Nickel(II) and Nickel(I) Complexes with Tripod Arsine Ligands

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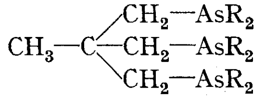
The co-ordinating ability of the two, tripod like, ligands 1,1,1-tris(dimethylarsinomethyl)ethane, L^1, and 1,1,1-tris-(diphenylarsinomethyl)ethane, L^2, toward nickel has been investigated. The ligand L^1 forms high-spin, six-co-ordinate, and low-spin, five- or four-co-ordinate nickel(II) complexes; with L^2 the two pseudo-tetrahedral nickel(I) complexes of the formula NiL^2Br and NiL^2I have been obtained.

THE triphosphine 1,1,1-tris(diphenylphosphinomethyl)-ethane (ppp) has a ' tripod ' structure and is potentially tridentate. It has been employed in several metal-complex systems and has shown particular versatility in its reactions with nickel, to the extent that stable complexes of nickel(II),[1] nickel(I),[2] and nickel(0)[3] can be prepared. We have investigated the analogous ligands (I), in which the three phosphorus atoms are replaced by arsenic atoms in order to see if they would also form unusual complexes with nickel.

(I) 

L^1, R = Me;
L^2, R = Ph

With the ligand L^1 complexes of the general formula $NiL^1_2X_2$ [X = Cl, Br, I, ClO_4, BF_4, or BPh_4] and a thiocyanate complex $NiL^1(NCS)_2$ have been prepared. The ligand L^2 gives, in the presence of the reducing agent sodium tetrahydroborate, the two complexes NiL^2Br and NiL^2I which are the first, recorded, examples of compounds of nickel(I) with a polydentate ligand having arsenic atoms as donors.

TABLE 1

Analytical and physical data for the complexes

Compound	Colour	Λ_M [a]	n [b]	μ_{eff}/B.M.	C [c]	H [c]	Ni [c]
$NiL^1_2Cl_2$	Emerald green	0(A), 8·3(B)	0·53(A), 0·50(B)	3·22	29·5 (29·4)	6·5 (6·1)	6·3 (6·5)
$NiL^1_2Br_2$	Green	50(B) [d]	1·0(C)	3·13	26·6 (26·8)	5·8 (5·5)	6·1 (6·0)
$NiL^1_2I_2$	Gold-yellow	75(B)	0·95(C), 0·53(B)	3·02	24·7 (24·5)	5·3 (5·0)	5·4 (5·4)
$NiL^1(NCS)_2$ [e]	Red-brown	0(A), 1·7(B)	0·99(A), 0·97(B)	0	27·5 (27·9)	4·9 (4·9)	10·3 (10·5)
$NiL^1_2(ClO_4)_2$	Tobacco	147(B)		0	26·0 (25·8)	5·6 (5·3)	5·7 (5·7)
$NiL^1_2(BF_4)_2$	Tobacco	151(B)		0	26·5 (26·4)	5·9 (5·4)	5·4 (5·8)
$NiL^1_2(BPh_4)_2$	Dark green	124(B)		0	56·7 (57·4)	7·0 (7·1)	4·1 (4·0)
$Ni(das)(L^1)(BF_4)_2$	Dark green	153(B)		0	28·2 (27·9)	5·0 (4·8)	6·7 (6·5)
NiL^2Br [f]	Yellow			2·11	54·6 (55·0)	4·4 (4·4)	6·6 (6·5)
NiL^2I [g]	Green-yellow			2·20	51·8 (52·1)	4·1 (4·2)	6·4 (6·2)

[a] Molar conductance, in Ω^{-1} cm^2 mol^{-1}, of *ca.* 10^{-3}M soln. in A, 1,2-dichloroethane and B, nitroethane at 20 °C. Reference values in 1,2-dichloroethane and nitroethane, respectively, are 19 and 70 for $Bu^n_4N)Br$, 14 and 130 for $(Bu^n_4N)_2ZnBr_4$. [b] Ratio of the found to the theoretical molecular weight for *ca.* 5 × 10^{-3}M soln. in A, 1,2-dichloroethane; B, nitroethane; and C, benzene. [c] Calculated value in parentheses. [d] Behaviour of conductivity in nitroethane on dilution: $\Lambda_M = 42(2{\cdot}8 \times 10^{-3}\text{M}), 49(1{\cdot}4 \times 10^{-3}\text{M}), 51(6{\cdot}9 \times 10^{-4}\text{M}), 56(3{\cdot}6 \times 10^{-5}\text{M}), 63(2{\cdot}0 \times 10^{-5}\text{M})$. [e] N: calc. 5·0; found 4·9%. [f] As: calc. 25·1; found 25·5%. [g] I: calc. 13·5; found 13·5%.

RESULTS AND DISCUSSION

Complexes of Nickel(II).—Analytical data and some of the physical properties of the compounds are given in Table 1. The nickel(II) compounds are air-stable. The halogeno-complexes have effective magnetic moments at room temperature in the range 3·02—3·22 B.M. Their diffuse reflectance and benzene solution spectra, which are practically identical (Table 2) show a band at *ca.* 8 000, a shoulder at *ca.* 13 000, and a band (or shoulder) at *ca.* 16 700 cm^{-1} in the region of the *d–d* transitions. The bromide and iodide complexes are monomeric in benzene solution.† Thus, the compounds dissolve unchanged in non-dissociating solvents. The spectral and magnetic data are consistent with a distorted octahedral structure in which there is no centre of symmetry, giving rise to bands in characteristic positions but with unusually high intensities (ε_{max} 40—210 l mol^{-1} cm^{-1}). Thus the available evidence points to a *cis*-octahedral structure, in which one arsenic atom of each ligand is non-co-ordinating. A structure in which the halide ligands are mutually *trans* can also be excluded on the grounds that such a structure would give rise to a diamagnetic compound, as for example occurs in $Ni(das)I_2$,[4] (das = *o*-phenylenebisdimethylarsine).

In the dissociating solvent nitroethane the conductivity and molecular weight measurements of the iodide salt of the ligand L^1 indicate that it is dissociated into $[NiL^1_2I]^+$ cations and iodide anions. The absorption spectrum, shown in the Figure, is characteristic of tetragonal complexes with ligands of this type. The spectrum of $Ni(tas)I_2$[5] is shown also in the Figure,

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† A solution of the chloro-complex in benzene rapidly becomes turbid.

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[5] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 1961, 4433.

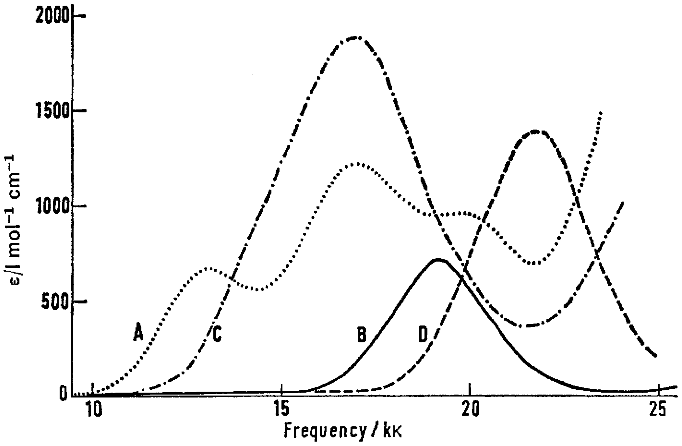
tas = bis(dimethylarsinopropyl)methylarsine, and by comparison with this it is clear that the complex $[NiL^1_2I]^+$ has a five-co-ordinate structure, probably a distorted square pyramidal one. The bromide salt exhibits similar properties except that the molar conductivity is lower and increases with dilution (Table 1) in a way that suggests the presence of an equilibrium of the type $NiL^1_2Br_2 \rightleftharpoons [NiL^1_2Br]^+ + Br^-$.

TABLE 2

Electronic spectra of the complexes

Compound		Absorption max., cm^{-1} (ε for soln., $l\,mol^{-1}\,cm^{-1}$)
$NiL^1_2Cl_2$	*a*	8 300sh, 9 800, 13 000, 16 700
	b	19 200 (700)
$NiL^1_2Br_2$	*a*	7 900sh, 9 400, 13 300sh, 16 700, 27 000sh
	c	7 900sh, 10 000sh (37), 13 300sh (58), 18 200 (108)
	d	17 600 (1 056)
$NiL^1_2I_2$	*a*	8 300sh(?), 9 500, 13 300sh, 16 700sh, 23 800
	c	9 500 (43), 13 200sh, 19 900 (220)
	d	17 300 (1 880)
$NiL^1(NCS)_2$	*a*	21 700
	d	21 700 (1 400)
$NiL^1_2(ClO_4)_2$	*a*	15 000, 22 200
	d	16 100 (677), 20 400 (1 533)
$NiL^1_2(BF_4)_2$	*a*	15 400, 21 700
	d	15 900 (664), 20 400 (1 558)
$NiL^1_2[BPh_4]_2$	*a*	16 700, 20 400
	d	16 000 (691), 20 400 (1 620)
$NiL^1(DAS)(BF_4)_2$	*a*	16 300, 23 400
	d	16 300 (210), 23 400 (1 800)
NiL^2Br	*a*	7 300, 15 300sh, 25 000sh
NiL^2I	*a*	5 700sh(?), 7 200, 14 700sh, 25 000sh
Ni(ppp)I [e]	*a*	6 900sh, 9 100, 14 300sh, 26 300sh

[a] Solid. [b] 1,2-Dichloroethane solution. [c] Benzene solution. [d] Nitroethane solution. [e] Ref. 2.



Absorption spectra in 1,2-dichloroethane solution of A, $[Ni(tas)I_2]$; B, $[NiL^1_2Cl_2]$; absorption spectra in nitroethane solution of C, $[NiL^1_2L_2]$; D, $[NiL^1(NCS)_2]$

The chloro-complex dissolves in 1,2-dichloroethane and in nitroethane to give a magenta solution with an intense absorption band at 19 200 cm^{-1}. The solutions are non-conducting and the molecular weight is half that expected for an undissociated monomer. One must therefore conclude that the compound dissociates into free ligand and the species NiL^1Cl_2; the absorption spectrum (Figure) seems to indicate a square-planar structure, though some low-spin five-co-ordinate nickel complexes have absorption spectra with only the band at *ca.* 20 000 cm^{-1}.[6]

The diamagnetic complex $NiL^1(NCS)_2$ is a monomeric non-electrolyte in 1,2-dichloroethane and nitroethane. It has a square-planar structure both in the solid state and in solution (Figure). The other complexes of this ligand with poorly co-ordinating anions such as ClO_4^-, BF_4^-, and BPh_4^- are all diamagnetic and 2 : 1 electrolytes in nitroethane, and have the general formula $NiL^1_2X_2$. The visible and u.v. spectra, which are practically identical, both in the solid state and in solution, have bands at *ca.* 16 000 and *ca.* 21 000 cm^{-1} (Table 2). They are rather similar, apart from the relative intensity of the peaks, to the spectra of the related compounds $Ni(ttas)_2(ClO_4)_2$ [7] and $Ni(tas)_2(ClO_4)_2$ [5] and to the square-pyramidal, five-co-ordinate, compound $Ni(ttas)(das)(ClO_4)_2$ [8] [ttas = bis(*o*-dimethylarsinophenyl)methylarsine]. The compound $Ni(das)(L^1)(BF_4)_2$ which we have also prepared for the purpose of comparison has a very similar spectrum (Table 2). It is therefore reasonable to conclude that the cations of these compounds are five-co-ordinate, $[NiL_2]^{2+}$, even though the ligands possess an additional arsenic atom which could be co-ordinated, but is not.

When the compound $NiL^1_2(BF_4)_2$ is titrated conductimetrically with tetraethylammonium halides, a sharp break is observed in the curves when one equivalent of bromide or iodide has been added, or when two equivalents of chloride have been added. The absorption spectra obtained at the equivalence point are exactly the same as those of the species discussed above, NiL^1Cl_2, $[NiL^1_2Br]^+$, and $[NiL^1_2I]^+$.

Addition of the ligand L^2 to solutions of nickel(II) salts does not bring about any colour change and no nickel(II) complexes of this ligand have been isolated. This is probably due to the low basicity of the arsenic atoms in this ligand.

Complexes of Nickel(I).—Ethanolic solutions of the nickel(II) complexes with the ligand L^1 change colour when treated with sodium tetrahydroborate, but all attempts to isolate products of reduction have been unsuccessful. However, when the ligand L^2 is used, crystalline compounds of the formula NiL^2X have been obtained (X = Br or I).* Analytical data and some of the physical properties of the compounds are given in Table 1; these compounds are moderately air-stable in the solid state but their solutions are unstable even in an

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* During the preparation of the bromo-complex traces of metallic nickel are sometimes formed; the preparation of a chloro-complex failed, metallic nickel being the main product.

[6] M. O. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1543.

[7] R. G. Cunninghame, R. S. Nyholm, and M. L. Tobe, *J.C.S. Dalton*, 1972, 229.

[8] B. Bosnich, R. Bramley, R. S. Nyholm, and L. Tobe, *J. Amer. Chem. Soc.*, 1966, **88**, 3926; B. Bosnich, R. S. Nyholm, P. J. Pauling, and M. L. Tobe, *ibid.*, 1968, **90**, 4741.

inert atmosphere and are rapidly decolourized by air. The i.r. spectra give no evidence for the presence of hydride ions.

The *X*-ray powder patterns of the two compounds are practically identical to those of the phosphorus analogues.[2] Since single crystal *X*-ray studies of the analogous phosphorus iodide compound have shown that it has a pseudo-tetrahedral configuration,[9] the arsenic compounds are very likely also to be pseudo-tetrahedral. The room temperature magnetic moments, which fall in the range 2·11—2·20 B.M., although slightly higher than usual for nickel(I) complexes [2,10] are fully consistent with a d^9 configuration in a field of approximately tetrahedral symmetry.[11] The reflectance spectra of the two compounds, very similar to those of phosphorus analogues, show the spectrochemical shifts expected when substituting arsenic for phosphorus, and iodide for bromide (Table 2).

EXPERIMENTAL

Synthesis of the Ligands.—The ligand L^1 was prepared by the method previously described.[12]

The ligand L^2 was prepared as follows: $Me{\cdot}C(CH_2{\cdot}Cl)_3$ [13] (0·015 mol), in dry tetrahydrofuran (50 ml) was added with continuous stirring to 0·045 mol of $KAsPh_2$,2(dioxan),[14] dissolved in tetrahydrofuran (200 ml). The solution was heated under reflux for 8 h and then concentrated to a small volume on a steam bath. All operations were carried out in a nitrogen atmosphere. The residue was treated cautiously with diethyl ether and water; the organic phase was separated, and the solvent removed *in vacuo*. Ethanol was then added and white crystals separated which were recrystallized from acetone (Found: C, 64·8; H, 5·5. Calc. for $C_{41}H_{39}As_3$: C, 65·1; H, 5·2%), m.p. 124—125 °C.

Preparation of the Complexes $NiL^1{}_2X_2$, X = Cl, Br, *or* I.—The ligand (2 mmol) dissolved in warm ethanol (5 ml), was added to a warm solution of anhydrous nickel halide (1 mmol) in absolute ethanol (5 ml). On cooling, crystals separated which were collected, washed with the solvent and light petroleum (b.p. 40—70 °C), and dried *in vacuo*.

$NiL^1(NCS)_2$.—The compound was obtained when equimolar amounts of nickel thiocyanate and the ligand were allowed to react by the method used to prepare the above halogeno-complexes.

$NiL^1{}_2(BPh_4)_2$.—To a solution of anhydrous nickel chloride (1 mmol), dissolved in ethanol (10 ml), was added the ligand (2 mmol) dissolved in ethanol (5 ml). The resulting solution was boiled. When solid sodium tetrahydroborate was added (2 mmol), crystals were obtained immediately. The compound was recrystallized from ethanol and acetone.

$NiL^1{}_2X_2$, X = ClO_4 *or* BF_4.—A solution of ligand (2 mmol) in warm ethanol (10 ml) was added to a warm solution of the appropriate nickel salt (1 mmol) in ethanol (10 ml). A crystalline product separated which was recrystallized from nitroethane and butanol.

$Ni(das)L^1(BF_4)_2$.—The compound was obtained when equimolar amounts of nickel tetrafluoroborate hexahydrate, triarsine, and diarsine were allowed to react by the method used to prepare $NiL^1{}_2(BF_4)_2$.

NiL^2X, X = Br *or* I.—All the operations were carried out in a atmosphere of either nitrogen or argon. Ligand (1 mmol) dissolved in diethyl ether (20 ml) was added to a solution of nickel halide (1 mmol) in butanol (10 ml). To the resulting solution sodium tetrahydroborate (1 mmol) dissolved in ethanol (10 ml) was added dropwise and the solution was shaken vigorously after each addition. A yellow crystalline product formed immediately and was filtered off, washed with absolute alcohol, water, alcohol again, and then light petroleum, before being dried in a current of nitrogen.

Materials and Physical Measurements.—All the solvents were purified and dried using standard procedures. The physical measurements were carried out as previously described.[15]

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