5)_3P)_2NiX_2$ compounds.[28]

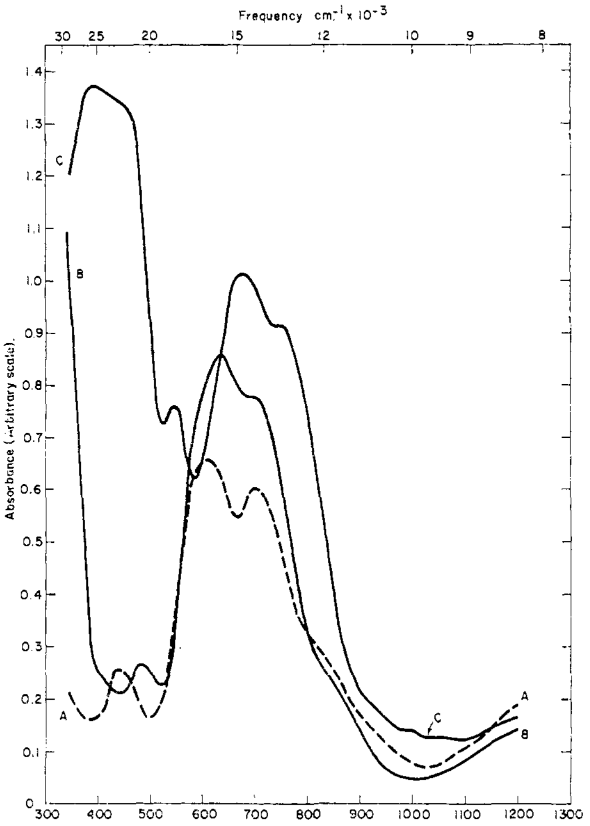

Fig. 1.—The electronic reflectance spectra of the solid compounds: A, $[(C_6H_5)_3PO]_2NiCl_2$; B, $[(C_6H_5)_3PO]_2NiBr_2$; C, $[(C_6H_5)_3PO]_2NiI_2$.

The next best characterized of the complexes reported here is the iodide, $[Ni(OP(C_6H_5)_3)_2I_2]$. The equivalent conductance in nitromethane, ∼34 mho at 24° in 10^{-3} molar solution leads us to believe that the substance is a non-electrolyte in the solid state but that there is some electrolytic dissociation, probably in the nature of

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(27) F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1873 (1960).

(28) F. A. Cotton, D. M. L. Goodgame, R. H. Holm and O. D. Faut, to be published.

$$[Ni(OP(C_6H_5)_3)_2I_2] = [Ni(OP(C_6H_5)_3)_2I]^+ + I^-$$

in nitromethane solution. Were the compound actually ionic, we should expect a much higher conductance, probably ~180 mho for a di-divalent electrolyte. Assuming, then, that the complex is a non-electrolyte, its tetrahedral conformation is attested by the electronic absorption spectra (Table I and Fig. 1) and its high magnetic moment (3.84 B.M. at 297°) following the same lines of reasoning as those given above for the homologous bromide. Again, the effects of the C_{2v} component of the ligand field are not marked.

The compound $[Ni(OP(C_6H_5)_3)_2Cl_2]$ has not been obtained in a state of high purity, but the spectral and magnetic data provide, here again, quite strong evidence for its pseudotetrahedral constitution. The reflectance spectrum (Fig. 1) agrees well with the Liehr–Ballhausen nomograph taking $D_q \approx 300$ cm.$^{-1}$ and the magnetic moment is high.

It has already been shown that the cobaltous compound, $Co(OP(C_6H_5)_3)_2Br_2$, is tetrahedral.[29] However, this and the corresponding Ni(II) complex are not isomorphous according to X-ray powder diagrams.[30] The diagrams are rather similar in the low angle region, suggesting similar short-range order in both cases, but in the higher angle region the two patterns are diverse indicating lack of identity of the lattices.

Acknowledgment.—The financial support of the United States Atomic Energy Commission, under Contract No. AT(30-1)-1965, is gratefully acknowledged.

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[30] Kindly obtained for us by Dr. I. Simon of Arthur D. Little Co.

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Tetrahedral Complexes of Nickel(II) Containing Triphenylarsine Oxide

BY DAVID M. L. GOODGAME AND F. ALBERT COTTON

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The preparation and properties of the compounds $((C_6H_5)_3AsO)_2NiCl_2$, and $((C_6H_5)_3AsO)_2NiBr_2$ are reported. Magnetilc and spectral data are adduced and interpreted to show that these compounds contain pseudotetrahedrally coördinated nickel (II) ions just as do the $((C_6H_5)_3PO)_2NiX_2$ compounds preciously described by us. Unsuccessful attempts to prepare analogous compounds with triphenylstibine oxide are described briefly.

Introduction

The preparation and characterization of complexes containing tetrahedrally coördinated nickel(II) are of unusual interest at the present time because of the relative rarity of such compounds. Aside from those instances where the nickel(II) ion is found in tetrahedral interstices in a giant superstructure over which it exerts little influence, *i.e.*, glasses[1] and host oxide lattices,[2,3] there are only the following discrete complexes which have been shown, either with complete certainty by X-ray study or virtual certainty from magnetic and spectral data, to contain tetrahedrally coördinated nickel(II). There are various solid salts containing tetrahalonickel(II) ions[4–6] and large cations. It also has been found that the tetrahedral $[Ni(NCS)_4]^{-2}$ anion exists in acetone solution, although it has not yet been possible to isolate a solid compound containing this anion.[7] These $[NiX_4]^{-2}$ species are truly tetrahedral in that they have by nature perfect or nearly perfect T_d symmetry of the ligand field. There are then a few authentic examples of pseudotetrahedral nickel(II) complexes, all, so far, of the type L_2NiX_2, where L is a neutral ligand and X a halide ion. Those heretofore reported are the compounds $((C_6H_5)_3P)_2NiX_2$ (X = Cl, Br, I)[8] and the compounds $((C_6H_5)_3PO)_2NiX_2$ (X = Cl, Br, I).[9]

We report here the preparation and properties of the compounds $((C_6H_5)_3AsO)_2NiCl_2$ and $((C_6H_5)_3AsO)_2NiBr_2$, the magnetic and spectral properties of which show them to be pseudotetrahedral nickel(II) complexes, quite similar to the analogous $((C_6H_5)_3PO)_2NiX_2$ compounds. Unsuccessful attempts have been made to prepare similar compounds containing $(C_6H_5)_3SbO$.

Experimental

Preparation.—Triphenylarsine oxide was prepared by the method of Shriner and Wolf.[10]

Triphenylstibine oxide was prepared from triphenylstibine by a method similar to that used for the preparation of triphenylarsine oxide. A solution of triphenylstibine (12 g., 0.034 mole) in acetone (240 ml.), contained in a 500 ml. round-bottomed flask, fitted with a stirrer and thermometer, was treated with 32% hydrogen peroxide (4.1 ml., 0.043 mole). The hydrogen peroxide was added dropwise over a period of about ten minutes, and at a rate such that the temperature of the reaction mixture was maintained at 25–30°. Triphenylstibine oxide began to separate as a colorless solid during the addition of the hydrogen peroxide. When the addition of the hydrogen peroxide was complete, the reaction mixture was stirred for a further 30 minutes and then cooled in an ice-water bath for 1 hr. On filtration, 3 g. of triphenylstibine oxide was obtained. The acetone was removed from the filtrate by distillation and the white solid residue treated with 25 ml. of benzene and filtered to give a further 7.6 g. of triphenylstilbine oxide. The product was air-dried. The total yield was 10.6 g. (84.5%).

Anal. Calcd. for $C_{18}H_{15}OSb$: C, 58.58; H, 4.10. Found: C, 58.46; H, 3.90.

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