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

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.

(29) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **32**, 1168 (1960).

(30) Kindly obtained for us by Dr. I. Simon of Arthur D. Little Co.

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

Tetrahedral Complexes of Nickel(II) Containing Triphenylarsine Oxide

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RECEIVED APRIL 9, 1960

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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(1) W. A. Weyl, Proceedings of the Tenth Solvay Conference, Brussels, 1956.

(2) D. S. McClure, *Phys. Chem. Solids*, **3**, 311 (1957).

(3) O. Schmitz-Dumont, H. Gössling and H. Brokopf, *Z. anorg. u. allgem. Chem.*, **300**, 159 (1959).

(4) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(5) F. A. Cotton and R. Francis, THIS JOURNAL, **82**, 2986 (1960).

(6) F. A. Cotton and R. Francis, *ibid.*, in press.

(7) F. A. Cotton and D. M. L. Goodgame, to be published.

(8) L. Venanzi, *J. Chem. Soc.*, 719 (1958).

(9) F. A. Cotton and D. M. L. Goodgame, THIS JOURNAL, **82**, 5771 (1960).

(10) R. L. Shriner and C. N. Wolf, *Organic Syntheses*, **30**, 97 (1950).

The compound melted and turned pale brown at 254–256°. Jensen[11] reports that triphenylstibine oxide prepared by heating $(C_6H_5)_3Sb(OH)_2$ above its melting point has a melting point of 295°.

Bis-(triphenylarsine oxide)-dichloronickel.—A solution of triphenylarsine oxide (3.0 g., 0.0093 mole) and hexaaquo nickel chloride (1.0 g., 0.0042 mole) in absolute ethanol (30 ml.) was placed in an evacuated desiccator over sulfuric acid for several days. The solid residue, which was dark green in color with a few small blue patches, was triturated with three 25 ml. portions of benzene to remove excess triphenylarsine oxide. The resultant blue powder was filtered and dried *in vacuo*. The yield was practically quantitative. The compound melted at 189°.

Anal. Calcd. for $C_{36}H_{30}As_2Cl_2NiO_2$: C, 55.86; H, 3.91; Ni, 7.58. Found: C, 56.04; H, 4.15; Ni, 7.51%. The compound is decomposed by water and glacial acetic acid in the cold and on warming in chloroform, acetonitrile, nitromethane and 2-nitropropane. It is insoluble in ethyl acetate, carbon tetrachloride, cold chloroform, ligroin, benzene, cyclohexane, *n*-hexane and diethyl ether. Green solutions are formed in alcohols. The compound may be recrystallized from acetone or chlorobenzene, the solutions being blue.

Bis-(triphenylarsine oxide)-dibromonickel.—A solution of triphenylarsine oxide (5.43 g., 0.0169 mole) and nickel bromide (2.05 g., 0.0075 mole) in absolute ethanol (40 ml.) was kept *in vacuo* over sulfuric acid for several days. A mixture of blue, green and orange solids was formed, when the green solution had evaporated to dryness. The crude product was dissolved in hot chlorobenzene (55 ml.) to give a deep blue solution. After filtration, the solution yielded blue crystals on cooling. These blue crystals were filtered off soon after the solution had cooled to room temperature, since, on further standing, orange crystals were formed along with the blue. The blue crystals were washed with cold chlorobenzene (20 ml.) and dried *in vacuo*. The yield was 2.55 g. (39%). The compound melted at 213°.

Anal. Calcd. for $C_{36}H_{30}As_2Br_2NiO_2$: C, 50.10; H, 3.50; Br, 18.52; Ni, 6.80. Found: C, 50.15; H, 3.19; Br, 18.45; Ni, 6.84.

The compound is slightly soluble in hot benzene forming a blue solution. Blue solutions also are formed in chloroform and hot dioxane. The compound is insoluble in toluene and xylene and is decomposed by dimethylformamide. Other solubility characteristics are similar to those described for bis-(triphenylarsine oxide)-dichloronickel.

Other Nickel(II) Complexes with Triphenylarsine Oxide.—When a hot solution of triphenylarsine oxide (4.82 g., 0.015 mole) in absolute ethanol (15 ml.) was added to a solution of nickel iodide (2.08 g. 0.0066 mole), also in absolute ethanol (15 ml.), the color of the solution changed to dark red, and a red-brown solid was precipitated on cooling. The solid product was filtered, washed twice with absolute ethanol and dried *in vacuo*. A further quantity of the red-brown solid was obtained by concentrating the filtrate *in vacuo* over sulfuric acid. A total yield of 5 g. was obtained, the compound having a melting point of 230° with decomposition. Repeated attempts to obtain a sample of the compound with a satisfactory analysis have been unsuccessful. Analyses on the impure samples indicate that the brown substance is mainly bis-(triphenylarsine oxide)-di-iodonickel.

Yellow complexes were obtained by evaporating ethanol solutions of triphenylarsine oxide and nickel perchlorate or nickel nitrate. These compounds were not further examined but are probably $[Ni((C_6H_5)_3AsO)_4](ClO_4)_2$ and $[Ni((C_6H_5)_3AsO)_2(NO_3)_2]$ analogous to the corresponding complexes with triphenylphosphine oxide previously described.[12,13]

Attempts to prepare complexes of triphenylarsine oxide with nickel sulfate and with nickel acetate were unsuccessful.

Attempts to Prepare Nickel(II) Complexes with Triphenylstibine Oxide.—Triphenylstibine oxide is only very slightly soluble in hot alcohols but is more so in hot acetone and is quite soluble in hot dimethylformamide.

The possibility of forming complexes of triphenylstibine oxide with nickel chloride, bromide, nitrate and perchlorate was investigated, using absolute ethanol, 1-butanol, acetone and dimethylformamide as solvents. In no case was there any indication of complex formation under these conditions. Either no reaction was observed, even on evaporating the solutions of the reactants to dryness, or pale green gelatinous basic products were formed.

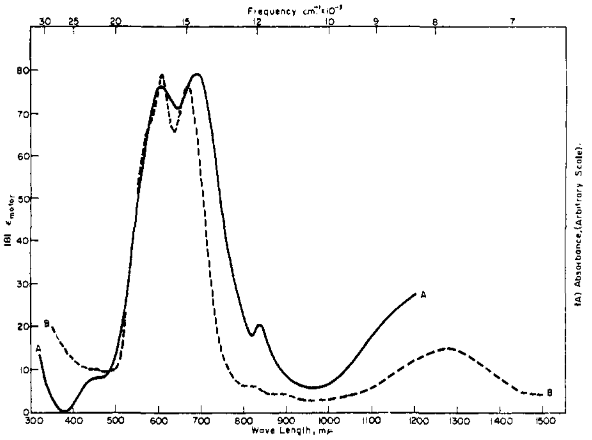

Fig. 1.—The electronic absorption spectrum of $[(C_6H_5)_3AsO]_2NiCl_2$: A, reflectance spectrum of solid; B, spectrum of 0.005 *M* solution in chlorobenzene.

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.

Compound	Molar conduct. 10^{-3} *M* in $C_6H_5NO_2$, ohm^{-1}	Temp., °C.
$[Ni((C_6H_5)_3AsO)_2Cl_2]$	6.9	26.7
$[Ni((C_6H_5)_3AsO)_2Br_2]$	7.0	27.8

Magnetic Measurements.—Bulk susceptibility measurements were made at room temperature using the Gouy method as previously described.[14] No dependence on field strength was observed. Mohr's salt and copper sulfate pentahydrate were used to calibrate the Gouy tubes. Duplicate determinations were carried out. Results:

	T, °K.	$\chi^{M}_{corr.} \times 10^6$	Diamagnetic corr. $\times 10^6$	μ (B.M.)
$[Ni((C_6H_5)_3AsO)_2Cl_2]$	298.5	6491	−450	3.95 ± 0.05
$[Ni((C_6H_5)_3AsO)_2Br_2]$	297.9	6527	−471	3.96 ± 0.05

The diamagnetic corrections were calculated using the measured value for the susceptibility of triphenylarsine oxide given by Foex.[15]

Electronic Spectra.—The reflectance spectra of the solid compounds were measured using a Beckman DU spectrophotometer with the standard Beckmann 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 Figs. 1 and 2.

Discussion

The data quoted in Table I, in the Experimental section and the electronic absorption spectra shown in Figs. 1 and 2, show that the compounds $((C_6H_5)_3AsO)_2NiX_2$, (X = Cl, Br), resemble very closely the compounds $((C_6H_5)_3PO)_2NiX_2$, (X = Cl, Br, I), previously reported,[9] in having a pseudotetrahedral configuration of ligands around the nickel(II) ion. As in the case of the corresponding complexes with triphenylphosphine oxide, the symmetry cannot be

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[11] K. A. Jensen, *Z. anorg. u. allgem. Chem.*, **250**, 245 (1943).

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

[13] E. Bannister and F. A. Cotton, *ibid.*, 2276 (1960).

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

[15] G. Foex, "Constantes Selectionées Diamagnetisme et Paramagnetisme," Masson et Cie., Paris, 1957.

TABLE I

ELECTRONIC ABSORPTION SPECTRA OF THE COMPLEXES

Compound	Medium	Position of absorption bands, mμ (Molar extinction coefficients, for solns.) sh = shoulder					
$((C_6H_5)_3AsO)_2NiCl_2$	Solid	~450(sh)		605	687	837	>1200
	0.005 *M* in PhCl		~575(sh)	607(79)	666(76.5)	815(6.5)~900(4)	1280(15)
$((C_6H_5)_3AsO)_2NiBr_2$	Solid	490		640	~680(sh)	855	~1300
	0.005 *M* in PhCl			630(184)	685(164)	~850(6)	1300(27)

T_d since the four ligands are not identical. However the C_{2v} component superimposed on the cubic hemihedral symmetry of the ligand field evidently is insufficient to cause any marked splitting in the electronic absorption bands or any substantial lowering of the magnetic moment, such as is found in the compounds $((C_6H_5)_3P)_2NiX_2$, (X = Cl, Br, I).

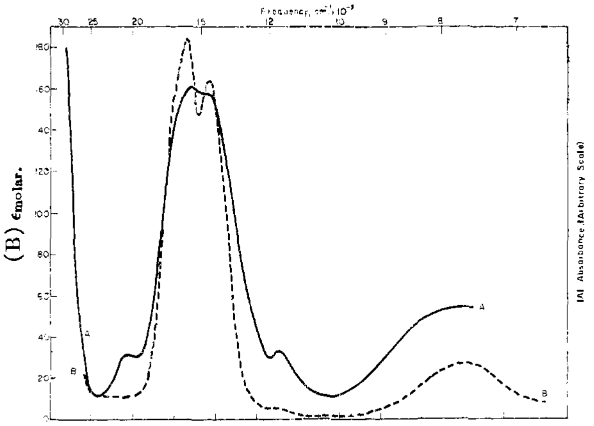

Fig. 2.—The electronic absorption spectrum of $[(C_6H_5)_3AsO]_2NiBr_2$: A, reflectance spectrum of solid; B, spectrum of 0.005 *M* solution in chlorobenzene.

Both $((C_6H_5)_3AsO)_2NiCl_2$ and $((C_6H_5)_3AsO)_2NiBr_2$ were found to have molar conductances of about 7 ohm^{-1} in 10^{-3} molar nitrobenzene solution. It is considered that this slight conductance is due to either solvolysis or decomposition in solution. In nitromethane the compounds dissolve to give a clear blue solution, which then rapidly deposits a gelatinous green solid. The compounds clearly are not of the type $[Ni((C_6H_5)_3AsO)_4][NiX_4]$ since for such a di-divalent electrolyte a molar conductance of approximately 50 ohm^{-1} would be expected for a 10^{-3} molar solution in nitrobenzene. It is therefore concluded that the compounds $((C_6H_5)_3AsO)_2NiX_2$ are non-electrolytes in the solid state.

The pseudotetrahedral nature of these complexes is apparent from the following: (1) There is good agreement between the energies of the bands observed in the electronic absorption spectra (Figs. 1 and 2 and Table I) and the energy level nomograph of Liehr and Ballhausen,[16] where B = 810 cm.$^{-1}$ $\lambda = -275$ cm.$^{-1}$ and $Dq \approx 400$ cm.$^{-1}$ for $((C_6H_5)_3AsO)_2NiCl_2$ and ≈ 350 cm.$^{-1}$ for $((C_6H_5)_3AsO)_2NiBr_2$. Thus the doublets in the region 600–700 mμ are assigned to the $\Gamma_1(^3T_{1g}) \rightarrow {}^3P$ transition and the bands at 1280 and 1300 mμ, respectively, to the $\Gamma_1(^3T_{1g}) \rightarrow {}^3\Gamma_5(^3F)$ transition. The weak bands at ~450 and 490 mμ, respectively, may be assigned to the $\Gamma_1(^3T_{1g}) \rightarrow {}^1\Gamma_3(^1G)$ transition, and the weak bands in the region 815–855 mμ to the $\Gamma_1(^3T_{1g}) \rightarrow {}^1D$ transition. (2) The molar extinction coefficients of the bands in the electronic absorption spectra, especially those assigned to the $\Gamma_1(^3T_{1g}) \rightarrow {}^3P$ transition, are high, being of the same order of magnitude as those reported for tetrahedral nickel anions[4–7] and for the corresponding complexes with triphenylphosphine oxide.[9] (3) The high magnetic moments at room temperature are in agreement with the theoretical predictions of Figgis[17] and also with those reported for other truly or psuedotetrahedral complexes of nickel(II).[4,5,9]

Comparison of the "average" Dq values as deduced from the electronic absorption spectra for the ligands in the complexes $((C_6H_5)_3AsO)_2NiX_2$, (X = Cl, Br) with those for corresponding complexes with $(C_6H_5)_3PO$ indicates that triphenylarsine oxide has a larger Dq than has triphenylphosphine oxide. Since steric factors are likely to be similar in both cases, it appears that the reduced electronegativity of the arsenic atom with respect to the phosphorus atom results in an increased ability for the oxygen atom to participate in σ-bonding with the nickel ion.

Attempts to isolate complexes of the type $((C_6H_5)_3SbO)_2NiX_2$ were unsuccessful. Triphenylstibine oxide is very little soluble in organic solvents, and this may indicate that the structure of this ligand is polymeric and thus different from $(C_6H_5)_3PO$ and $(C_6H_5)_3AsO$. To our knowledge no structural investigations have been reported for triphenylstibine oxide.

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

[16] A. D. Liehr and C. J. Ballhausen, *Ann. Physik*, **6**, 134 (1959).

[17] B. N. Figgis, *Nature*, **182**, 1568 (1958).