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Metal Complexes of Tridentate Hybrid Ligands. V. Nickel Complexes of Ligands Containing the Donor Sequence As-N-N(heterocyclic)

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The compounds obtained by the interaction of four new hybrid tridentate ligands, each containing the donor sequence As-N-N, with nickel(II) salts are described. The four ligands were obtained by the Schiff base condensation of a o-dialkylarsinoaniline and either pyridine-2-aldehyde or 6-methylpyridine-2-aldehyde.

The main types of complex obtained were:

(i) bis-ligand complexes of the type $Ni(ligand)_2Y_2$ *(where Y =* ClO_4 *or* BPh_4 *and for some ligands* NO_3*).*

(ii) mono-ligand complexes of the type Ni ligand X_2 *(where X = Cl, Br, I or NCS and for some ligands* NO_3*).*

All the physical measurements undertaken indicate that the bis-complexes are high-spin octahedral in structure.

The mono-complexes appear to possess a high-spin five-coordinate stereochemistry in the case of the chloro and bromo-complexes. The iodides all appear to possess the same structure, except for one case in which a diamagnetic four-coordinate stereochemistry obtains.

The thiocyanate complexes all appear to be polymeric octahedral compounds.

Introduction

Previous papers reported on the complexes formed by nickel(II) and cobalt(II) salts with hybrid tridentates with the donor atom sequences of As-N-O[1], As-N-S[2] and As-N-N[3]; all the ligands being derived from Schiff base reactions of o-dialkylarsinoanilines and suitable aldehydes.

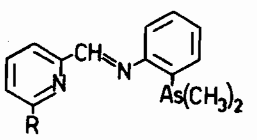
We now report the results of a study of the nickel complexes of the four new As-N-N(heterocyclic) hybrid tridentate ligands. The cobalt complexes of these ligands have been described in a previous paper[4]:

(i) 1-(2′-pyridyl)-2-(o-dimethylarsinobenzene)-2-azaethene (I; NNAs).

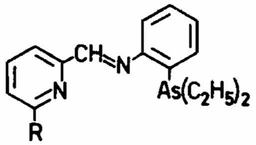
(ii) 1-(6′-methyl-2′-pyridyl)-2-(o-dimethylarsinobenzene)-2-azaethene (II; MeNNAs).

(iii) 1-(2′-pyridyl)-2-(o-diethylarsinobenzene)-2-azaethene (III; NNAsEt).

(iv) 1-(6′-methyl-2′-pyridyl)-2-(o-diethylarsinobenzene)-2-azaethene (IV; MeNNAsEt).



R = H NNAs I
R = Me MeNNAs II



R = H NNAsEt III
R = Me MeNNAsEt IV

Results

Bis-ligand complexes of nickel(II) (see Table I). The bis-ligand nickel(II) complexes are all brown to pinkish-brown in color, and have the general formula: $[NiL_2]\ Y_2nH_2O$ (I. = I-IV, Y = I, ClO_4, BPh_4; L = I, III, Y = NO_3; n = 0-2). Iodide complexes are prepared from the interaction of either 1:1 or 2:1 mole ratios of ligand to nickel iodide in ethanol solutions. The bis-complex has a lower solubility than the corersponding mono-ligand complex in ethanol, and thus is preferentially precipitated setting up an equilibrium in favor of its formation. On the other hand, nitrate and perchlorate compounds are prepared from 1:1 mole ratio reactions, but only ligands I and III give rise to bis-ligand complexes of nickel(II) nitrate. The tetraphenylborate salts are obtained from mixtures of equimolar solutions of the corresponding ligand and nickel salt (usually nitrate) by the addition of a solution of $LiBPh_4$ or $NaBPh_4$. It is worth mentioning that all attempts to prepare the tris-ligand complexes of nickel(II) using 3:1 mole ratio of ligand to nickel salt were unsuccessful.

The magnetic moments of all the bis-ligand complexes at room temperature fall within the range 2.86 to 3.28 B.M. (Table IIb), while the molar conductivities in nitromethane are typical of 1:2 electrolytes,

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Table I. Analytical Results and Preparation Methods for Nickel(II) Complexes.

		Analysis (%)				
Complex		C	H	N	Ni	prepn. *
Nickel(II)-NNAs(I)						
$Ni(NNAs)Cl_2\frac{1}{2}C_6H_6$	Found	44.7	4.1	5.9	12.9	EBu-B
	Calc.	45.0	4.0	6.2	12.9	
$Ni(NNAs)Br_2EtOH$	Found	34.5	3.8	5.3	10.8	EBu
	Calc.	34.9	3.8	5.3	10.8	
$Ni(NNAs)Br_22H_2O$	Found	31.0	3.9	5.3	10.8	EMe
	Calc.	31.0	3.5	5.2	10.8	
$Ni(NNAs)I_2$	Found	28.1	2.5	4.6	9.6	E/EBu-f
	Calc.	28.0	2.5	4.7	9.9	
$Ni(NNAs)(NCS)_2$	Found	41.8	3.5	11.9	13.1	E
	Calc.	41.5	3.3	12.2	12.8	
$Ni(NNAs)_2(NO_3)_2$	Found	44.6	4.1	10.9	7.9	EH
	Calc.	44.5	4.0	11.1	7.8	
$Ni(NNAs)_2(NO_3)_2\frac{1}{2}H_2O$	Found	44.0	4.0	11.0	7.8	E
	Calc.	43.9	4.0	11.0	7.7	
$Ni(NNAs)_2(ClO_4)_2$	Found	40.1	3.7	6.6	7.1	E
	Calc.	40.5	3.6	6.7	7.1	
$Ni(NNAs)_2(ClO_4)_22H_2O$	Found	38.8	3.4	6.9	6.7	E(Cl + ClO_4
	Calc.	38.7	4.0	6.5	6.8	
$Ni_3(NNAs)_4(NCS)_62H_2O$	Found	43.7	3.7	11.4	10.6	E
	Calc.	43.7	3.8	11.5	10.4	
$Ni(NNAs)_2I_2$	Found	38.1	3.5	6.5	6.7	2E
	Calc.	38.0	3.4	6.3	6.7	
$Ni(NNAs)_2(BPh_4)_2\frac{1}{2}H_2O$	Found	71.3	5.5	3.9	4.7	2E/3E
	Calc.	71.5	5.6	4.4	4.6	
$Ni(NNAs)(NAs)Cl_2H_2O$	Found	42.6	5.0	6.7	9.3	E-H-R(E)
	Calc.	41.9	4.6	6.7	9.3	
Nickel(II)MeNNAs(II)						
$Ni(MeNNAs)(MeNAs)Cl_23H_2O$	Found	39.8	4.8	6.6		E
	Calc.	39.5	5.0	6.3		
$Ni(MeNNAs)(MeNAs)I_2$	Found	33.7	3.4	5.4		E-R(E)
	Calc.	33.3	3.4	5.3		
$Ni(MeNNAs)Cl_2$	Found	42.0	4.1	6.3	13.5	E/BH
	Calc.	41.8	4.0	6.5	13.6	
$Ni(MeNNAs)Cl_2CH_3OH$	Found	41.3	4.7	6.0	12.6	E-R(EMe)
	Calc.	41.6	4.6	6.1	12.6	
$Ni(MeNNAs)Br_2$	Found	34.5	3.2	5.5	11.1	E/E-R(EMe)
	Calc.	34.7	3.3	5.4	11.3	
$Ni(MeNNAs)Br_2\frac{1}{2}H_2O$	Found	34.1	3.3	5.3	11.3	E/H
	Calc.	34.1	3.4	5.3	11.1	
$Ni(MeNNAs)I_2$	Found	29.7	3.4	4.5	9.8	E
	Calc.	29.3	2.8	4.6	9.6	
$Ni(MeNNAs)(NCS)_2$	Found	42.7	3.9	11.2	12.1	E
	Calc.	43.0	3.6	11.9	12.4	
$Ni(MeNNAs)(NO_3)_2$	Found	37.3	3.6	11.5	12.0	E/EHB
	Calc.	37.2	3.5	11.6	12.1	
$Ni(MeNNAs)(NO_2)_2H_2O$	Found	36.0	4.0	10.9	11.6	E
	Calc.	35.9	3.8	11.2	11.7	
$Ni(MeNNAs)_2I_2$	Found	39.8	4.3	5.8	6.3	E/2E
	Calc.	39.4	3.8	6.1	6.4	
$Ni(MeNNAs)_2(ClO_4)_2$	Found	41.9	4.1	6.5		E
	Calc.	41.9	4.1	6.5		
$Ni(MeNNAs)_2(ClO_4)_22H_2O$	Found	40.3	4.1	5.9	6.3	0.5E
	Calc.	40.3	4.3	6.3	6.6	
$Ni(MeNNAs)_2(BPh_4)_2$	Found	72.3	5.8	4.2	4.7	E, 3E
	Calc.	72.2	5.8	4.3	4.5	
Nickel(II)-NNAsEt(III)						
$Ni(NNAsEt)Cl_2$	Found	43.6	4.6	6.0	13.1	EBH-f
	Calc.	43.1	4.3	6.3	13.2	
$Ni(NNAsEt)Br_2H_2O$	Found	33.6	3.8	5.1	10.1	EBBu-H
	Calc.	33.7	4.0	4.9	10.3	
$Ni(NNAsEt)I_2$	Found	30.9	2.9	4.5	9.1	E-f-R(E)
	Calc.	30.6	3.0	4.5	9.4	
$Ni(NNAsEt)(NCS)_2$	Found	44.2	4.1	11.3	12.0	EB
	Calc.	44.1	3.9	11.4	12.0	
$Ni(NNAsEt)_2I_2$	Found	40.6	4.1	6.0		2E
	Calc.	40.8	4.0	6.0		
$Ni(NNAsEt)_2(NO_3)_2H_2O$	Found	46.5	4.8	9.9	7.1	EBH-f
	Calc.	46.3	4.8	10.1	7.1	
$Ni(NNAsEt)_2(ClO_4)_2$	Found	42.9	4.3	6.3	6.7	EB
	Calc.	43.3	4.3	6.3	6.6	
$Ni(NNAsEt)_2(BPh_4)_2$	Found	72.5	6.1	4.1	4.5	E
	Calc.	72.4	5.9	4.2	4.4	

Table I. (Continued).

Nickel(II)-MeNNAsEt(IV)						
Ni(MeNNAsEt)Cl$_2$	Found	44.8	4.8	6.2	12.7	EB
	Calc.	44.5	4.6	6.1	12.8	
Ni(MeNNAsEt)Br$_2$	Found	37.3	4.0	5.0	10.8	EB
	Calc.	37.3	3.8	5.1	10.7	
Ni(MeNNAsEt)I$_2$	Found	32.0	3.4	4.7	9.3	E
	Calc.	31.8	3.3	4.4	9.2	
Ni(MeNNAsEt)(NCS)$_2$	Found	45.5	4.3	11.3	11.4	E
	Calc.	45.2	4.2	11.1	11.6	
Ni(MeNNAsEt)(NO$_3$)$_2$	Found	40.3	4.4	10.8	11.5	EB
	Calc.	39.9	4.1	10.9	11.5	
Ni(MeNNAsEt)$_2$(ClO$_4$)$_2$	Found	44.2	4.9	6.5	6.5	E
	Calc.	44.6	4.6	6.1	6.4	
Ni(MeNNAsEt)$_2$(BPh$_4$)$_2$	Found	72.2	6.2	4.0	4.6	E
	Calc.	72.3	6.1	4.1	4.3	

Table IIa. Magnetic susceptibility data of mono-ligand complexes of Nickel(II).

Complex	T°K	$10^6\chi_g$	$10^6\chi_M'$	μ_{eff} (B.M.)
Halides				
Ni(NNAs)Cl$_2$½C$_6$H$_6$	295.3	9.42	4504	3.27
Ni(NNAs)Br$_2$EtOH	296.3	7.76	4510	3.28
Ni(NNAs)Br$_2$2H$_2$O	302.3	7.05	4186	3.21
Ni(NNAs)I$_2$	295.3	6.91	4302	3.20
Ni(MeNNAs)Cl$_2$	295.3	10.65	4800	3.39
Ni(MeNNAs)Cl$_2$CH$_3$OH	294.3	8.82	4312	3.21
Ni(MeNNAs)Br$_2$	298.5	7.92	4352	3.23
Ni(MeNNAs)Br$_2$½H$_2$O	296.3	8.00	4469	3.27
Ni(MeNNAs)I$_2$	296.3	6.93	4558	3.31
Ni(NNAsEt)Cl$_2$	294.3	9.53	4450	3.17
Ni(NNAsEt)Br$_2$2H$_2$O	294.3	6.47	3966	3.06
[Ni(NNAsEt)I]I	294.3	—0.29	103	diam.
Ni(MeNNAsEt)Cl$_2$	293.3	8.36	4080	3.11
Ni(MeNNAsEt)Br$_2$	293.3	7.30	4262	3.15
Ni(MeNNAsEt)I$_2$	293.3	6.83	4691	3.32
Thiocyanate and Nitrate				
Ni(NNAs)(NCS)$_2$	297.3	8.73	4243	3.20
Ni$_3$(NNAs)$_4$(NCS)$_6$2H$_2$O	302.0	7.41	4490*	3.27*
Ni(MeNNAs)(NCS)$_2$	299.4	8.32	4185	3.19
Ni(NNAsEt)(NCS)$_2$	293.3	7.35	3933	3.05
Ni(MeNNAsEt)(NCS)$_2$	293.3	7.70	4145	3.13
Ni(MeNNAs)(NO$_3$)$_2$	295.3	8.74	4428	3.25
Ni(MeNNAs)(NO$_3$)$_2$H$_2$O	298.4	8.32	4390	3.26
Ni(MeNNAsEt)(NO$_3$)$_2$	293.3	7.43	4065	3.10

* calculated values per Nickel(II) atom.

Table IIb. Magnetic susceptibility data of bis-ligand complexes of Nickel(II)

Complex	T°K	$10^6\chi_g$	$10^6\chi_M'$	μ_{eff} (B.M.)
Ni(NNAs)$_2$I$_2$	295.3	3.88	3842	3.03
Ni(NNAs)$_2$(NO$_3$)$_2$	302.6	5.11	4214	3.19
Ni(NNAs)$_2$(NO$_3$)$_2$½H$_2$O	297.3	4.95	4150	3.18
Ni(NNAs)$_2$(ClO$_4$)$_2$	301.8	4.50	4103	3.15
Ni(NNAs)$_2$(ClO$_4$)$_2$2H$_2$O	295.3	4.13	3989	3.11
Ni(NNAs)$_2$(BPh$_4$)$_2$½H$_2$O	299.3	2.22	3536	2.92
Ni(MeNNAs)$_2$I$_2$	296.3	4.32	4484	3.28
Ni(MeNNAs)$_2$(ClO$_4$)$_2$	299.8	4.33	4130	3.15
Ni(MeNNAs)$_2$(ClO$_4$)$_2$2H$_2$O	296.3	4.02	4046	3.11
Ni(MeNNAs)$_2$(BPh$_4$)$_2$	299.3	2.76	4303	3.20
Ni(NNAsEt)$_2$(NO$_3$)$_2$H$_2$O	293.3	4.78	4212	3.15
Ni(NNAsEt)$_2$(ClO$_4$)$_2$	293.3	3.73	3703	2.96
Ni(NNAsEt)$_2$(BPh$_4$)$_2$	294.3	2.68	4300	3.20
Ni(MeNNAsEt)$_2$(ClO$_4$)$_2$	293.3	3.89	3980	3.06
Ni(MeNNAsEt)$_2$(BPh$_4$)$_2$	294.3	1.98	3420	2.86

and range from 130 to 200 mho/mole. The somewhat lower values of tetraphenylborate salts ($\Lambda_M = 120$-140 cm^2 ohm^{-1} mole^{-1}) are presumably due to low mobilities of the bulky anion.

Table III. Infrared data of ionic nitrate and perchlorate group in nickel(II) complexes.

Nitrate ion	ν_3(cm^{-1})	ν_2(cm^{-1})	ν_4(cm^{-1})
$Ni(NNAs)_2(NO_3)_2$	1360vs 1331vs	830m vs	707w
$Ni(NNAs)_2(NO_3)_2\frac{1}{2}H_2O$	1361vs 1331vs	830m vs	707w
$(NiNNAsEt)_2(NO_3)_2H_2O$	1345vs br	830m vs	715w
Perchlorate ion		A_1 sym.	
$Ni(NNAs)_2(ClO_4)_2$	ν_3(cm^{-1})	breathing str.	ν_2(cm^{-1})
$Ni(NNAs)_2(ClO_4)_2 2H_2O$	1098vs br	937w	621s s
$Ni(MeNNAs)_2(ClO_4)_2$	1092vs br	930w	624s s
$Ni(MeNNAs)_2(ClO_4)_2 2H_2O$	1093vs br	930vs	624s s
$Ni(NNAsEt)_2(ClO_4)_2$	1090vs br	930vw	625s s
$Ni(MeNNAsEt)_2(ClO_4)_2$	1090vs br	931vs	624s s

The structures of both the solid and solution spectra of these bis-complexes are essentially the same, suggesting that these complexes are of the same stereochemistry both in the solid state and in solution. Thus the spectra in both states exhibit two main peaks; one at 11.5-13.0 kK with a shoulder at 10.0 kK, and a very intense band at 20.0-21.5 kK.

On the evidence of magnetic moments, molar conductivities and spectra, coupled with the tridentate capacity of the ligands, we conclude that these bis-compounds possess octahedral stereochemistry. The ligand field strengths of the ligands (I-IV) can be approximately deduced from the position of the ν_1 band in the electronic spectra. This gives the relative order of ligand field strength as:

ligand	10 Dq	ref.
NO_2	12,730	this work
NNAsEt	13,590	5
NNAs	12,700	this work
1,10-phenanthroline	12,700	6
MeNNAs	11,800	this work
MeNNAsEt	11.600	this work
ethylenediamine	11,500	6

The infrared spectra of the anions as perchlorate and nitrate exhibit the characteristic patterns[7,8] of the uncoordinated anions (Table III). Thus the uncomplexed perchlorate ion exhibits a strong band at approx. 1090 cm^{-1} (ν_3) and a sharp and strong band at approx. 625 cm^{-1} (ν_4), while the ionic nitrate also displays a strong broad band at aprox. 1360 cm^{-1} (ν_3), a very sharp band at approx. 830 cm^{-1} (ν_2) and also a weak combination band at approx. 2370 cm^{-1} ($\nu_1 + \nu_3$).

Mono-ligand complexes of nickel(II) see (Table I). Nickel(II) chloride and bromide. The interaction of equimolecular quantities of the ligands, I, II, III, or IV with nickel(II) chloride or bromide in absolute ethanol or a mixed solvent such as ethanol/butanol leads to the formation of pale yellowish-green to green crystalline compounds. These are soluble without colour change to orange upon dissolution in ethanol.

Spectral data in the ligand field region indicate that the same stereochemistry may be assigned to these bromide and chloride complexes in the solid state and in solution (except $Ni(NNAsEt)Br_2$ in solution) on the basis of the close spectral similarities. As the complexes are effectively non-electrolytes in solution and the ligands are potentially tridentate, the coordination number of nickel would apepar to be five, unless six-coordination occurs through bridging by halogen atoms or in some cases by coordination of solvate.

Since the complexes are of the high-spin type with magnetic moments ranging from 3.1 to 3.4 B.M. (Table IIa), a square-planar structure is unlikely. Furthermore, the spectral data cannot be consistently interpreted on the basis of a pseudo-tetrahedral structure, which would be derived by coordinaion of only two donor atoms from a tridentate ligand.

These mono-complexes exhibit bands (Figure 1) at about 14.5-15.5 kK and sometimes shoulders at 20.5-23.0 kK in the solid state, while in solution, frequencies of peaks occur at 5.0, 8.6-8.9 and 14.5-15.7. These spectra appear to be very similar to those of other high-spin complexes to which a five-coordinate structure has been attributed. In particular, the bands at

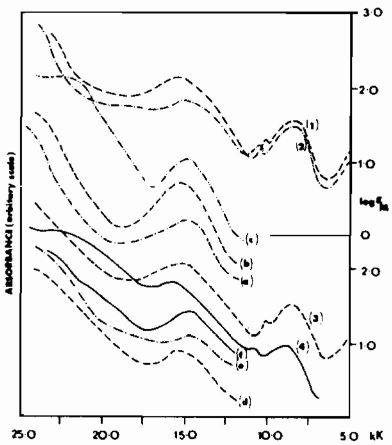

Figure 1. Spectra of Nickel(II) halide complexes of ligands containing the donor atom sequence N-N-As. Solution spectra in $CHCl_3$: (1) $Ni(MeNNAs)Br_2$; (2) $Ni(MeNNAs)Cl_2$; (3) $Ni(MeNNasEt)Br_2$; (4) $Ni(NNAs)Br_2$. Reflectance spectra of $Ni(MeNNAsEt)X_2$: (a) X = Cl, (b) X = Br, (c) X = I; $Ni(NNAs)X_2$: (d) X = Cl, (e) X = Br; $Ni(NNAsEt)Br_2$: (f)

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8.7-8.9 and 14.5-15.7 kK for these complexes can be correlated with those at 8.7-9.3 kK and 13.9-15.2 kK for the high-spin five-coordinate,[9] Ni(NNP)Br_2 and Ni(NNAs)Br_2 (NNP, NNAs = tridentate donor sets), which also have similar donor atom sets.

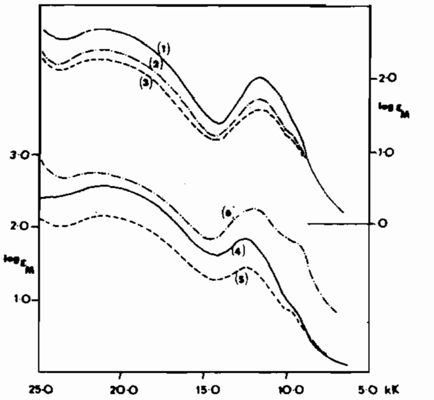

Figure 2. Solution spectra of Nickel(II) complexes

No.	Complex	Solvent
(1)	Ni(MeNNAs)$_2$(ClO_4)$_2$	$MeNO_2$
(2)	Ni(MeNNAs)(NO_3)$_2$	MeOH
(3)	Ni(MeNNAs)Cl_2	MeOH
(4)	Ni(NNAs)$_2$(ClO_4)$_2$	$EtNO_2$
(5)	Ni(NNAs)Br_2H_2O	MeOH
(6)	[Ni(NNAs)$_2$]$_2$[Ni(NCS)$_6$]	MeOH

In a coordinating solvent such as methanol, the solution spectra of all the halide complexes (Figure 2) are quite diferent to solid state and inert solvent (such as nitromethane and chloroform) spectra (Figure 1). The spectra of the orange solutions in methanol are very similar to those of the bis-ligand complexes [NiL_2]Y_2 and have the same maximum frequencies but with the extinction coefficients aproximately half those of the latter compounds. These compounds also have higher molar conductivities in methanol solution. Further evidence which supports the contention that the bis-ligand compounds are formed in methanol, is provided by the isolation of the compound [NiL_2](ClO_4)$_2$ (L = MeNNAs, NNAs) from the methanolic solution of $NiLX_2$ and $NaClO_4$.

Nickel(II) iodide complexes. Nickel(II) iodide complexes of the ligands I-IV are obtained as large black crystals, which are green when finely ground. Only the ligand NNAsEt(III) gave rise to a diamagnetic compound. Other ligands I, II and IV gave paramagnetic complexes with magnetic momentes in the range 3.20-3.32 B.M. (see Table IIa).

The diamagnetic compound, Ni(NNAsEt)I_2 is a typical 1:1 electrolyte in nitromethane, and its solution spectrum in nitromethane also exhibits the characteristic pattern of a square-planar nickel(II) compound. Thus it does not give a band below about 13,000 cm^{-1}. Its solution spectrum is shown in Figure 3, along with the spectrum of the diamagnetic square-planar complex of [Ni(NAs)$_2$](ClO_4)$_2$ (NAs = o-dialkylarsino-aniline).

The reflectance spectra of the paramagnetic iodo-compounds (Figure 1) are much the same as the corresponding nickel chloride and bromide complexes, and it is thus reasonable to suggest an analogous high-spin five-coordinate stereochemistry for these paramagnetic complexes in the solid state. However, Ni(NNAs)I_2 exhibits conductivities characteristic of a tvpical 1:1 electrolyte in nitromethane and in nitrobenzene, and its spectrum in nitromethane is practically indistinguishable from that of square-planar [Ni(NNAsEt)I]I (see Figure 3). This latter compound possess the same donor atom set of N_2AsI and has almost the same values of the molar extinction coefficient.

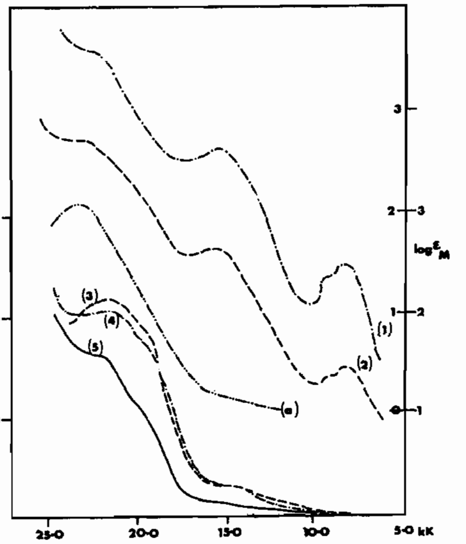

Figure 3. Solution spectra of Nickel(II) iodide complexes in nitromethane. (1) Ni(MeNNAs)I_2EtOH (right hand inside scale); (2) Ni(MeNNAs)I_2½EtOH (right hand outside scale); (3) [Ni(NNAsEt)I]I (left hand scale); (4) Ni(NNAs)I_2 (left hand scale); (5) Ni(NNAsEt)Br_2 in $CHCl_3$ (ε_M = half of left hand scale); (a) Reflectance spectrum of square-planar Ni(NAs)$_2$(ClO_4)$_2$ (arbitrary scale).

The greater tendency of these ligands NNAs(I) and NNAsEt(III) to form square-planar nickel(II) complexes compared to ligands II and IV is probably due to:

(i) the probably stronger ligand field strength of ligands I and III, and

(ii) the presence of the 6-methyl group on the pyridine ring of II and IV may well block the coordination of the iodide ion to the square-planar corner.

Thiocyanate complexes. The interaction of the ligands (I-IV) with nickel(II) thiocyanate in ethanolic solution leads to almost quantitative formation of light green complexes of the type NiL(NCS)$_2$ These compounds are not sufficiently soluble in common organic solvents for the measurement of molar conductivities and absorption spectra. The magnetic moments for mono-ligand complexes fall within the range 3.05-3.20 B.M. at room temperature (Table IIa).

Their diffuse reflectance spectra are quite different from those of their halide analogues, and exhibit two maxima at approx. 11.0 kK and 16.0 kK, and a shoul-

Table IV. Infrared spectral data of anions in nickel(II) complexes $NiLY_2$ (Y = NCS, NO_3).

Anions			
Thiocyanate		ν(C-N)	δ(N-C-S)
$Ni(NNAs)(NCS)_2$		2096vs, 2138s s	476m
$Ni(MeNNAs)(NCS)_2$		2092vs, 2138s s	478m
$Ni(NNAsEt)(NCS)_2$		2086vs, 2130s s	475m
$Ni(MeNNAsEt)(NCS)_2$		2100vs, 2134s s	471m
$[Ni(NNAs)_2]_2[Ni(NCS)_6]2H_2O$		2088vs br	475m
Nitrate	ν_3(N-O str)	ν_2	$\nu_1+\nu_3$
$Ni(MeNNAs)(NO_3)_2$	1438vs 1300vs	815m	2315w, 2470w
$Ni(MeNNAs)(NO_3)_2(H_2O)$	1440vs 1300vs	815s	2320w, 2460w
$Ni(MeNNAsEt)(NO_3)_2$	1300s 1460s	809s	2300w, 2480w
	1280s 1500s	813s	2280w, 2520w

Intensity: vs very strong, s strong, m medium, w weak, br broad.

der at approx. 21.5 kK. These peaks are attributable to the transitions $\nu_1[^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)]$, $\nu_2[^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)]$ and $\nu_3[^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)]$ in an O_h symmetry field.

The octahedral configuration is probably attained by means of polymeric thiocyanate bridges, as has often been found in other thiocyanate complexes.[10] The infrared spectra (Table IV) support this contention as they exhibit two bands at 2082-2100 cm^{-1} and 2130-2138 cm^{-1} which can be assigned to C-N stretching. The C-S stretching frequencies are obscured by the ligand bands but NCS bending modes appear around 470 cm^{-1} and no appreciable band occurs in the range 440-400 cm^{-1}. This value of the NCS bending mode might be indicative of the N-bonding of terminal thiocyanate groups even though the values of both C-N frequencies are found in the range of S-bonded group (ν_1 2080-2120 cm^{-1}) rather than that of the N-bonded group (ν_1 2040-2080 cm^{-1}).

The fact that values of these frequencies are also higher than those found for monomeric complexes of nickel thiocyanate[11] is presumably due to the thiocyanate groups acting as bridging linkages. The insolubility of these complexes in inert solvents, such as nitrobenzene and nitromethane, is in accordance with the hypothesis that six-coordination is achieved via intermolecular bridging (Ni-NCS-Ni) of the thiocyanate groups.

It is interesting to note that the direct mixing of millimolar quantities of the ligand NNAs and nickel thiocyanate in a relatively small volume of ethanol (30 ml) resulted in the immediate separation of a brown compound, which has the empirical formula $Ni_3(NNAs)_4(NCS)_62H_2O$, and is moderately soluble in methanol.

The value of the molar conductivity of this complex in nitrobenzene is slightly less than that of a 1:2 electrolyte and the magnetic moment is 3.27 B.M. per nickel(II) atom. The solution spectrum in methanol (Figure 2) is indistinguishable from those of the bis-complexes, $NiL_2(ClO_4)_2$, except for a shoulder at 9.6 kK which corresponds to the band of the octahedral $[Ni(NCS)_6]^{4-}$ anion of low molar intensity ($\varepsilon_M <$ 10).[12]

The infrared spectrum (Table IV) exhibits only one strong and broad band at 2088 cm^{-1} which may be indicative of N-bonded thiocyanate, supporting the contention that this complex contains only one kind of bonding mode of the thiocyanate group.[13] It is thus reasonable to assume that this compound consists of two bis-ligand metal cations and one hexaisothiocyanatonickel(II) anion, *i.e.*, $[Ni(NNAs)_2]_2$ $[Ni(NCS)_6]$-$2H_2O$.

Nickel(II) nitrate complexes. When equimolar quantities of ligands (I-IV) and nickel(II) nitrate were reacted in ethanol, only ligands II and IV gave a green mono-ligand complex of the type $NiL(NO_3)_2$-nH_2O (L = II, n = O or 1; L = IV, n = O). Ligands I and III gave only bis-ligand complexes of formula $NiL_2(NO_3)_2nH_2O$, (n = O, 1/2, or 1).

The patterns of the reflectance spectra of the mono-ligand nitrate complexes are very similar to those of the corresponding thiocyanate complexes. Bands appear at aprox. 11.0, 16.0 and 22.0 kK which may be respectively assignable to the transitions ν_1, ν_2 and ν_3 in the field of octahedral symmetry. The magnetic moments of these compounds also fall in the range expected for octahedral nickel(II) complexes (3.10-3.25 B.M.) (Table IIa).

The infrared spectra (Table IV) of the nitrate complexes show clearly the absence of ionic nitrate in these compounds. The two bands of the compounds $Ni(MeNNAs)(NO_3)_2 . nH_2O$, (n = O, I) at 1300 and 1440 cm^{-1} indicate the presence of monodentate nitrate groups. These two compounds also show a broad band at 3400 cm^{-1} which indicates the presence of water. The achievement of six-coordination in these compounds ma be achieved by a tridentate ligand, two monodentate nitrate groups and a water molecule.

The infrared spectrum of the complex $Ni(MeNNAsEt)(NO_3)_2$ shows four strong bands in the 1200-1500 cm^{-1} region; the two bands at 1280 and 1500 cm^{-1} with a splitting of 220 cm^{-1} have been assigned to a bidentate nitrate group and those at 1300 and 1460 cm^{-1}, with a splitting of 160 cm^{-1}, to a monodentate

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nitrate group. On this basis it may be concluded that the octahedral structure of his complex is achieved via a monodentate nitrate group and a bidentate nitrate group, as has been observed in similar complexes.[14]

It should be noted that the assignment of frequencies of coordinated nitrate groups in the 1400-1500 cm^{-1} region are very difficult due to the presence of relatively intense ligand bands.

The conductivities of the complexes, $Ni(MeNNAs)(NO_3)_2nH_2O$ (n = 0, 1), in nitrobenzene solution indicate that they are essentially non-electrolytes in this solvent, but are 1:1 electrolytes in nitromethane solution. Spectra in nitromethane, in contrast with the previously described nickel(II) iodide complexes of the ligand I, do not show the characterised pattern exhibited by square-planar nickel(II) complexes.

The absorption spectra in nitromethane retain essentially the same band shape and are only slightly shifted to lower frequencies compared to the reflectance spectra of the same compounds. These compounds are assigned octahedral configuration. It is thus reasonable to suggest that the compound $Ni(MeNNAs)(NO_3)_2$ has been solvolyzed in nitromethane and still retains its octahedral moiety:

$$\begin{gathered}Ni(MeNNAs)(NO_3)_2 + solv. \rightarrow \\ Ni(MeNNAs)(NO_3)(Solv.)_n + NO_3^-\end{gathered}$$

It is noticeable that the analogous compound, $Ni(MeNNAsEt)(NO_3)_2$ is slightly disociated in nitromethane ($\Lambda_M = 23$ cm^2 ohm^{-1} $mole^{-1}$).

Experimental Section

General procedure for the preparation of metal complexes. The warm and deaerated ligand solution was slowly added to the apropriate hot metal salt solution (code (i)) in aproximately 40 ml of absolute ethanol or mixed solvent (code (ii)).

(i) When the metal complex compound separated during refluxing of the solution for 20 min. it was digested for another 10-20 minutes and the solution was then allowed to cool to room temparture.

(ii) When the metal complex compound did not appear to separate within aprox. 20 min., the solvent was slowly evaporated until crystals started to separate, or evaporated to approx. 20 ml. and allowed to cool either to room temperature, or in an ice-bath.

(iii) When procedure (ii) did not yield the desired metal complex, the solution was warmed and another solvent (10-40 ml) slowly added followed by procedure (i) or (ii).

The metal complexes were collected and washed with appropriate solvents and finally with hexane. If necessary, the metal complex compounds were recrystallized from the appropriate solvent. When undesired products or imprities separated during the procedure (i), (ii) or (iii), the solution was filtered while hot.

Code (i). (a) The number in front of the solvent indicates mole ratio of the ligand and metal salt; no arabic number indicates 1:1 mole ratio. (b) -f: filtered while hot. (c) -R(   ): recrystallized from solvents in the bracket. (d) -: change of solvent.

(ii) The code for solvents used for the preparation and the recrystallization of the complex compounds is as follows:

B	benzene
Bu	1-butanol
E	ethanol
Me	methanol
H	hexane
W	water

(iii) Examples of the codes for the preparation of metal complexes:

(a) EB-f: 1:1 mole ratio of ligand and metal salt was used in a mixed solvent of absolute ethanol and benzene and filtered while hot to remove the undesired products.

(b) 2E-R(Me): The complex compound was prepared from a 2:1 mole ratio of ligand to metal salt in ethanol solution and recrystallized from methanol.

(c) $E(NO_3 + BPh_4)$: A tetraphenylborate salt was added to equimolecular quantities of metal(II) nitrate and ligand in ethanol.

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