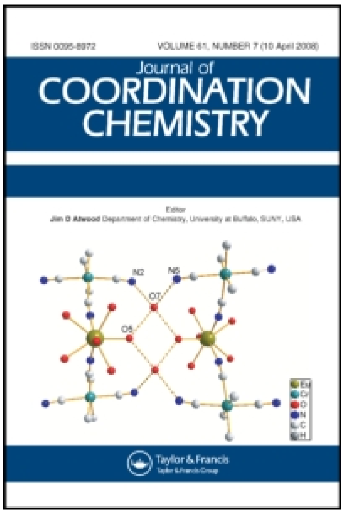

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NICKEL(II) COMPLEXES WITH AN OPEN-CHAIN TETRADENTATE NITROGEN-ARSENIC LIGAND

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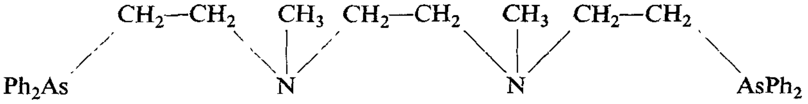
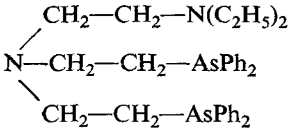
The open-chain tetradentate ligand *N,N'*-bis(2-diphenyl-arsinoethyl)-*N,N'*-dimethylethylenediamine, (AsNNAs), forms four-coordinate nickel(II) complexes with the formulae [Ni(AsNNAs)]Y_2 ($Y = ClO_4$, BPh_4, BF_4) and [Ni(AsNNAs)I]Y ($Y = BPh_4$, I). Octahedral complexes of the general formula Ni(AsNNAs)Y_2 are formed in the presence the more strongly coordinating anions, Y = Br, I, NCS, $CH_3COO/2$, $NO_3/2$. The octahedral complexes may dissociate in solution to give an equilibrium mixture containing also tetrahedral species. The coordinating behaviour of the ligand is compared with that of a ligand which has the same donor-atom set but a tripod structure, and with that of its phosphorous analogue PNNP.

INTRODUCTION

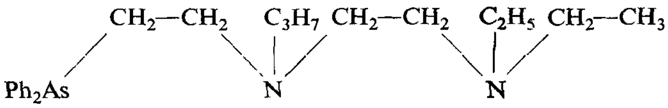
The coordinating behaviour of "tripod" and "open-chain" forms of tetradentate ligands has been recently subjected to a comparative study. Donor-atom sets examined include P_4,[1] As_4,[2] and N_2P_2.[3] We now extend this study to an open-chain ligand with the potential donor-atom set (AsNNAs) namely, *N,N'*-bis(2-diphenylarsinoethyl)-*N,N'*-dimethylethylenediamine, I.



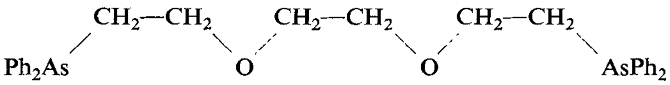
Complexes of I with Ni(II) have been prepared using a variety of anions, and the mode of interaction has been compared with that obtaining when the tripod ligand *N, N*-bis(2-diphenylarsinoethyl)-*N*-(2-diethylaminoethyl) amine, II, (N-NAs_2) having the same donor-atom set, is used.[4]



For the purposes of comparison the tridentate ligand *N,N*-diethyl-*N'*-(2-diphenylarsinoethyl)-N' (*n*-propyl) ethylenediamine, III, (NNAs), and some of its nickel complexes have also been prepared



In addition the potentially tetradentate open-chain ligand 1,8-bis(diphenylarsino)-3,6-dioxaoctane (IV) (AsOOAs) and a nickel complex have been prepared and characterized.



EXPERIMENTAL

Synthesis of the Ligands

The ligands were prepared by treating the corresponding chlorides with $KAsPh_2.2dioxan$ in tetrahydrofuran (THF) solution:[5]

$$R—Cl + KAsPh_2 \longrightarrow R—AsPh_2 + KCl$$

N,N'-bis(2-diphenylarsinoethyl)-N,N'-dimethylethylenediamine (AsNNAs)(I) 0.10 moles of the chloro-amine, prepared as described previously,[3] were dissolved in a small amount of dry THF and the solution, after standing over BaO, was added dropwise and with stirring to an orange solution of $KAsPh_2$.2dioxan in THF. The decoulorized mixture was boiled under reflux for ten minutes, and most of the solvent was removed by heating the mixture on a steam bath. A precipitate of KCl, formed by the addition of ether, was removed by filtration, and the remaining solvent removed by distillation under reduced pressure. The ligand was recrystallized from ethanol as a white crystalline powder. (M.p. 87–89°C; calcd. for $C_{32}H_{38}N_2As_2$ C, 64.09; H, 6.39; N, 4.67; As, 24.80; found: C, 63.52; H, 6.37; N, 4.60; As, 24.38%).

N,N-diethyl-N'-(2-diphenylarsinoethyl)-N'-(n-propyl)ethylenediamine, (NNAs), (III) The preparation of the chloro-amine has been described elsewhere.[6] The ligand was prepared by the same method as above, and was obtained as an oil by distillation under reduced pressure. (B.p. 178–180°C at 0.2 torr; calcd. for $C_{23}H_{35}N_2As$: C, 66.70; H, 8.53; N, 6.75; As, 18.10; found: C, 65.96; H, 8.64; N, 6.69; As, 17.91%).

1,8-bis(diphenylarsino)-3,6-dioxaoctane, (AsOOAs), (IV) The chloro-ether was prepared as follows. 47 g of $SOCl_2$ were added to 15 g of triethyleneglycol in 15 g of benzene and the mixture was heated under reflux on a steam bath at *ca.* 50°C for 8 hr. After the solvent and excess thionylchloride had been removed by distillation under reduced pressure, the chloroether was distilled at 135°C (50 torr) as a colourless oil, and purified by a further distillation. The ligand was obtained by the usual procedure and recrystallized from ehtanol at −20°C. (M.p. 34–35°C; calcd. for $C_{30}H_{32}O_2As_2$: C, 62.80; H, 5.63; As, 26.13; found C, 62.46; H, 5.60; As, 25.83%).

Preparation of the complexes 1 mmole of ligand in 10 ml of butan-1-ol was added to a solution of the appropriate nickel salt in 10 ml of hot butan-1-ol. The solution was filtered and concentrated until crystallization occurred. In some cases cyclohexane had to be added to induce precipitation. Ochre crystals of $[Ni(AsNNAs)I_2]$ were only obtained after letting the solution stand for two days. To obtain the violet crystals of $[Ni(AsNNAs)(NCS)_2].CHCl_3$ the ligand was dissolved in chloroform. The $[NiLX]BPh_4$ complexes were obtained by adding sodium tetraphenylborate to the butan-1-ol solutions. All the complexes were filtered on a sintered glass funnel, recrystallized and dried *in vacuo* at 70°C. The analytical data for the complexes are given in Table I. Details of the magnetic, conductance and spectral properties are given in Table II.

Materials and Physical Measurements All solvents were reagent grade. Physical measurements were carried out as described previously.[4,7]

RESULTS AND DISCUSSION

The type of complex formed with the ligand I depends considerably upon the nature of the anion present. The discussion is therefore divided into separate sections according to the behaviour of the anion *Y*.

$Y = ClO_4$, BPh_4, BF_4 These anions are non-coordinating and the compounds formed are ionic $[Ni(AsNNAs)]Y_2$. The complexes are diamagnetic and are assigned a square-planar structure with donor-atom set As_2N_2 both in the solid state and in solution (Figure 1).

TABLE I

Analytical data for the complexes

Compound	Colour	M.p.	% C		% H		% N		% Ni	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(1) Ni(AsNNAs)Br_2]	Pale green	138	46.92	47.35	4.67	4.67	3.42	3.46	7.16	6.80
(2) [Ni(AsNNAs)I_2]	Violet	179	42.30	42.17	4.20	4.63	3.07	3.02	6.43	6.07
(3) [Ni(AsNNAs)I_2]	Ochre	167–170	42.30	42.40	4.20	4.19	3.07	3.09	6.43	6.13
(4) [Ni(AsNNAs)I]BPh_4	Violet	120–122	60.85	60.20	5.30	5.12	2.54	2.50	5.24	5.62
(5) [Ni(AsNNAs)]$(ClO_4)_2$	Gold Yellow	279–281	44.70	44.75	4.46	4.48	3.26	3.30	6.48	6.27
(6) [Ni (AsNNAs)]$(BPh_4)_2$	Gold Yellow	212–214	74.20	74.00	5.93	6.50	2.16	2.10	4.50	4.44
(7) [Ni(AsNNAs)]$(BF_4)_2$	Gold Yellow	175–180	46.20	46.00	4.60	4.90	3.37	3.34	7.05	6.88
(8) [Ni(AsNNAs)$(NCS)_2$]	Turquoise Green	238	56.26	56.32	4.95	5.29	7.22	7.16	7.57	7.93
(9) [Ni(AsNNAs)$(NCS)_2$]$\cdot CHCl_3$	Violet	138–140	46.99	47.06	4.39	4.54	6.26	6.33	6.56	6.40
(10) [Ni(AsNNAs)(CH_3COO)]BPh_4	Turquoise Green	220	67.15	67.50	5.92	6.16	2.70	2.79	5.66	5.22
(11) [Ni(AsNNAs)NO_3]BPh_4	Blue	148–150	64.65	64.86	5.62	5.60	4.04	4.20	5.64	5.24
(12) [Ni(AsOOAs)I_2]	Brown	179–182	40.62	40.00	3.63	3.59			6.62	6.62
(13) [Ni(NNAs)Cl]BPh_4	Pink	197–199	68.20	67.83	6.70	6.95	3.38	3.47	7.09	6.80
(14) [Ni(NNAs)Br]BPh_4	Purple	192–193	64.75	65.34	6.35	6.77	3.21	3.38	6.72	6.61
(15) [Ni(NNAs)I]BPh_4	Violet	192–194	61.50	61.94	6.03	6.32	3.05	3.08	6.38	6.20
(16) [Ni(NNAs)$(NCS)_2$]	Pale Green	172–173	51.00	50.98	6.00	6.10	9.51	9.23	9.98	9.71

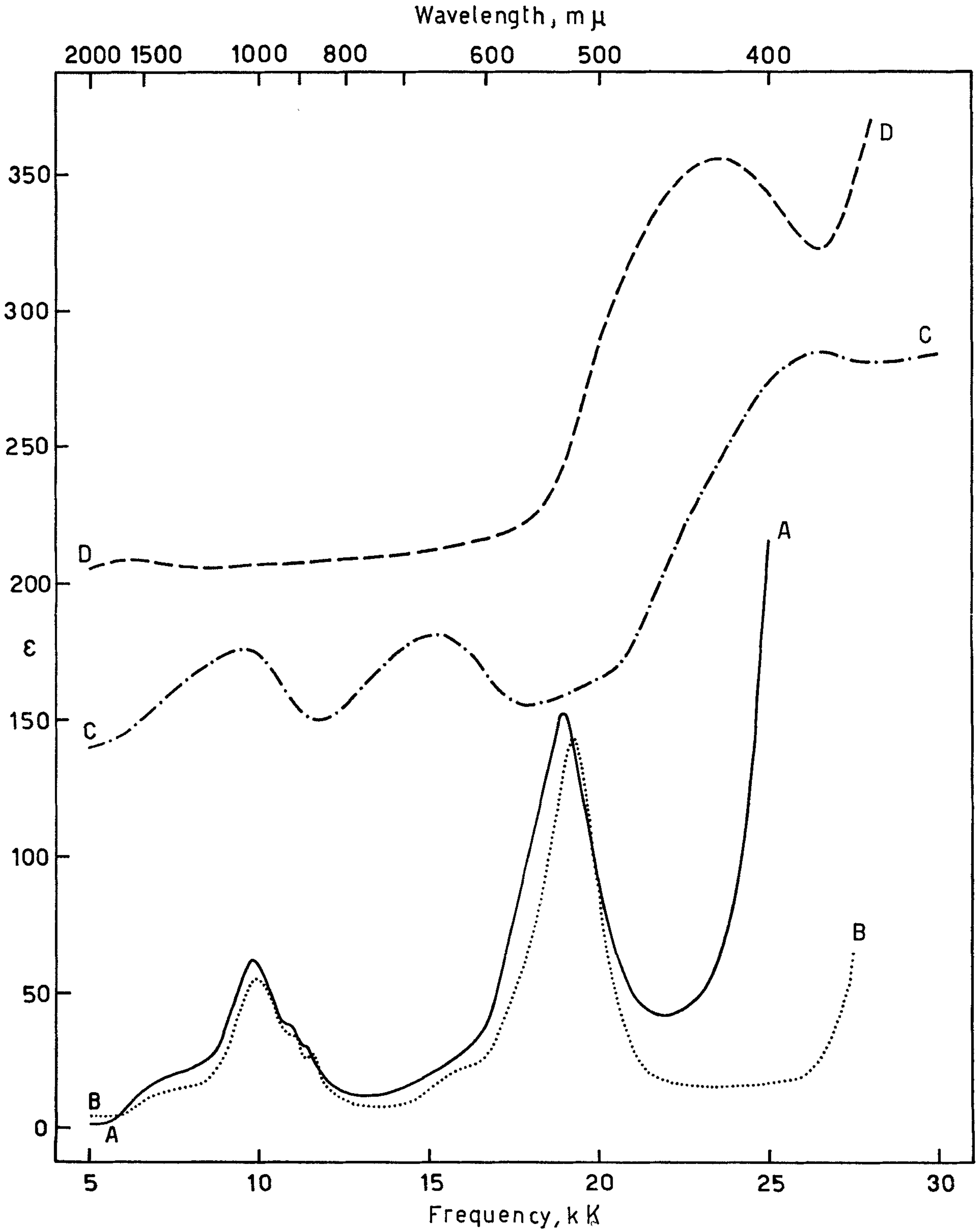


FIGURE 1 Absorption spectrum of 1,2-dichloroethane solution of: A, $[Ni(Me_2NCH_2CH_2NMe_2)Br_2]$; B, $[Ni(AsNNAs)Br_2]$. Reflectance spectra of: C, $[Ni(AsNNAs)Br_2]$; D, $[Ni(AsNNAs)](BPH_4)_2$.

TABLE II

Physical data for the complexes

Compound	μ_{eff}(B.M.)[a]	Λ_M* (cm^2 ohm^{-1}) D[b]	N[b]	State[b]	Absorption max. (kcm^{-1}) with ϵ_M for soln. in parentheses.[c]
(1) [Ni(AsNNAs)Br_2]	3.35 (25)	—	20	R	9.6br, 15.2, 26.3
				D	9.8(62), 11(36)sh, 11.4(31)sh, 15.4sh 19(158)
(2) [Ni(AsNNAs)I_2]	diam. (22)	10	65	R	10.5sh, 14.8, 19
				D	9.5(40), 14.3sh, 18(388)
(3) [Ni(AsNNAs)I_2]	3.14 (22)	11	67	R	9.5br, 14.8, 22.2sh
				D	9.5(23), 14.3sh, 17.8(453)
(4) [Ni(AsNNAs)I]BPh_4	diam. (20)	18	57	R	10sh, 14.2, 18.5
				D	13.4(70), 17.9(470)
(5) [Ni(AsNNAs)]$(ClO_4)_2$	diam. (22)	11	132	R	23.2
				D	22.5(435)
(6) [Ni(AsNNAs)]$(BPh_4)_2$	diam. (22)			R	23.2
				N	22.7(480)
(7) [Ni(AsNNAs)]$(BF_4)_2$	diam. (22)			R	23.2
				N	22.7(475)
(8) [Ni(AsNNAs)$(NCS)_2$]	3.10 (25)	*d*	*d*	R	9.6br, 16.1
(9) [Ni(AsNNAs)$(NCS)_2$]$CHCl_3$	3.08 (22)	—	—	R	11.4, 18.2
				D	10.2sh, 11.6(48), 17.9(35)
(10) [Ni(AsNNAs)(CH_3COO]BPh_4	3.11 (23)	23	50	R	10.2br, 16.4
				D	9.5sh, 10.6(48), 16.7(40)
(11) [Ni(AsNNAs)(NO_3)]BPh_4	3.07 (21)	21	50	R	10.9br, 17.2
				D	10.7(47), 17.5(51)
(12) [Ni(AsOOAs)I_2]	diam. (20)	—	—	R	13.3sh, 20.4sh
				D	14.7(490), 20.4(3200)
(13) [Ni(NNAs)Cl]BPh_4	diam. (26)	23	58	R	19.6
				D	19.4(715)
(14) [Ni(NNAs)Br]BPh_4	diam. (25)	23	59	R	19.1
				D	18.9(670)
(15) [Ni(NNAs)I]BPh_4	diam. (26)	23	58	R	13.7sh, 18.2
				D	13.2(28), 18.0(576)
(16) [Ni(NNAs)$(NCS)_2$]	3.18 (26)	—	—	R	8.6br, 10.9sh, 16.0, 20.8
				D	5.7br(32), 10.3(27), 15.1(32) 20.8(69)

* For *ca.* 10^{-3} *M* soln. at 20°. Ref. values: [Bu^n_4N]BPh_4, 22(D), 58(N); [Bu^n_4N]$_2$[$NiBr_4$], 14(D), 125(N).

[a] Temp. (°C) in parentheses.

[b] R = Diffuse reflectance, N = nitroethane, D = 1, 2-dichloroethane.

[c] sh = shoulder, br = broad.

[d] Not soluble.

Y = Br, CH_3COO, NO_3 On the basis of the electronic spectra and magnetic moments these complexes must be assigned an octahedral structure. The ratio of the frequencies (1.58) and shape of the bands, ν_1 and ν_2 of the complex [Ni(AsNNAs)Br_2] are similar to those of the complexes [Ni(AsNNAs)(CH_3COO)]BPh_4 and [Ni(AsNNAs)(NO_3)]BPh_4 which are monomeric and 1:1 electrolytes ($\nu_2/\nu_1 = 1.6$). The presence of bidentate acetate and nitrate ligands in the latter complexes suggests a *cis* configuration and we tentatively assign a *cis* configuration to the bromo-complex too.

The solution spectra of the bromo-complex differ from its reflectance spectrum and are similar to the spectra of the complexes [Ni($Me_2NCH_2CH_2NMe_2$)Br_2] (Figure 1) and dibromo *cis-endo-N,N'*-di(4-methylbenzylidene)-*meso*-2,3-butanediamine nickel(II) which has been shown by X-ray methods to be pseudotetrahedral.[8]

This suggests that the chromophore present in these solutions is tetrahedral NiN_2Br_2, the two arsenic atoms not being coordinated to the metal. ^1H nuclear magnetic spectra reveal that the octahedral and tetrahedral species are in equilibrium since the phenyl proton signals are not in the diamagnetic position as it would be expected for the tetrahedral species where the As atoms are not bound to the paramagnetic centre. Addition of bromide ions to a solution containing the diamagnetic $[Ni(AsNNAs)]^{2+}$ ion causes a bathochromic shift of the band at 22.7kK, and when one equivalent of bromide ion has been added the resulting spectrum is practically identical with that of the complex [Ni(NNAs)Br] BPh_4 containing the tridentate ligand NNAs, III. The latter complex is monomeric and a 1:1 electrolyte and must therefore have a square-planar geometry with the donor-atom set N_2AsBr. Thus it seems reasonable to suggest that the complex ion $[Ni(AsNNAs)Br]^+$ is formed by the addition of bromide to $[Ni(AsNNAs)]^{2+}$ and that it is a square-planar species containing the chromophore NiN_2AsBr. Further addition of bromide gives the tetrahedral species described earlier. A pictorial representation of these equilibria is given in Figure 2.

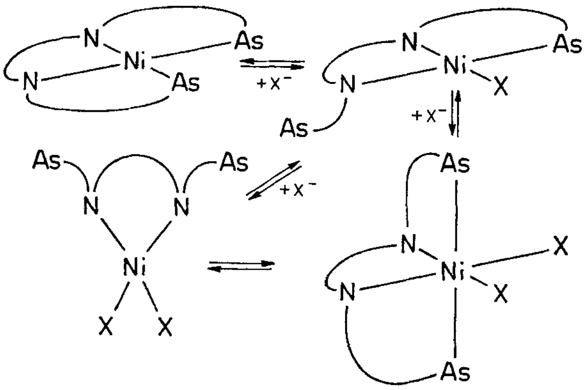


FIGURE 2 A pictorial representation of the equilibria in solutions of $[Ni(AsNNAs)]^{2+}$ containing different amounts of X^- (X = Br, I).

Y = *I* The ochre form of $[Ni(AsNNAs)I_2]$ is paramagnetic and octahedral in the solid state. As in the case of the dibromide a *cis*-configuration can be tentatively assigned to this compound on the basis of the resemblance of its spectrum and those of the nitrato and acetato complexes. Its behaviour in solution is identical to that of the violet form. The solid compounds $[Ni(AsNNAs)I]BPh_4$ and the violet form of the diiodide are diamagnetic and must be formulated as square-planar complexes with the chromophore NiAsNNI; the reflectance spectra of both compounds closely resemble the spectrum of the complex $[Ni(NNAs)I]BPh_4$ to which a square-planar geometry must be assigned (Figure 3), with bands at much lower frequencies than those of cation $[Ni(AsNNAs)]^{2+}$.

In dichloroethane the spectra of $[Ni(AsNNAs)I]BPh_4$ are identical with each other, showing that the species present in solution is predominantly the square-planar one. The spectrum of [Ni(AsNNAs)I]I contains an additional band at 9.5kK which is indicative of the presence of a tetrahedral species having the chromophore NiN_2I_2, in which the arsenic atoms are not coordinated. A similar band is found in the spectrum of $[Ni(Me_2NCH_2CH_2NMe_2)I_2]$.[8] The presence of a neutral, tetrahedral species is supported by the conductivity data, which are intermediate between the expected values for a 1:1 electrolyte and a non-electrolyte, and by the value of the ratio M_{found}/M_{calcd} (M = molecular weight) $\bar{n} = 0.78$ in dichloroethane.

The equilibrium between planar and tetrahedral species shifts towards the latter with increasing temperature (Figure 4). Bands characteristic of tetrahedral species also appear in the spectra of solutions of $[Ni(AsNNAs)I]BPh_4$, $[Ni(NNAs)I]BPh_4$ and $[Ni(AsNNAs)](BPh_4)_2$ in the presence of added iodide ions.

Y = *NCS* Both the violet and turquoise-green forms of the complex $[Ni(AsNNAs)(NCS)_2]$ are paramagnetic and can be assigned an octahedral structure. The solution and the reflectance spectra of the violet form are identical. The infrared spectrum shows a single CN stretching band at 2080 cm^{-1} indicative of N-bonded thiocyanate.[9] The value of $\bar{n}$ of 0.86 in dichloroethane suggests a monomeric species. A *trans*-octahedral structure is proposed for the violet form since more than one CN stretching band would be expected for a *cis* complex, and since its electronic spectrum is closely similar to that of $[Ni(PNNP)(NCS)_2]^3$ which has also been assigned a *trans*-configuration.

The insoluble turquoise-green form shows three bands in the CN stretching region at 2132, 2119 and 2062 cm^{-1}, values characteristic of both N- and S-bonded thiocyanate. A polymeric

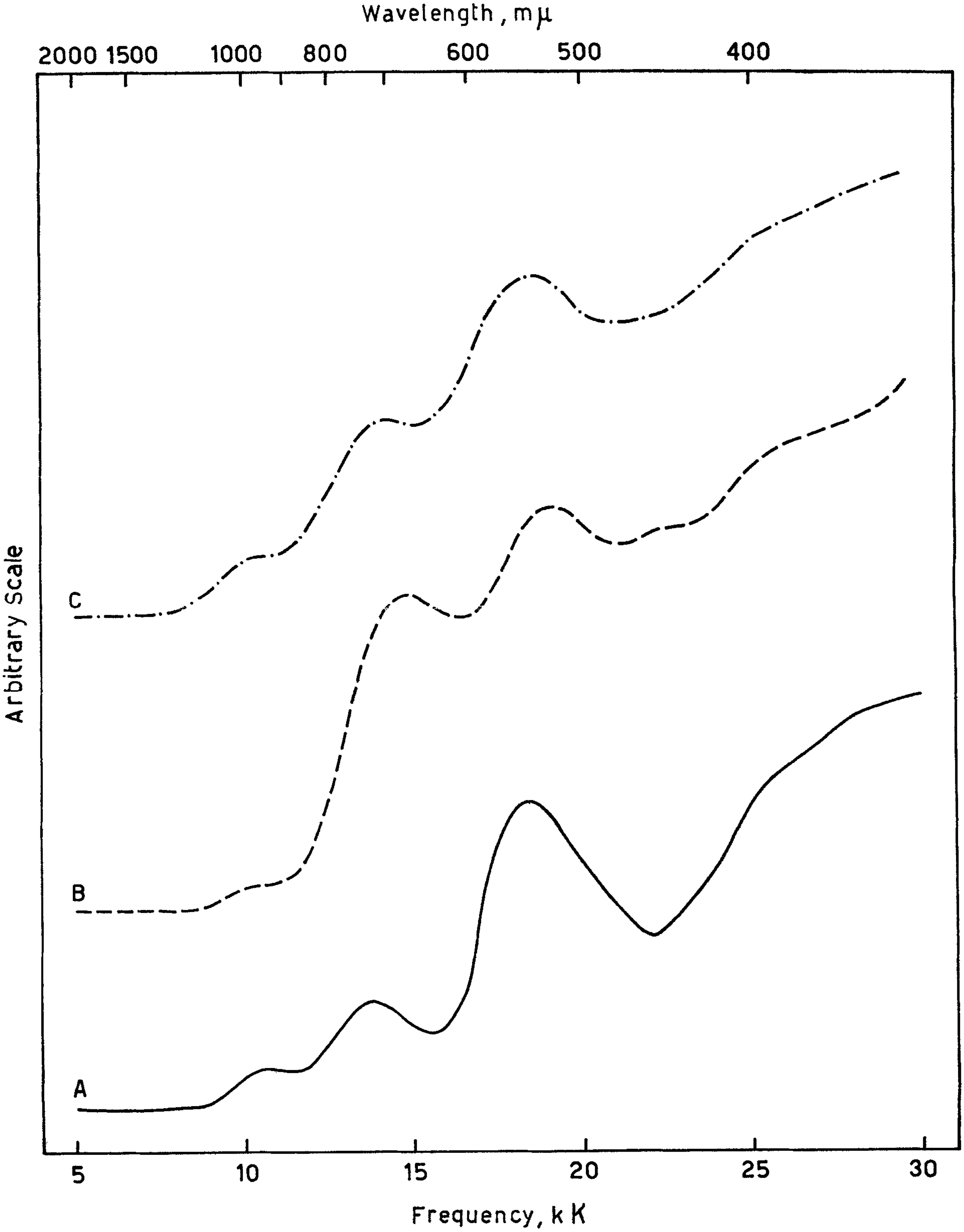


FIGURE 3 Reflectance spectra of: A, [Ni(NNAs)I]BPh_4; B, [Ni(AsNNAs)I]I; C, [Ni(AsNNAs)I]BPh_4.

structure with bridging thiocyanate is therefore suggested for this compound. This implies that AsNNAs is behaving as a tridentate ligand with a non-bonded arsenic atom. Similar behaviour was found with the tetradentate ligand N—N_2As, whose nickel complexes were shown by X-ray methods [10,11] to contain donor sets $N_3(NCS)$ or $N_3(NCS)_2$.

The thiocyanate complex of the Ligand III, $[Ni(NNAs)(NCS)_2]$ has a polymeric octahedral structure in the solid state with a CN stretching frequency at 2123 cm^{-1} which confirms the presence of a bridging thiocyanate group. In chloroform the spectral evidence shows an equilibrium is present between octahedral and five-coordinate species with increasing temperature (Figure 5).

Ni(AsOOAs)I_2 The electronic spectrum of the nickel complex of ligand IV is similar to that of the phosphorous analogue $[Ni(POOP)I_2]$.[12] The structure of the arsenic complex is therefore likely to be a distorted square-planar structure similar to the one found by X-ray methods.

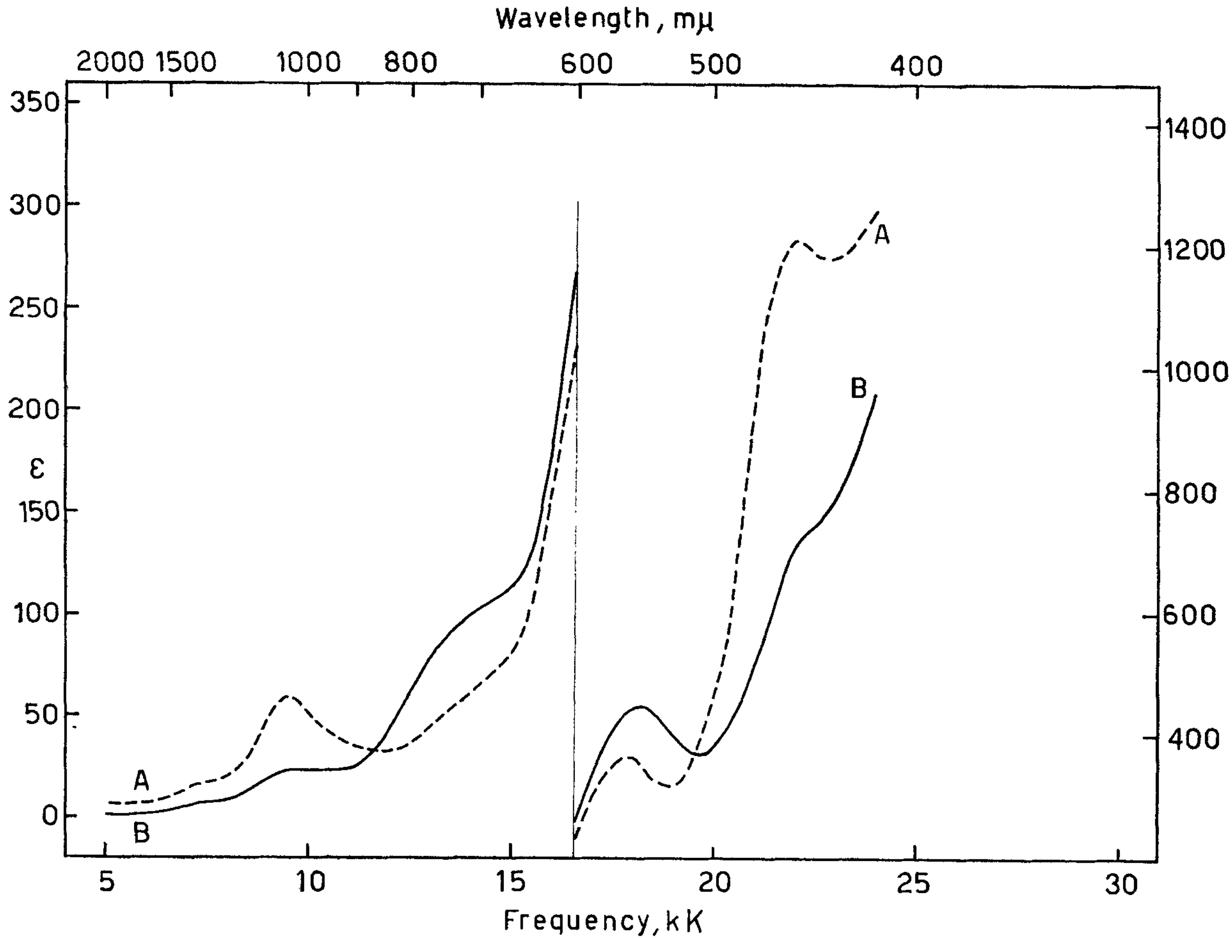


FIGURE 4 Absorption spectra of $[Ni(AsNNAs)I_2]$ in 1,2-dichlorothane solution at A, O and B, 50°C.

CONCLUSIONS

The ligand I may coordinate in a variety of modes, partly because the open-chain geometry does not impose any particular stereochemistry upon the complexes formed, and partly because the two kinds of potential donor-atom differ widely in their donor ability. Indeed, nickel(II) would be expected to bond more readily to the more electronegative and less polarizable nitrogen atoms than to the arsenic atoms[13].

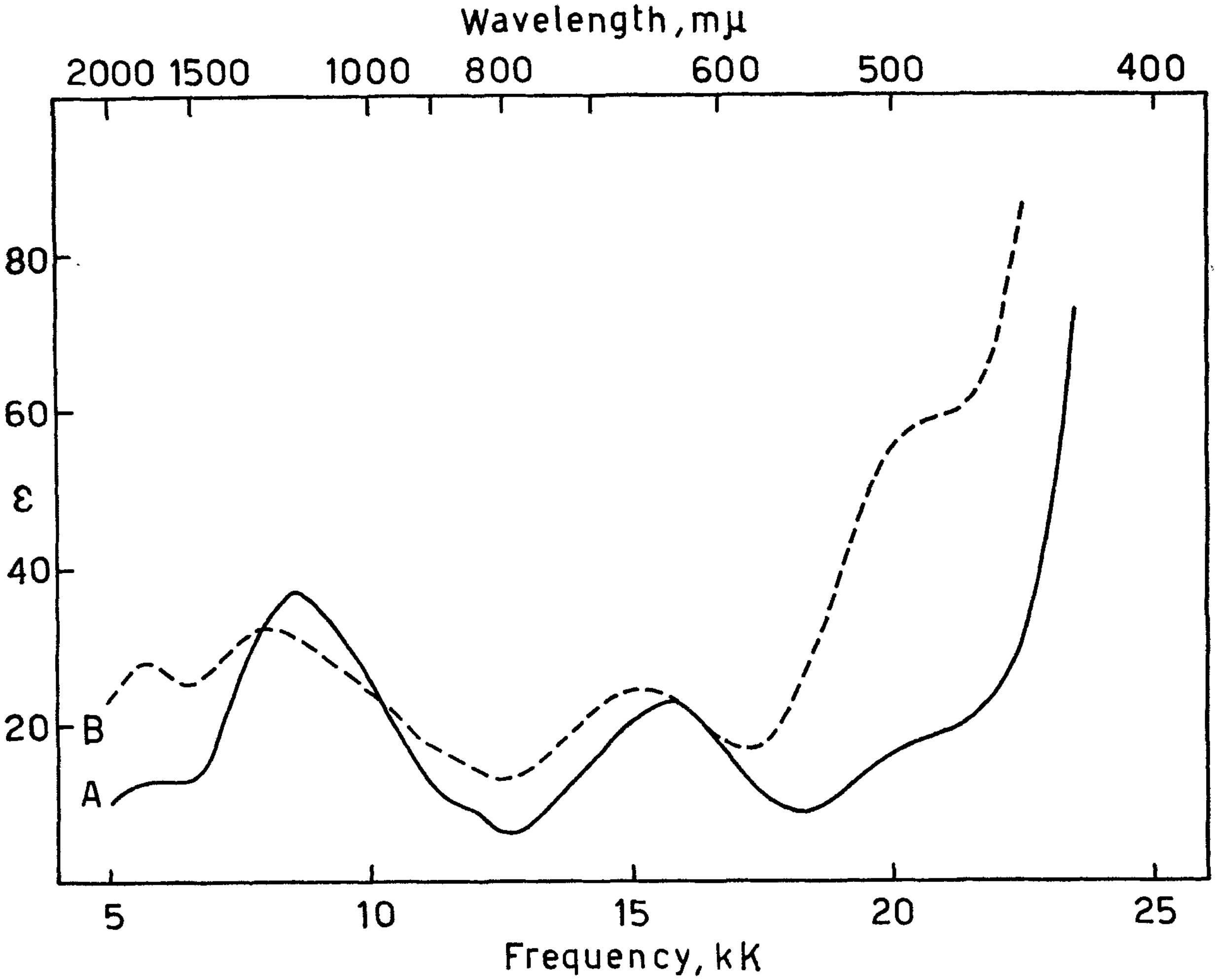


FIGURE 5 Absorption spectra of [Ni(NNAs)(NCS)$_2$] in chloroform at A, 21 and B, 51°C.

When the anions present are non-coordinating the square-planar species with donor-atom set N_2As_2 is formed and its stability may be slightly enhanced by the chelate effect. In the presence of halide ions, Y, one or both of the arsenic atoms may be displaced from the coordination sphere, depending on the concentration of the halide ions, to give donor-atom sets N_2YAs_2, N_2Y_2; in the solid state the octahedral complexes with donor-atom set $N_2As_2Y_2$ may be stabilized by lattice forces. Bromide ions slightly favour the formation of tetrahedral species, set N_2Br_2, whereas iodide ions which are less electronegative and more polarisable than bromide, and more comparable with arsenic as regards polarizability, tend to favour the square-planar species with set N_2AsI. Surprisingly, no evidence for five-coordinate species such as NiN_2As_2Y was found. Probably both the steric hindrance from the bulky $AsPh_2$ groups and small tendency of nickel(II) to bond to arsenic cooperatively reduce the stability of the five-coordinate species with respect to four- and six-coordinate species. The tridentate ligand III, NNAs, does form five-coordinate species in solution, perhaps because this ligand has only one bulky $AsPh_2$ group.

The tripod ligand II always functions as a tridentate ligand with one arsenic atom non-bonding.[4] For example, with iodide it gives a square-planar species, donor set N_2AsI, and with thiocyanate it gives a polymeric octahedral species. The principal difference, then, between the open-chain ligand I and the tripod ligand II seems to result from the fact that II is less flexible and cannot, for example, use both arsenic atoms as donors to form a monomeric square-planar species with donor-atom set N_2As_2 as can I. By contrast, the phosphorous analogue of I, PNNP, which has the same open-chain structure,[3] always behaves as a tetradentate ligand as perhaps expected in view of the higher coordinating power towards nickel of phosphorous as compared with arsenic.

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