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Metal Complexes of Tridentate Hybrid Ligands. III. Cobalt and Nickel Complexes of Ligands Containing the Donor Sequence As-N-N

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The compounds obtained from the interaction of four new hybrid tridentate ligands, each containing the donor atom sequence N-N-As, with cobalt(II) and nickel(II) salts is described. The four ligands, obtained by the Schiff's base condensation of o-dimethyl- or o-diethyl-arsinoaniline and a suitable aldehyde, possess a terminal nitrogen donor present in (i) an NMe_2 *group, (ii) an* $NHMe_2$ *group, or (iii) a pyrrole ring.*

With ligands of the first two types, compounds of formula $[MligandX_2]$ *(where X = halogen, NCS or* NO_3*; M = Co or Ni) can be prepared. In the cases where X = halogen, five-coordination is proposed, while the thiocyanate and nitrate compounds may be five-coordinate or octahedral depending upon the ligand and the metal present.*

Complexes derived from the ligand of type (iii) may posses either protonated or deprotonated ligand residues, and a number of different types of nickel(II) and cobalt(III) compounds were isolated.

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] and As-N-S;[2] all the ligands deing derived from Schiff-base reactions of *o*-dialkylarsinoanilines and suitable aldehydes.

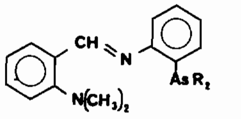
We now report the results of a study of the nickel(II) and cobalt(II) complexes of the four new As-N-N hybrid tridentate ligands:

(i) (2′-dimethylarsinophenyl)-2-N′,N′-dimethylaminobenzylideneimine (I, Me_2NNAs).

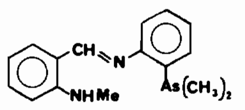
(ii) (2′-diethylarsinophenyl)-2-N′,N′-dimethylaminobenzylideneimine (II, $Me_2NNAsEt$).

(iii) (2′-dimethylarsinophenyl)-2-N′-methylamino-benzylideneimine (III, MeNHNAs).

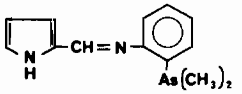
(iv) (2′-dimethylarsinophenyl)-2-pyrrolealdimine (IV, NHNAs).



$R = CH_3$ Me_2NNAs (I)
$R = C_2H_5$ $Me_2NNAsEt$ (II)



MeNHNAs (III)



NHNAs (IV)

The metal complexes of the ligands derived from N-substituted *o*-aminobenzaldehyde and N,N-dialkyl-substituted diamines have been recently reported.[6] In such cases the metal halides form high-spin five-coordinate compounds.

The ligand Me_2NNAs is very closely related to (2′-N′N-dimethylaminophenyl)-2-N′N′-dimethylaminobenzylideneimine,[3] where one terminal nitrogen atom is replaced by an arsenic donor atom.

It sould be noted that even though some metal complexes of the bidentate[4] and tetradentate ligands[5] derived from the interaction of 2-pyrrolealdehyde and alkyl amines or alkylenediamines have been well characterised in the solid state and in solution, metal complexes of the analogous tridentate ligand seem to be unknown.

Nickel(II) Complexes of Me_2NNAs *and* Me_2NNAs*-Et.* All the complexes (Table I) were prepared from the interaction of 1:1 mole ratios of the corresponding ligand and nickel(II) salt. All attempts to prepare the bis-ligand complexes by using various solvents were unsuccessful and only gave rise to oily

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(1) B. Chiswell and K.W. Lee, *Aust. J. Chem.*, *22*, 2315 (1969).

(2) B. Chiswell and K.W. Lee, *Inorg. Chim. Acta*, submitted for publication.

(3) P. Bamfield, R. Price, and R.G.J. Miller, *J. Chem. Soc.*, (*A*), 1447 (1969).

(4) R.H. Holm, A. Chakravorty, and L.J. Theriot, *Inorg. Chem.*, *5*, 625 (1966).

(5) J.H. Weber, *Inorg. Chem.*, *6*, 258 (1967).

(6) L. Sacconi, I. Bertini, and R. Morassi, *Inorg. Chem.*, *6*, 1548 (1967).

(7) M. Ciampolini and J. Gelsomini, *Inorg. Chem.*, *6*, 1821 (1967). M. Ciampolini and N. Nardi, *Inorg. Chem.*, *6*, 445 (1967). Z. Dori and H.B. Gray, *Inorg. Chem.*, *7*, 889 (1968).

(8) M. Ciampolini, N. Nardi, and G.P. Speroni, *Coord. Chem. Revs.*, *1*, 222 (1966) and references therein.

(9) L. Sacconi and I. Bertini, *Inorg. Chem.*, *7*, 1178 (1968).

(10) M. Ciampolini and G.P. Speroni, *Inorg. Chem.*, *5*, 45, (1966).

Table I. Analytical Data of Nickel(II) Complexes of the Ligands Me$_2$NNAs, Me$_2$NNAsEt and MeNHNAs.

Complex Nickel(II)-Me$_2$NNAs		Analysis (%) C	H	N	Ni	Method of prepn.*
Ni(Me$_2$NNAs)Cl$_2$	Found.	44.1	4.8	6.1	12.7	E
	Calc.	44.5	4.8	6.1	12.8	
Ni(Me$_2$NNAs)Br$_2$	Found.	37.8	4.3	5.4	10.5	E
	Calc.	37.2	3.9	5.1	10.7	
Ni(Me$_2$NNAs)I$_2$	Found.	31.5	3.3	4.3	9.2	E-f
	Calc.	31.8	3.3	4.4	9.2	
Ni(Me$_2$NNAs)(NCS)$_2$	Found.	45.4	4.2	11.1	11.5	F
	Calc.	45.2	4.2	11.1	11.7	
Ni(Me$_2$NNAs)(NO$_3$)$_2$	Found.	40.2	4.6	10.9	11.3	E
	Calc.	39.4	4.1	10.9	11.5	
Nickel(II)-Me$_2$NNAsEt						
Ni(Me$_2$NNAsEt)Cl$_2$	Found.	46.8	5.2	5.4	12.0	EBH
	Calc.	46.8	5.1	5.8	12.1	
Ni(Me$_2$NNAsEt)Br$_2$	Found.	40.1	4.7	5.0	10.0	EBH
	Calc.	39.6	4.3	4.8	10.3	
Ni(Me$_2$NNAsEt)I$_2$	Found.	34.6	4.1	4.1	8.8	EBH
	Calc.	34.1	3.8	4.2	8.8	
Ni(Me$_2$NNAsEt)(NCS)$_2$	Found.	47.1	4.8	10.3	11.1	EBH
	Calc.	47.4	4.7	10.5	11.0	
Ni(Me$_2$(NNAsEt)(NO$_3$)$_2$	Found.	42.4	4.8	11.0	11.3	
	Calc.	42.2	4.6	10.4	10.9	
Nickel(II)-MeNHNAs						
Ni(MeNHNAs)Br$_2$½H$_2$O	Found.	35.4	3.9	5.3		Ef-f-Et
	Calc.	35.4	3.7	5.2		
Ni(MeNHNAs)I$_2$EtOH	Found.	31.5	3.7	4.6		EB-f
	Calc.	32.0	3.7	4.2		
Ni(MeNHNAs)(NCS)$_2$½H$_2$O	Found.	43.3	4.2	11.0	11.6	EB
	Calc.	43.3	4.0	11.2	11.8	
Ni(MeNHNAs)(NCS)$_2$3H$_2$O	Found.	39.7	4.5	9.8		E
	Calc.	39.7	4.5	10.3		

* See experimental section.

masses. The complexes obtained are crystalline and air stable. They are, excepting the thiocyanate complexes, fairly soluble in common organic solvents such as nitromethane.

The magnetic moments at room temperature are listed in Table II together with other physical properties. The complexes are all of the high-spin type, and in each case the orbital contributions are relatively small.

The values of molar conductivity, measured at 25° C in approx. 10^{-3} M solutions indicate that the complexes are appreciably dissociated in nitromethane. An increase in the order $Cl<Br<I$ in the molar conductivity is apparent, but the values obtained are much less than those of typical 1:1 electrolytes.

The reflectance spectra of the nickel halide complexes, Ni-LX$_2$ (X = Cl, Br, I) are very similar, both in the frequency of their maxima and in their shape. Also the solution spectra of the corresponding bromide complexes, measured in the range 1750-400 nm in nitromethane are similar to their solid spectra. It therefore seems that the halide complexes have the same setreochemistry in both solid state and solution.

The single absorption bands (Figure 1) in the regions 1200 nm and 750 nm, and two intense bands (or often one broad band) around 450-550 nm, are in similar positions to those of other complexes shown in Figure 2, for which five-coordinate configurations have been proposed on the basis of their physical properties.

It is thus reasonable to suggest an analogous high-spin five-coordinate stereochemistry for these complexes, Ni(Me$_2$NNAs)X$_2$ and Ni(Me$_2$NNAsEt)X$_2$ (X = Cl, Br, I).

The diffuse reflectance spectra (Figure 3) of the nitrate and thiocyanate complexes are very similar to the solution spectra of the nitrate complexes in nitromethane. These display bands a 950 nm (ε_M =

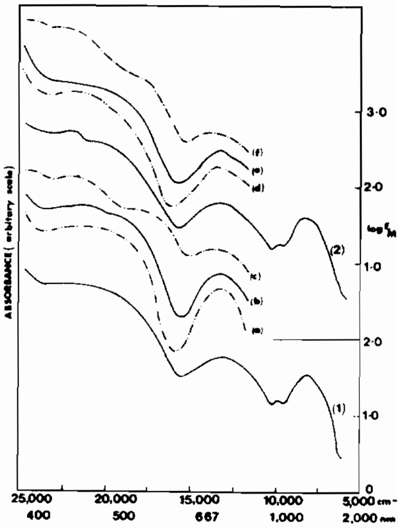

Figure 1. Spectra of nickel(II) halide complexes of ligands Me$_2$NNAs and Me$_2$NNAsEt.
Reflectance spectra of Ni(Me$_2$NNAs)X$_2$: (a) X = Cl (b) X = Br (c) X = I; (NiMe$_2$NNAsEt)X$_2$: (d) X = Cl (e) X = Br (f) X = I; Solution spectra of NiLBr$_2$ in nitromethane: (1) L = Me$_2$NNAs (2) L = Me$_2$NNAsEt.

45-48) and about 600 nm ($\varepsilon_M = 23$) and a very intense band around 400-450 nm. These latter bands might be overlapped by the tail of a charge transfer band. They are quite different from the analogous halide complexes, and very similar to other six-coordinate complexes of nickel nitrate or thiocyanate.

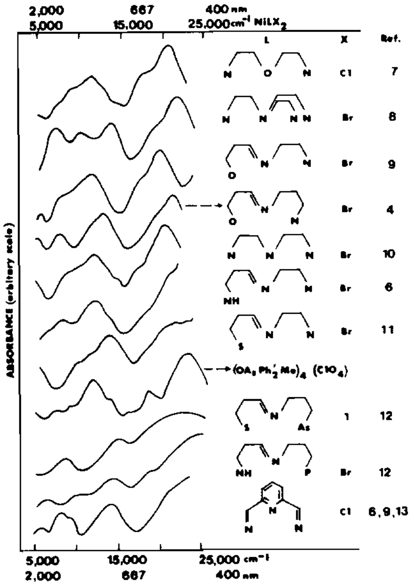

Figure 2. Some reflectance spectra of five-coordinate complex of nickel(II).

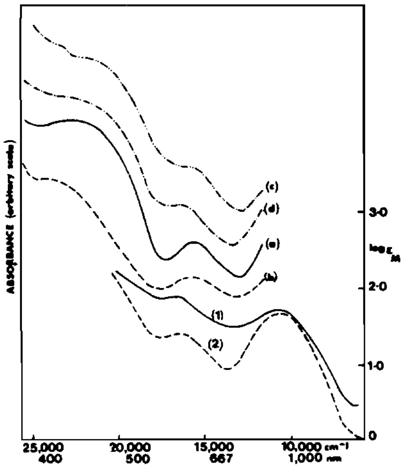

Figure 3. Spectra of nickel(II) thiocyanate and nitrate complexes of ligands Me_2NNAs and $Me_2NNAsEt$. Solution spectra in $MeNO_2$ (1) $Ni(Me_2NNAs)(NO_3)_2$ (2) $Ni(Me_2NNAsEt)(O_3)_2$; Reflectance spectra: (a) $Ni(Me_2NNAs)(NO_3)_2$ (b) $Ni(Me_2NNAsEt)(NO_3)_2$ (c) $Ni(Me_2NNAs)(NCS)_2$ (d) $Ni(Me_2NNAsEt)(NCS)_2$.

It is therefore reasonable to assume that the bands at 950 nm and 600 nm can be safely assigned as $\nu_1(^3A_{2g}\rightarrow{}^3T_{2g})$ and $\nu_2(^3A_{2g}\rightarrow{}^3T_{1g}(F))$ respectively, and the intense band at higher frequencies as $\nu_3(^3A_{2g}\rightarrow{}^3T_{1g}(P))$ in terms of octahedral symmetry. The ratio of the band frequencies ν_2 to ν_1 is, as expected for O_h symmetry,[14] about 1.6 and the magnetic moments fall in the range expected for octahedral nickel(II).

Further evidence for six-coordination is provided by the infrared spectra of the thiocyanate and nitrate groups. The thiocyanate complex in the C-N stretching region shows two bands i.e. at 2072±10 cm^{-1} (strong, broad) and at 2118 cm^{-1} (strong, sharp); these are in the range of those found for polymeric octahedral complexes of nickel thiocyanate.[15] Thus these can be assigned as the C-N stretching frequencies of an N-bonded terminal thiocyanate and a bridging thiocyanate group. The insolubility of these complexes in common organic solvents such as nitromethane is in accordance with a polymeric octahedral structure which is achieved via intermolecular bridging of the thiocyanate groups.

Even though the absence of a strong band of an ionic nitrate[13] group near 1350 cm^{-1} clearly indicates that all nitrate groups are coordinated to nickel(II), it has not been possible to deduce whether the bonding mode of the coordinated nitrate group is monodenate or bidentate, or both, because these compounds exhibit two very strong and broad poorly resolved bands at around 1300 cm^{-1} and at 1460-1500 cm^{-1}.

Nickel(II) Complexes of MeNHNAs. The preparation of nickel(II) complexes of the ligand MeNHNAs in absolute ethanol or mixed solvents was difficult.

The treatment of nickel salts (excepting thiocyanate) with the ligand in ethanol gave a deep brown solution, which upon refluxing and concentration always yielded the compound of the formula, $Ni(NAs)_2X_2$ (where NAs = *o*-dimethylarsinoaniline and X = Cl, Br, I, ClO_4). These hydrolyzed compounds can be readily prepared for comparison from the intermixing of nickel salts and the ligand *o*-dimethylarsinoaniline. They are very insoluble in common organic solvents and thus immediate precipitation of almost quantitative yields occurs.[16]

The fact that the compounds of type $Ni(NAs)_2X_2$ are not immediately isolated from the solution of the ligand MeNHNAs and nickel(II) salts may indicate that the complexes NiX_2-MeNHNAs which are of high solubility in ethanol are at first formed, and are then slowly hydrolyzed by water to give the insoluble $Ni(NAs)_2X_2$ during the refluxing of solutions.

This situation also occurs in other similar ligand systems; thus the ligand derived from *o*-dimethylarsinoaniline and diacetyl or acetylacetone readily hydrolyses in the presence of metal salts. It is also worth noting that the complexes, $Ni(NAs)_2X_2$ (X = Cl, Br, I) prepared from the hydrolysis of the Schiff base tridentate ligands, give larger crystals than those prepared directly from nickel salts and the ligand NAs. This suggests that the hydrolysis reaction is relatively slow giving time for the insoluble precipitate to form large crystals.

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(11) L. Sacconi and P.G. Speroni, *Inorg. Chem.*, 7, 295 (1968).

(12) L. Sacconi, G.P. Speroni, and R. Morassi, *Inorg. Chem.*, 7, 1521 (1968).

(13) L. Sacconi, R. Morassi, and S. Midollini, *J. Chem. Soc.* (*A*), 1510 (1968).

(14) A.B.P. Lever, «Inorganic Electronic Spectroscopy», Elsevier, Amsterdam (1968), pp. 333-349.

(15) D.C.M. Mitchell and R.J.P. Williams, *J. Chem. Soc.*, 1912, (1960).

(16) B. Chiswell and K.A. Verrall, *Inorg. Chim. Acta*, accepted for publication 1972; K.A. Verrall, Ph.D. Thesis, University of Queensland, 1971.

The nickel(II) complexes of the ligand MeNHNAs are few and are listed in Table I. Other compounds were obtained but did not give satisfactory analytical results. All attempts to prepare the nickel nitrate complexes were unsuccessful; the attempt to dry the brown mass, which was isolated by the addition of diethyl ether to the concentrated solution of nickel(II) nitrate and the ligand MeNHNAs in a dry nitrogen stream, resulted in the change of the brown colour to green and the formation of a tar. The complex, Ni(MeNHNAs)$Br_2 \cdot \frac{1}{2}H_2O$, was prepared by the addition of anhydrous diethyl ether (dried over sodium metal) to the solution from which the precipitate Ni(NAs)$_2$Br$_2$ had already been filtered off.

The interaction of nickel thiocyanate with the ligand MeNHNAs in a mixed solvent (ethanol-benzene) and refluxing of the solution for 1.5 hr does not give the hydrolyzed mauve complex Ni(NAs)$_2$(NCS)$_2$,[16] but instead yellow crystals of Ni(MeNHNAs)(NCS)$_2$nH$_2$O ($n = \frac{1}{2}$ or 3) slowly separated as the solution was concentrated.

The infrared spectrum of Ni(MeNHNAs)X$_2$ n solvate (X = Br, Cl, NCS) in the N-H stretching region displays a medium strength broad band at 3140 cm^{-1} which is lowered by 210 cm^{-1} with respect to the value of 3350 cm^{-1} found for the analogous ligand[6] derived from *o*-methylaminobenzaldehyde and N,N-dimethylethylenediamine the complexes of which show the N-H stretching frequency shifted to lower frequencies by 80-120 cm^{-1} except for the chloride complex which shows a larger shift of 190 cm^{-1}. The lowering of 210 cm^{-1} in Ni(MeNHNAs)X$_2$ (X = Cl, Br, NCS) may indicate metal-nitrogen bonding and is presumably also caused by stronger hydrogen bonding.

The reflectance spectra (Figure 4) in the visible region of the halide complexes Ni(MeNHNAs)X$_2$ (X = Br, I) are very similar, but there is an appreciable difference in the nitromethane solution spectra of the bromide and iodide complexes.

The bromide complex exhibits maxima at 1180 and 715 nm in both the solid and solution spectrum. This is characteristic of a five-coordinate high-spin nickel(II), while the iodide complex Ni(MeNHNAs)I$_2$ EtOH in nitromethane displays only a shoulder at approx. 715 nm and no appreciable band below 800 nm.

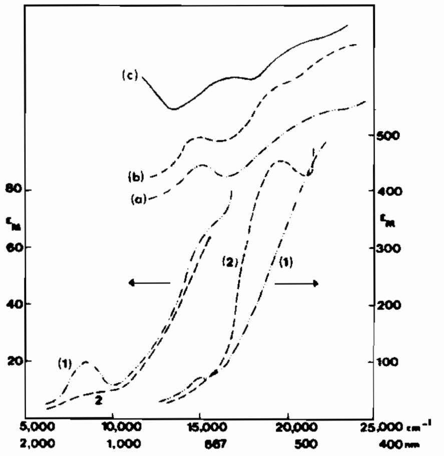


Figure 4. Spectra of nickel(II) complexes of ligand MeNHNAs. Reflectance spectra: (a) Ni(MeNHNAs)Br$_2$½H$_2$O (b) Ni(MeNHNAs)I$_2$EtOH (c) Ni(MeNHNAs)(NCS)$_2$ ½H$_2$O. Solution spectra in MeNO$_2$: (1) compound (a) (2) compound (b).

This suggests that the iodide complex is dissociated in nitromethane solution ($\Lambda_M = 79$ cm^2 ohm^{-1} mole^{-1}) (Table II) to give a four-coordinate square-planar complex.

The thiocyanate complexes, Ni(MeNHNAs)(NCS)$_2$. nH$_2$O ($n = \frac{1}{2}$ or 3), are paramagnetic in the solid state and insoluble in organic solvents such as ethanol and nitromethane. The reflectance spectrum shows bands at approx. 1000 and 600 nm which are similar to those shown by other six-coordinate thiocyanate complexes. The infrared spectrum exhibits two bands 2118 (s), 2110 (s) in the C-N stretching region, supporting the supposition of six-coordination by intermolecular bridging[15] thiocyanate group.

Nickel(II) Complexes of NHNAs. The reaction of the ligand NHNAs with nickel(II) salts in the presence of alkali (KOH or NaOEt) in ethanol or aqueous ethanol yields a deep red-brown solution from which the required yellow brown deprotonated complex [Ni(L-H)$_2$]^0 (L = NHNAs) separates, either on concentration or by addition of water. The deprotonated complexes are very soluble in common organic solvents such as acetone, ethanol and chloroform, but are insoluble in water. They are best recrystallized by homogeneous precipitation from acetone-water solution from which acetone is allowed to slowly evaporate (Table III).

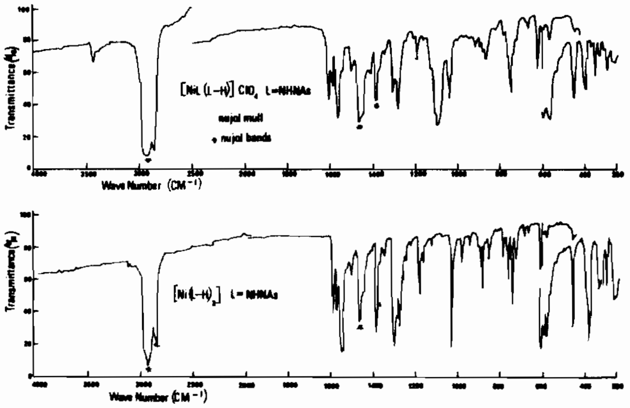


Figure 5. Infrared spectra of deprotonated nickel(II) complexes.

The deprotonated complexes, [Ni(L-H)$_2$]^0, are paramagnetic at room temperature and practically nonelectrolytes in nitromethane. The infrared spectra (Figure 5) exhibit no band in the N-H stretching region, suggesting that the deprotonated ligand in [Ni(L-H)$_2$]^0 is acting as a tridentate.

It is therefore reasonable to suggest that six-coordinate octahedral coordination of the metal ion in the deprotonated complexes is achieved with two deprotonated tridentate ligands. Further evidence of such coordination can be deduced from the electronic spectra (Figure 6) which show bands at approx. 900, 560

Table II. Physical properties of nickel(II) complexes of the ligands Me_2NNAs, $Me_2NNAsEt$ and MeNNHAs.

Complex	Magnetic Data*				Solid Reflectance Spectra
	$10^6\chi_g$	$10^6\chi'_M$	μ_{eff}(B.M.)	Λ_M**	$\nu_{max}\times10^3$, cm^{-1}
$Ni(Me_2NNAs)Cl_2$	9.08	4414	3.25	13.0	13.4, 18.5sh, 21.5, 27.0
$Ni(Me_2NNAs)Br_2$	8.12	47.02	3.35	19.0	13.3, 18.5sh, 22.0, 27.0
$Ni(Me_2NNAs)I_2$	6.75	4619	3.32	37.6	12.2, 14.2, 17.0, 21.5, 25.0
$Ni(Me_2NNAs)(NCS)_2$	8.48	4259	3.28	i.s.	~10.0, 16.5, 20.5, 23.0, 27.0
$Ni(Me_2NNAs)(NO_3)_2$	7.70	4175	3.16	41.5	~10. 15.5, 20.5, 23.0, 27.0
$Ni(Me_2NNAsEt)Cl_2$	8.67	4484	3.25	1.7	13.5, 18.5sh, 21.0, 27.0
$Ni(Me_2NNAsEt)Br_2$	7.32	4679	3.33	9.3	13.2, 18.0sh, 21.0, 26.0
$Ni(Me_2NNAsEt)I_2$	4.81	3626	2.93	29.8	13.0, 14.5sh, 18.0sh, 21.5, 24.5
$Ni(Me_2NNAsEt)(NCS)_2$	7.31	4210	3.17	i.s.	~10, 16.0, 20.0sh, 22.0, 26.0
$Ni(Me_2NNAsEt)(NO_3)_2$	7.45	4275	3.18	19.8	~10, 16.0, 20.0sh, 23.5, 27.0
$Ni(MeNHNAs)Br_2{}^1\!/\!_2H_2O$	7.08	4096	3.11	14.6	14.3, 18.0sh, —24.0
$Ni(MeNHNAs)I_2EtOH$				79.1	
$Ni(MeNHNAs)(NCS)_2{}^1\!/\!_2H_2O$	7.04	3778	3.00	i.s.	10.0, 16.2, 19.8sh, 23.0
$Ni(MeNHNAs)(NCS)_23H_2O$	8.43	4854	3.39	i.s.	~10, 16.5sh, 20.0sh, 24.0

* measured at 290°K. ** measured in *ca.* 10^{-3} *M* nitromethanc solution; ohm^{-1}cm^{2}mole^{-1}. i.s. insufficiently soluble. sh. shoulder.

Table III. Analytical data and magnetic properties of nickel(II) complexes of NHNAs.

Analytical Data	C	H	N	Ni	X	Method of prepn.	proposed formula*	Magnetic Data^a $10^6\chi_g$	$10^6\chi_M$	param/diamg Ni(II)	μ_{eff}/param (B.M.)
Deprotonated complexes											
Found	43.3	4.3	7.6	8.1	5.2	E-f	$[NiL(L\text{-}H)]ClO_4H_2O^b$	diamag.			
Calc.	43.1	4.5	7.7	8.1	4.9						
Found	51.5	4.8	9.2	9.6		EW-R(A,W)	$[Ni(L\text{-}H)_2]^{\circ\,c}$	6.10	39.80		3.08
Calc.	51.5	4.7	9.3	9.7							
Purple complexes											
Found	43.5	4.4	7.4	11.3	9.7	EB-f-H	$Ni_3L_2(L\text{-}H)_2Cl_4H_2O$	2.30	4010	1/2	3.07
Calc.	43.5	4.4	7.4	12.3	9.9						
Found	46.3	4.2	8.4	11.8	9.3	E-B	$Ni_3L_2(L\text{-}H)_2(C_5H_5N)Cl_4$	2.44	4370	1/2	3.21
Calc.	46.0	4.3	8.5	11.8	9.5						
Found	35.1	4.1	5.9	9.6	25.3	E	$Ni_3L_4Br_63H_2O$	3.84	7080	2/1	3.07
Calc.	34.6	3.7	6.2	9.8	26.6						
Found	30.8	3.3	5.0	8.3	36.5	E-R(E,C)	$Ni_3L_4I_52H_2O$	3.60	8355	2/1	3.16
Calc.	30.3	3.1	5.4	8.6	37.5						
Found	32.7	3.1	5.8	9.1	35.1	3E	$Ni_3L_3(L\text{-}H)I_5$	1.95	4597	1/2	3.29
Calc.	32.8	3.2	5.9	9.3	33.3						
Found	46.6	3.8	11.2	10.4		EB-f-BuE	$Ni_5L_4(L\text{-}H)_4(NCS)_6$ U	2.79	9420	2/3	3.34
Calc.	46.6	4.2	10.9	10.4							

* L = Ligand NHNAs; L-H Deprotonated ligand NHNAs-H. ^{a} measured at 295°K. ^{b,c} the value of molar conductivity (Λ_M, cm^{2}ohm^{-1}mole^{-1}): 90.5 for *b* and 5.0 for *c* in approx. 10^{-3} nitromethane solution.

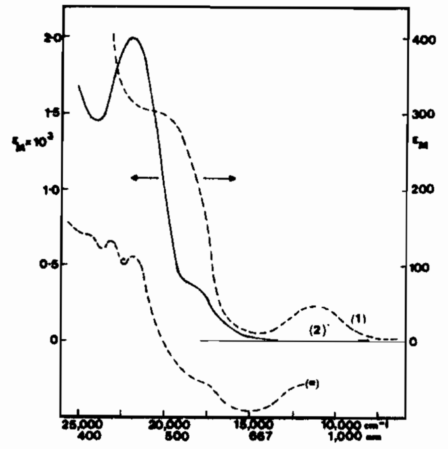


Figure 6. Spectra of deprotonated nickel(II) complexes. Reflectance spectrum: (a) $Ni(NHNAs\text{-}H)_2$ (arbitrary scale); Solution spectra: (1) $Ni(NHNAs\text{-}H)_2$ in $CHCl_3$ (2) Ni-(NHNAs)(NHNAs-H)ClO_4H_2O in $MeNO_2$.

nm and an intense band around 430 nm in the solid state. These first two bands can be safely assigned as ν_1 and ν_2, and the absorption frequencies ratio $\nu_2/\nu_1 = 1.58$ is close to 1.6 which is characteristic of spectra of nickel(II) ions with octahedral configuration.[14]

It is interesting to note that the intense band around 430 nm is clearly split into three components at 459, 433 and 408 nm in the reflectance spectrum of $[Ni(NHNAs\text{-}H)_2]^0$.

It should be noted that the ligand field strength of the deprotonated ligand, NHNAs-H, is comparable with that of the analogous ligand, ONAs (N-*o*-dimethylarsinophenylsalicylaldimine).[1]

The interaction of nickel(II) perchlorate with the ligand NHNAs in ethanol yields a deep brown complex having the empirical formula [Ni(NHNAs)-(NHNAs-H)ClO_4H_2O.

The complex is diamagnetic in the solid state and is a typical 1:1 electrolyte in either nitromethane or dimethylsulfoxide solution. The infrared spectrum displays a medium sharp band at 3440 cm^{-1} in the N-H stretching region which may indicate an un-deprotonated N-H stretching frequency of an uncoordinated pyrrole ring nitrogen.

The configuration of nickel(II) in this complex, therefore, may be low-spin five-coordinate in which the deprotonated ligand, NHNAs-H, acts as a tridentate and the neutral ligand, NHNAs as a bidentate with pyrrole nitrogen uncoordinated.

A low-spin square-pyramidal structure may be proposed and is supported by the facts that

(1) in the metal complexes of multidentate ligands containing the pyrrole moiety, the deprotonated pyrrole nitrogen is always coordinated to the metal ion whereas the neutral un-deprotonated pyrrole nitrogen is not coordinated to the metal ion;[17,18]

(2) the calculated nucleophilic reactivity constant [$\Sigma n^0 = 29.90$) for the donor atom set N_3As_2 falls within the range ($\Sigma n^0 = 25.5$-37.2) found for low-spin five-coordinate nickel(II) complexes;[19]

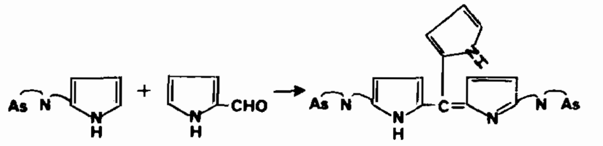
(3) the electronic spectra (Figure 6) of $[Ni(NHNAs)(NHNAs\text{-}H)]ClO_4$ in nitromethane exhibit bands at 555, 455 and ~380 nm. These bands are very intense due to overlapping by the charge transfer band but very similar in the band position and shape to those of low-spin square-pyramidal nickel(II) complexes,[20] $[Ni(diars)_2X]^+$ but different to those of low-spin trigonal bipyramidal complexes.

Purple Complexes of Nickel(II)-NHNAs. The interaction of equimolecular quantities of the ligand NHNAs and nickel(II) salts in ethanol gives a deep red-brown solution, which upon refluxing and concentration yields black crystals. These are almost insoluble in ethanol, and water, slightly soluble in hot ethanol, nitromethane and chloroform and moderately soluble in N,N-dimethylformamide and dimethylsulfoxide, in which they give a deep violet-purple solution.

These complexes obtained are listed in Table III, along with their most probable empirical formula which is deduced on the basis of the analytical data and the magnetic moments.

It can be seen that the ratio of Ni^{II}: L (where L = ligand NHNAs) moiety in these complexes is 3:4; excepting the thiocyanate complex which has a ratio of 5:8. In the chloride and thiocyanate complexes half of the ligands present in the proposed formula are deprotonated and the bromide and iodide complexes have the general formula $Ni_3L_4X_6nH_2O$ with all un-deprotonated ligand.

In the compounds $Ni_3L_2(L\text{-}H)_2(C_5H_3N)Cl_4$ it seems likely that two NHNAs ligands are coupled by a pyrrole aldehyde:



A similar coupling reaction in pyrrole readily occurs in the presence of acid or metal ion.[21]

The magnetic moments of these compounds at room temperature are anomalous ranging from 1.78 to 2.57 B.M. per nickel ion. By assuming that all the nickel atoms are in the bivalent state and that no atoms are present with intermediate moments between the values shown by high-spin and low-spin nickel(II), the magnetic moments per paramagnetic nickel(II) were calculated on the basis of the ratio of paramagnetic to diamagnetic nickel(II) as shown in Table III. They ranged from 3.07 to 3.34 B.M. per paramagnetic nickel(II).

Their stereochemistry may be one of square-planar, five-coordinate or tetragonal in cases of diamagnetic nickel(II), and one of tetrahedral, five-coordinate and/or octahedral in cases of paramagnetic nickel(II). It has not been possible to deduce the stereochemistry of these nickel complexes because the solid reflectance spectra display complete absorption in the visible region and solution spectra and molar conductivities cannot be measured due to low solubility in non-coordinating solvents.

Cobalt(II) Complexes of Ligands Me_2NNAs and $Me_2NNAsEt$. Complexes of empirical formula $Co(Me_2NNAs)X_2$ (X = Cl, Br, I, NCS and NO_3 were obtained as large brown crystals upon the reaction of the appropriate cobalt(II) salt with the ligand Me_2NNAs in ethanol under nitrogen. A series of the analogous cobalt(II) complexes $Co(Me_2NNAsEt)X_2$ were prepared in mixed solvents of ethanol-benzene-heptane (2:1:1) under nitrogen (Table IV).

The perchlorate, $Co(Me_2NNAs)_2(ClO_4)_2 3H_2O$ was prepared by treating cobalt(II) perchlorate with two equivalents of the ligand Me_2NNAs in ethanol, but the attempt to prepare the analogous complex containing the ligand $Me_2NNAsEt$ gave a brown sticky material which is very soluble in ethanol producing a brown colour. It was not further characterized.

All the complexes obtained are soluble in the common organic solvents such as acetone, alcohols and inert solvents.

The values of the molar conductivities for the mono-ligand complexes in nitromethane solution suggest that the complexes containing the ligand Me_2NNAs are appreciably dissociated whilst the corresponding complexes of the ligand $Me_2NNAsEt$ are practically non-electrolytes in that solvent. The perchlorate complex exhibits a molar conductivity typical of a 1:2 electrolyte in nitromethane solution.

The magnetic moments of the mono-ligand complexes at room temperature (Table V) are typical of the high-spin configuration of cobalt(II), and range from 4.33 to 4.62 B.M.

The reflectance spectra of the mono-ligand complexes of cobalt(II) in the visible region are much the same for both ligands Me_2NNAs and $Me_2NNAsEt$ except in the case of the nitrate complexes where it was observed that, while $Co(Me_2NNAsEt)(NO_3)_2$ has a reflectance spectrum which is very similar to those

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(17) H. Henning and R. Daute, *Z. Chem.*, *9*, 275 (1969).
(18) F. Ferguson and B.O. West, *J. Chem. Soc. (A)*, 1565, 1569 (1966).
(19) L. Sacconi, *J. Chem. Soc. (A)*, 248 (1970).
(20) M. Green and P.A. Tasker, *J. Chem. Soc. (A)*, 3105 (1970).
(21) G.F. Smith, «Advances in Heterocyclic Chem.», *2*, 287 (1963); A.H. Conwin, «Heterocyclic Compounds», *1*, 227 (1950); A.E. Martell, *Revs. Pure and App. Chem.*, *17*, 129 (1968).

Table IV. Analytical Data of Cobalt(II) Complexes of the ligands Me_2NNAs and $Me_2NNAsEt$.

Complex		Analysis (%) C	H	N	Co	Method of prepn.*
Cobalt(II)-Me_2NNAs						
$Co(Me_2NNAs)Cl_2$	Found	44.0	4.8	6.0	12.6	E
	Calc.	44.5	4.6	6.1	12.8	
$Co(Me_2NNAs)Br_2 \frac{1}{2} EtOH$	Found	37.7	4.5	4.5	20.4	E
	Calc.	37.8	4.2	4.9	10.3	
$Co(Me_2NNAs)I_2 2H_2O$	Found	29.8	3.5	4.6	8.4	E
	Calc.	30.1	3.7	4.1	8.7	
$Co(Me_2NNAs)(NCS)_2$	Found	45.5	4.6	11.1	11.8	E
	Calc.	45.2	4.2	11.1	11.7	
$Co(Me_2NNAs)(NO_3)_2$	Found	40.2	4.8	10.9	11.7	E-Bu
	Calc.	39.9	4.1	10.7	11.5	
$Co(Me_2NNAs)_2(ClO_4)_2 3H_2O$	Found	42.1	5.4	5.4	6.2	E-f
	Calc.	42.2	5.0	5.8	6.1	
Cobalt(II)-$Me_2NNAsEt$						
$Co(Me_2NNAsEt)Cl_2$	Found	46.5	5.3	5.4	12.2	EBH
	Calc.	46.8	5.1	5.8	12.1	
$Co(Me_2NNAsEt)Br_2$	Found	40.0	4.5	4.9	10.1	EBH
	Calc.	39.6	4.3	4.9	10.2	
$Co(Me_2NNAsEt)I_2$	Found	34.6	3.9	4.5	8.6	EBH
	Calc.	34.1	3.7	4.2	8.8	
$Co(Me_2NNAsEt)(NCS)_2$	Found	47.6	5.0	9.9	10.2	EBH
	Calc.	47.4	4.7	10.5	11.1	
$Co(Me_2NNAsEt)(NO_3)_2$	Found	42.2	4.7	10.1	11.1	EBH
	Calc.	42.2	4.6	10.4	10.9	

* see experimental section

Table V. Physical properties of Cobalt(II) complexes of the ligands Me_2NNAs and $Me_2NNAsEt$.

Compliex	$10^6\chi$	Magnetic Data* $10^6\chi'_M$	μ_{eff}(B.M.)	Λ_M**	Solid Reflectance Spectra $\nu_{max} \times 10^3$, cm^{-1}
$Co(Me_2NNAs)Cl_2$	19.00	8964	4.62	29.2	14.5sh, 15.9, 18.0sh, 21.5sh, 26.0
$Co(Me_2NNAs)Br_2 \frac{1}{2} EtOH$	16.25	8957	4.62	33.8	13.5sh, 15.0, 17.5, 20.5, 25.0
$Co(Me_2NNAs)I_2 2H_2O$	11.83	8225	4.43	54.4	12.5, 13.6sh, 14.5, 20.5, 24.5
$Co(Me_2NNAs)(NCS)_2$	16.92	8789	4.57	57.2	14.1, 16.5, 17.5sh, 21.5, 26.0
$Co(Me_2NNAs)(NO_3)_2$	16.75	8815	4.58	65.0	3.8, 16.3sh, 17.3, 19.5sh, 23.0
$Co(Me_2NNAs)_2(ClO_4)_2 3H_2O$	9.72	9905	4.85	136.0	
$Co(Me_2NNAsEt)Cl_2$	16.22	8164	4.45	6.5	~10sh, 12.5, 15.8, 17.4, 18.2, 21.9
$Co(Me_2NNAsEt)Br_2$	14.52	8657	4.53	9.1	~11, 12.4sh, 15.0, 17.5, 20.5sh
$Co(Me_2NNAsEt)I_2$	12.40	8630	4.53	27.1	~11, 13.9, 16.1, 17.7sh, 21.0, —24.0
$Co(Me_2NNAsEt)(NCS)_2$	13.70	7560	4.33	6.4	14.0sh, 16.1sh, 17.0, 23.0
$Co(Me_2NNAsEt)(NO_3)_2$	14.28	7975	4.36	13.1	13.0sh, 14.6, 18.4sh, 21.5, —26.0

* Measured at 295°K. ** Measured in ca. $10^{-3} M$ nitromethane solution ($cm^2 ohm^{-1} mole^{-1}$).

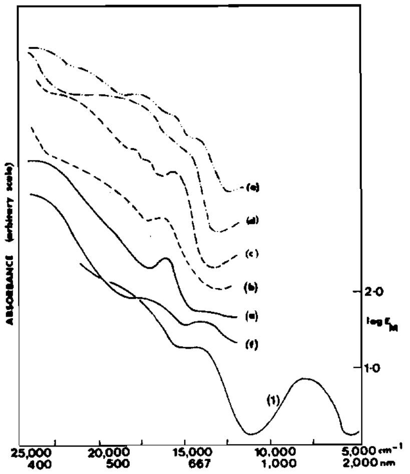

Figure 7. Spectra of Cobalt(II) complexes of Me_2NNAs and $Me_2NNAsEt$. Reflectance spectra of $Co(Me_2NNAsEt)X_2$: (a) X = NO_3 (b) X = NCS (c) X = Cl (d) X = Br (e) X = I; Reflectance spectra (f) and solution spectrum (1) of $Co(Me_2NNAs)(NO_3)_2$ in $MeNO_2$.

of the analogous halide and thiocyanate complexes formed by both ligands, the reflectance spectrum of $Co(Me_2NNAs)(NO_3)_2$ is quite different (Figure 7).

The hypothesis for a five-coordinate stereochemistry in these mono-ligand cobalt(II) complexes can be provided by the infrared spectra:

(i) The infrared spectra of the complexes $CoLX_2$ (L = Me_2NNAs, $Me_2NNAsEt$, X = Cl, Br, I) are almost indistinguishable in the frequencies and relative intensities of the bands from those of the corresponding nickel(II) complexes which have been shown to have a five-coordinate stereochemistry on the basis of their physical properties.

(ii) The infrared spectra of the thiocyanate complexes, $CoL(NCS)_2$ (L = Me_2NNAs, $Me_2NNAsEt$) are very similar to those of the halide complexes except for the absorption regions of the anions, but different from those of the corresponding nickel(II) complexes for which polymeric octahedral configurations were established (Figure 8b). In particular, differences are obvious in the C-N stretching region (2000-2200 cm^{-1}), the region 600-900 cm^{-1} and metal -NCS stretching region (250-400 cm^{-1}).

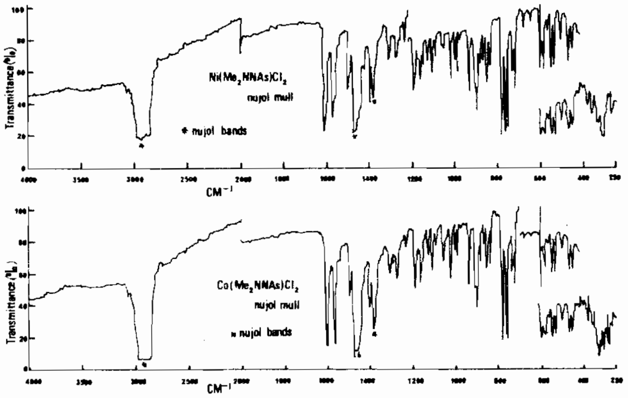

Figure 8a. Infrared spectra of Cobalt(II) and Nickel(II) chloride complexes of ligand Me$_2$NNAs.

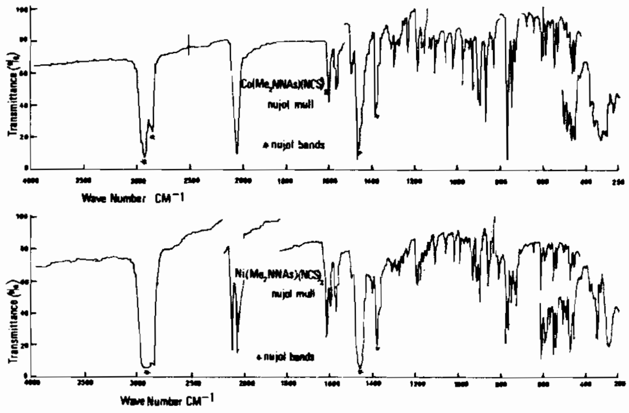

Figure 8b. Infrared spectra of Cobalt(II) and Nickel(II) thiocyanate complexes of ligand Me$_2$NNAs.

It should be noted that the cobalt thiocyanate complexes are soluble in organic solvents and are non-ionic, whilst the corresponding nickel complexes are almost insoluble in common organic solvents.

Regarding the possibility of the tetrahedral configuration in which the ligand would be acting as a bidentate ligand, it was noted that the solution spectra were different from those in the solid state. Furthermore, the solution spectra of the bromide complexes (Figure 9) displayed a band at 1480 nm and a structural band at approx. 667 nm which are very similar to those of the wellknown tetrahedral cobalt(II) complexes such as [CoX$_4$]$^{2-}$ and CoL$_2$X$_2$ (X = halide; L = PPh$_3$). It is therefore reasonable to assume that in nitromethane solution these halide complexes have tetrahedral configurations with two halide donors and a ligand in which one of the terminal donor atoms, N or As, may be detached from the cobalt(II).

On the basis of the above argument, the mono-ligand cobalt(II) complexes, CoLX$_2$ (L = Me$_2$NNAs, MeNNAsEt; X = Cl, Br, I and NCS), may be regarded as having five-coordinate structures in the solid state and four-coordinate tetrahedral structures in nitromethane solution.

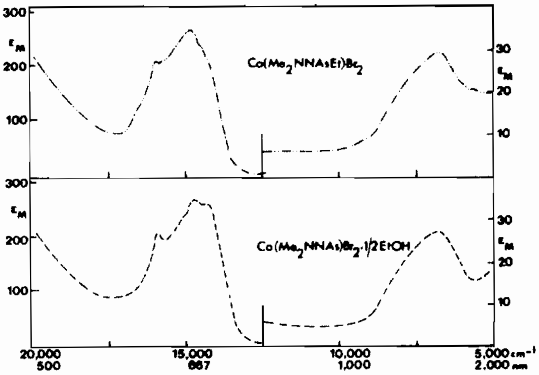

Figure 9. Spectra of Cobalt(II) bromide complexes of Me$_2$NNAs and Me$_2$NNAsEt in nitromethane solution.

The fact that the nickel(II) thiocyanate complexes are polymeric octahedral and the corresponding cobalt (II) complexes are five-coordinate is compatible with the greater tendency of cobalt(II) to form complexes with this configuration, as has often been observed in thiocyanate complexes.

The nitrate complex of the ligand Me$_2$NNAs shows the same spectral pattern in both solid and nitromethane solution, displaying a weak band at 1250 and two bands at 714 and ~570 nm. The spectra are different from those of the corresponding bromide complexes. Because of the low intensity ($\varepsilon_M \simeq 9$) in the near infrared band, it may be assigned as the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ in regular or slightly distorted octahedral cobalt(II) complexes.[13] The fact that this complex is appreciably dissociated in solution leads to the conclusion that the nitrate groups may be replaced by the solvent molecules.

The molar conductivity of the bis-ligand perchlorate complex Co(Me$_2$NNAs)$_2$(ClO$_4$)$_2$3H$_2$O is typical of a 1:2 electrolyte in nitromethane, and the value of the room temperature magnetic moment is 4.85 B.M., suggesting high-spin octahedral cobalt(II).

It is interesting to note that the tridentate ligands having N-N-As donor sequences which have a heterocyclic terminal nitrogen atom give rise to low-spin octahedral bis-ligand cobalt(II) complexes,[22] whilst the ligand Me$_2$NNAs which has the same donor sequence N-N-As but with a terminal bulky aliphatic nitrogen donor atom gives the bis-ligand cobalt(II) complex of the high-spin type. The formation of the high-spin cobalt(II) complex Co(Me$_2$NNAs)$_2$(ClO$_4$)$_2$-3H$_2$O is presumably due to the low ligand field strength resulting from the two bulky terminal groups on the nitrogen and arsenic donors, which would increase the cobalt(II)-ligand bond lengths.

Cobalt Complexes of Ligand NHNAs. The interaction of cobalt(II) salts with the ligand NHNAs (derived from *o*-dimethylarsinoaniline and pyrrole-2-aldehy-

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(22) K.W. Lee, Ph.D. Thesis, University of Queensland, 1971.

Table VI. Analysis and physical data for the deprotonated cobalt complexes of NHNAs(L).

Complex ^{c}		Analysis (%)				Method of	Magnetic data ^{a}			
		C	H	N	Co	prepn.	$10^6\chi_g$	$10^6\chi'_M$	μ_{eff}(B.M.)	Λ_M ^{b}
$[Co(L\text{-}H)_2]_2[CoCl_4]$	Found	44.1	4.0	7.7	12.5	3EBH	6.44	9820	4.82	150
	Calc.	44.0	4.2	7.9	12.5	Bu-f				
$[Co(L\text{-}H)_2]_2[CoBr_4]$	Found	40.0	4.0	7.1	10.6	E	5.97	10113	4.91	144
	Calc.	39.4	3.6	7.1	11.1					
$[Co(L\text{-}H)_2]_2[CoI_4]\frac{1}{2}C_6H_6$	Found	36.7	3.8	6.8	9.5	E-f-H	5.03	9790	4.82	182
	Calc.	36.3	4.0	6.2	9.7					
$[Co(L\text{-}H)_2]_2[Co(NCS)_4]$	Found	45.5	3.8	11.3	11.7	2E;E	5.35	8716	4.55	159
	Calc.	45.0	3.8	11.3	11.9					
$[Co(L\text{-}H)_2]_2[Co(NO_3)_4]2EtOH$	Found	42.4	3.9	10.5	11.1	0.9E	5.73	8756	4.57	150
	Calc.	42.1	4.3	10.5	11.1					
$[Co(L\text{-}H)_2]ClO_4 2H_2O$	Found	42.3	4.2	7.6	7.9	E	diamagnetic			85
	Calc.	42.1	4.3	7.6	8.0					
$[Co(L\text{-}H)_2]ClO_4EtOH$	Found	44.7	4.2	7.6	7.7	2E-f-R(D)	diamagnetic			82
	Calc.	44.7	4.5	7.5	7.8					
$[Co(L\text{-}H)_2]BPh_4$	Found	64.6	5.3	6.0		E-f	diamagnetic			82
	Calc.	64.9	5.4	6.2						
$[Co(L\text{-}H)_2]I\frac{1}{2}EtOH$	Found	40.1	3.7	6.9		E	diamagnetic			75
	Calc.	40.4	4.0	6.9						

^{a} measured at 295°K; ^{b} measured in approx. $10^{-3}M$ nitromethane solution ($cm^2ohm^{-1}mole^{-1}$). ^{c} L-H = ligand NHNAs minus a proton.

de) in ethanol under a nitrogen atmosphere gives green solutions in the case of cobalt(II) halides and thiocyanate and brown solutions in the case of the nitrate and perchlorate. On refluxing the solutions for 30 minutes and concentrating, they gave (Table VI):

(i) brown compounds of the type $[Co(L\text{-}H)_2]_2[CoX_4]$ (L = NHNAs; L-H = NHNAs minus a proton; X = Cl, Br, I, NCS and NO_3);

(ii) red-brown compounds of the type $[Co(L\text{-}H)_2]Y$. n solvate (Y = I, ClO_4, BPh_4).

Attempts to prepare a neutral cobalt(II) complex of the type $Co(L\text{-}H)_2$ were unsuccessfull.

All the complexes are slightly hygroscopic but stable in dry air. Both types of complexes are soluble in common organic solvents such as alcohols and nitromethane.

The infrared spectra of all the complexes display no bands due to the N-H stretching vibration in the 3000-3500 cm^{-1} region, suggesting that the ligand NHNAs(L) is deprotonated (L-H) and acts as a tridentate chelating agent.

The molar conductivities of the brown compounds of the type (i) in nitromethane solution show values typical of 1:2 electrrolytes (Λ_M = 144-182 $cm^2ohm^{-1}mole^{-1}$) on the basis of the formula weight of $[Co(L\text{-}H)_2]_2[CoX_4]$, whilst those of the red-brown compounds of the type (ii) $[Co(L\text{-}H)_2]Y$ are typical of 1:1 electrolytes (Λ_M = 75-85 $cm^2ohm^{-1}mole^{-1}$). Thus the conductivities of the complexes in nitromethane support the proposed formulations.

The room-temperature magnetic moments of the red-brown compounds, $[Co(L\text{-}H)_2]y$, indicate diamagnetism which is typical of octahedral complexes of cobalt(III). The magnetic moments of the anions in the $[Co(L\text{-}H)_2]_2[CoX_4]$ complexes were calculated assuming that the cation $[Co(L\text{-}H)_2]^+$ contain diamagnetic cobalt(III), and are listed in Table VI. They are all within the range 4.55-4.91 B.M. and are closely comparable to those found for the tetrahedral cobalt(II) complexes of the corresponding anions.[23] Furthermore, the absorption spectra of the red-brown cobalt(III) complexes exhibit intense bands near 500 nm in the solid state, but in nitromethane solution they give rise to a single intense band at 424 nm (Figure 10). On the other hand the spectra of the complexes $[Co(L\text{-}H)_2]_2[CoX_4]$ (X = Cl, Br, I, NCS) in both solid and solution are essentially that of the combination of the octahedral cobalt(III) cation and the tetrahedral cobalt(II) anion, as shown in Figure 10, for the solid state.

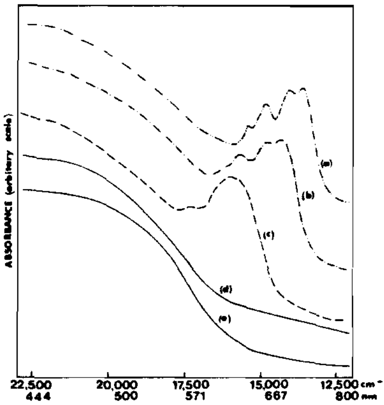

Figure 10. Reflectance spectra of deprotonated cobalt(II,III) complexes of ligand NHNAs(L). (a) $[Co(L\text{-}H)_2]_2[CoBr_4]$, (b) $[Co(L\text{-}H)_2]_2[CoCl_4]$, (c) $[Co(L\text{-}H)_2]_2[Co(NCS)_4]$, (d) $[Co(L\text{-}H)_2]_2[Co(NO_3)_4]$, (e) $[Co(L\text{-}H)_2]ClO_4$. L-H = ligand NHNAs minus a proton).

The fact that the spectrum of $[Co(L\text{-}H)_2]_2[Co(NO_3)_4]$ is practically identical with those of $[Co(L\text{-}H_2]Y$, may be explained by the hypothesis that the

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(23) J. Lewis, *Science Prog.*, *51*, 450 (1963); R.H. Holm and F.A. Cotton, *J. Chem. Phys.* *31*, 788 (1959).

highly intense bands of the $[Co(L\text{-}H)_2]^+$ cation obscured that of the $[Co(NO_3)_4]^{2-}$ anion which would be observed near 540 nm in the visible region.[24]

Although the deprotonation of protonated metal complexes is usually achieved by the aid of alkaline solution, in all the cobalt complexes the ligand NHNAs is deprotonated without the aid of alkali and coordinates only to the cobalt(III) ion.

In its ready ability to oxidize cobalt(II) salts and form cobalt(III) complexes by auto-deprotonation, the tridentate ligand NHNAs exhibits a similarity of action to the deprotonatable ligands such as 2-pyridinealdehyde-2-pyridylhydrazone (paphy)[25] and 1-10-phenanthroline-2-amidoxime,[26] but the action is different from that of ligands such as o-dimethylarsinoaniline[16] and o-phenylenebis(dimethylarsine)[27] which readily form cobalt(III) complexes by air oxidation.

The preferential formation of the cobalt(III) complex cation $[Co(L\text{-}H)_2]^+$ is not surprising because the ligand NHNAs can lose the somewhat acidic imino-proton of the N-heterocyclic pyrrole residue when it is bonded to a metal of high charge and small volume such as cobalt(III), which would be provided from the cobalt(II) salt by the auto-oxidation accompanied by the deprotonation of salt by the auto-oxidation of ligand or possibly by air oxidation. This proton loss can occur readily without the necessity of deprotonation with alkali.

The fact that the treatment of $[Co(L\text{-}H)_2]ClO_4$ with aqueous potassium hydroxide (2*M*) gave no evidence at all for the hydrolysis of the ligand NHNAs and the formation of cobalt(III) hydroxide reflects the high stability of these deprotonated compounds.

Experimental Section

General procedure for the preparation of metal complexes. The warm and deaerated ligand solution was slowly added to the appropriate hot metal salt solution (code (i)) in approx. 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 temperature.

(ii) When the metal complex compound did not appear to separate within approx. 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 impurities 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: Bu 1-butanol; E ethanol; Et diethyl ether; B benzene; A acetone; C chloroform; H hexane; W water.

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

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

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

Preparation of Ligands. All of the ligands were found to be oils of high boiling point and were not characterized. Stock solutions of the ligand were obtained by taking equimolecular quantities of the o-dialkyl-arsino-aniline[1] and the appropriate aldehyde, mixing them in ethanol and benzene, and refluxing the solution for 30 minutes. Most of the solvent was then distilled off and the residue diluted to a known volume with ethanol.

Spectra. (i) Infrared spectra were obtained using a Perkin-Elmer model 457 spectrometer. Samples were examined in the range 4000-400 cm^{-1} as mulls, in either nujol or hexachlorobutadiene, supported between potassium bromide discs. In the range 600-250 cm^{-1} nujol mulls were supported on polythene, and a further polythene strip was placed in the reference beam.

(ii) A Unicam SP 800 and a Cary model 14 spectrophotometer were used to record the electronic spectra of the complexes in solution. The Unicam SP 800 with the diffuse reflectance attachment SP 890 was used to record the spectra of complexes in the solid state.

Conductance Measurements. Two platinized platinum electrodes in the form of a "dip type" conductivity cell were used. The cell constant was checked using a potassium chloride solution of known specific conductance. The resistance of the solutions were measured using a Philips PR 9500 resistance bridge. Nitrobenzene (A.R.) was distilled and nitromethane (A.R.) was dried over anhydrous calcium sulfate and fractionally distilled. The concentrations of the solutions in nitromethane and nitrobenzene were ap-

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(24) F.A. Cotton and T.G. Dunne, *J. Amer. Chem. Soc.*, *84*, 2013 (1962).
(25) B. Chiswell, J.F. Geldard, A.T. Phillip, and F. Lions, *Inorg. Chem.*, *3*, 1272 (1964).
(26) H.A. Goodwin and F.E. Smith, *Aust. J. Chem.*, *23*, 1545 (1970).
(27) R.S. Nyholm, *J. Chem. Soc.*, 2071 (1950).

proximately 10^{-3} *M*. Molar conductivities Λ_M) were expressed in ohm^{-1} cm^2 $mole^{-1}$ and quoted for temperatures between 20°C and 28°C.

Magnetic susceptibility measurements. Most of the results were obtained by the Gouy method. The magnetic field was produced by a permanent magnet with a field strength of approximately 4 kG and the force developed on the sample measured using a Mettler balance with micrometer graduations of 0.05 mg. Measurements were made at room temperature using pyrex glass tubes packed with solid materials. The apparatus was calibrated using mercury(II) tetrathiocyanatocobaltate(II), $HgCo(NCS)_4$, and was checked with Mohr's salt, $(NH_4)_2SO_4Fe(SO_4)6H_2O$.

For the results obtained by the Faraday method, the magnetic field was produced by a 1.78 cm pole diameter, Newport Instruments' watercooled electromagnet with standard Faraday pole pieces. The vertical force developed by a sample on application of the magnetic field was measured by a Cahn RG electrobalance. Mercury(II) tetrathiocyanatocobaltate(II) was used for the determination of the magnetic field gradient. For the variable temperature result, the temperature was controlled by a Varian V—4557 variable temperature accessory. None of the measurements reported has been corrected for the temperature independent paramagnetism. Diamagnetic corrections were calculated from the Pascal constants.[28] Molar susceptibilities have been expressed in cm^3mole^{-1} using the unrationalized c.g.s. e.m.r. system.

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(28) B.N. Figgus and J. Lewis, «Modern Coordination Chemistry», Interscience, N.Y., 1960, p. 403.