

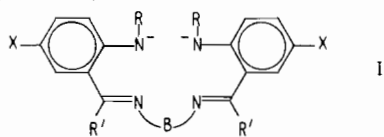
The Structure and Redox Properties of Some Planar $[M^{II}N_4]$ Chelate Compounds of Cobalt and Nickel. Part II.¹ The Effect on Molecular Properties of Substituents on the Quadridentate Ligands

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The preparations are reported of a series of cobalt(II) and nickel(II) compounds with quadridentate dianionic ligands related to 1,2-bis-(*o*-iminobenzylideneamino) ethane. This new series of planar $[M^{II}N_4]$ compounds includes species with electron-withdrawing and electron-donating substituents, and various bridging central chelate rings in place of the dimethylene bridge of the parent compound {5-Cl on the *o*-iminobenzaldehyde moiety; Me or Ph on the azomethine carbon; and $-CH_2-CHMe-$, $-CH_2-CMe_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$, and 3-NO₂ and 4-NO₂-*o*-phenylene for the chelate "bridge"}. Half-wave oxidation potentials have been measured for most of the compounds and these show that electron-withdrawing substituents raise $E_{1/2}$ while electron-donating ones lower it – apparently independently of the position of the substituent on the ligand. All solid compounds were characterised by their X-ray powder diffraction patterns (and i.r. spectra), a few were dimorphic, and several also gave crystalline solvates when recrystallised from DMF. About 60% of the solids can be classified into two structural groups from the X-ray diffraction patterns. The cobalt(II) compounds have a low intensity band at $\sim 10 \times 10^3 \text{ cm}^{-1}$ which in one case moves by $1.5 \times 10^3 \text{ cm}^{-1}$ between the solid state and solution. This change is associated with conformational changes in the molecule. In addition to the monomeric species, a cationic nickel(II) dimer of a mono-de-protonated ligand has been characterised.

Introduction

Previous work^{1–3} has shown that the metal(II) (Co, Ni and Cu) compounds of the ligands I differ quite significantly from those of the related salicylaldiminates.



The $[MN_4]$ species show a marked preference for planar structures, and are readily oxidised (low half-wave potentials). The cobalt(III) products have been isolated and shown to be unusual paramagnetic five-coordinate species.

Here we report a further extension of the work on the metal(II) species, with particular reference to the effect on structure and redox properties of a change in the various substituents of the ligands I (both electron-withdrawing and electron-donating) and the middle chelate ring (B of I).

Experimental

The abbreviations used for the ligands are defined in Table I.

Preparation of Compounds

The ligands generally were not isolated. Those derived from the aldehydes form readily in solution and the solutions were used directly for the preparation of the metal species. Those derived from the ketones were much slower to form. The method² used for most of our preparations (iii) below is much less efficient than that described in (vi) below and should be used in any future preparations.

The metal compounds which were usually red-brown were prepared by a variety of methods, as detailed below. All cobalt(II) compounds were prepared under N₂, but filtration and washing of the solids could be carried out in the air, in which they were indefinitely stable. It was often not necessary to recrystallise the products. Only those so noted in Table I were recrystallised, and these from DMF.

(i) *o*-Aminobenzaldehyde and the diamine in MeOH were treated with the metal acetate in MeOH. Crystallisation of the product usually occurred quickly, although in a few cases a short period of heating was found useful.

TABLE I. The Compounds Prepared, Abbreviations for the Ligands, Methods of Preparation, and the Analyses.

Compound	Key to Ligand Abbreviations ^a				Methods of Preparation ^b	Analyses		Calculated							
	R	R'	X	B		Found		C	H	N	Others	C	II	N	Others
						C	H								
[Co(abn)]	H	H	H	(CH ₂) ₃	(ii), c	60.6	5.5	16.9			60.5	5.4	16.6		
[Ni(abn)]	H	H	H	CH ₂ C(Me) ₂	(i), f	61.8	5.9	16.4			61.6	5.8	16.0		
[Co(abn)]					(ii)	61.6	5.9	16.1			61.6	5.7	16.0		
[Co(caben)]	H	H	Cl	(CH ₂) ₂	c										
[Ni(amen)]	H	Me	H	(CH ₂) ₂	(v), c	61.8	5.8	16.2			61.6	5.8	16.2		
[Co(amen)]					(v), c	61.7	5.9	16.1			61.6	5.7	16.2		
[Ni(maben)]	Me	H	H	(CH ₂) ₂	c, e										
[Co(maben)]					c, e										
[Ni(apen)]	H	Ph	H	(CH ₂) ₂	(iii), (v), c, d, f	70.0	5.2	11.3			70.8	5.1	11.8		
[Co(apen)]					(iii), (vi), c, f	71.0	5.4	11.6			70.8	5.1	11.8		
[Ni(appn)]	H	Ph	H	CH ₂ CH(Me)	(iii), d	71.5	5.7	11.5			71.2	5.4	11.5		
[Co(appn)]					(iii), (vi)	71.4	5.7	11.6			71.2	5.4	11.5		
[Ni(aptn)]	H	Ph	H	(CH ₂) ₃	(iv), d	70.9	5.7	11.6			71.2	5.4	11.5		
[Co(aptn)]					(iv), d	70.4	5.7	11.4			71.2	5.4	11.5		
[Ni(capen)]	H	Ph	Cl	(CH ₂) ₂	f	61.8	4.4	10.3		Cl, 13.1	61.8	4.1	10.3		Cl, 13.0
[Co(capen)]					(iii)	62.0	4.3	10.5		Cl, 12.9	61.8	4.1	10.3		Cl, 13.0
[Ni(capen)]DMF					d	60.3	5.0	11.4		Cl, 11.5	60.3	4.7	11.4		Cl, 11.5
[Co(capen)]DMF					d	60.0	4.8	11.4		Cl, 11.7	60.3	4.7	11.3		Cl, 11.5
[Ni(cappn)]	H	Ph	Cl	CH ₂ CH(Me)	(iii)	62.2	4.6	9.6		Cl, 12.7	62.4	4.3	10.0		Cl, 12.7
[Co(cappn)]					(iii)	62.5	4.5	10.1		Cl, 12.7	62.4	4.3	10.0		Cl, 12.7
α -[Ni(captn)]	H	Ph	Cl	(CH ₂) ₃	(iv), d, f	62.6	4.5	10.0		Cl, 12.7	62.4	4.3	10.0		Cl, 12.7
β -[Ni(captn)]					(iv), d, f	61.4	4.6	10.3		Cl, 12.7	62.4	4.3	10.0		Cl, 12.7
[Co(captn)]					(iv)	62.6	4.6	9.8		Cl, 12.8	62.4	4.3	10.0		Cl, 12.7
[Ni(3'-NO ₂ -abph)]	H	H	H	3-NO ₂ -C ₆ H ₃	(i), f	57.1	3.7	17.0			57.7	3.6	16.8		
[Ni(3'-NO ₂ -abph)]DMF					d	56.7	4.6	17.8			58.4	4.7	17.8		
[Ni(4'-NO ₂ -abph)]	H	II	II	4-NO ₂ -C ₆ H ₃	(i)	57.6	3.8	17.1			57.7	3.6	16.8		
α -[Co(4'-NO ₂ -abph)]					(i), f	57.4	4.0	17.1			57.7	3.6	16.8		
β -[Co(4'-NO ₂ -abph)]					d, f	56.3	4.8	17.1			56.5	4.5	17.2		
α -[Co(4'-NO ₂ -abph)]DMF					d, f	56.8	4.6	17.4							
β -[Co(4'-NO ₂ -abph)]DMF					f	58.2	6.2	13.9			58.4	5.9	13.6		
[Ni ₂ (abbnH) ₂](OAc) ₂	H	H	H	CH ₂ C(Me) ₂	f	48.3	4.9	12.8		Cl, 8.0	47.9	4.7	12.4		Cl, 7.9
α -[Ni ₂ (abbnH) ₂](ClO ₄) ₂					f	48.4	4.8	12.6		Cl, 7.9					
β -[Ni ₂ (abbnH) ₂](ClO ₄) ₂					f										

^a Refer to diagram I. ^b Letters refer to subscript comments. Italic Roman numerals refer to the separate methods of preparation given in the Experimental. ^c Previously prepared by Green and Tasker (refs. 2 and 3). ^d Recrystallised from DMF.

^e These products were not analytically pure, but are included because useful physicochemical data were obtained. ^f See special comments in the Experimental.

(ii) In some cases, crystallisation from MeOH, as in (i) did not occur, but reasonable yields were obtained when *one-half* of the calculated amount of NaOMe was added. Addition of the full quantity, as in refs. 2 and 3, almost invariably caused contamination with other basic metal species.

(iii) A mixture of the ketone and the diamine was heated at 120°C for 24 hr², usually with a trace of ZnCl₂. A further quantity of the amine was then added and the heating continued. The product was dissolved in MeOH, it usually being necessary to filter off unreacted ketone, the solution was heated to boiling and a hot solution of the metal acetate was added. In most cases, the product crystallised out readily, but in a few cases:

(iv) it was necessary to add NaOMe (half quantity). After most of our products had been obtained we found that ligand preparation was much more efficient under reflux conditions, as in (vi).

(v) The components of the ligand and the metal acetate were heated together in MeOH. Ethylene glycol was then added, and the mixture distilled until the temperature reached 100°C. The product crystallised when the remaining solution was cooled.

(vi) The components of the ligand were mixed and heated under reflux with a trace of ZnCl₂ until significant darkening occurred (usually ~15 min). This crude ligand was dissolved in hot DMF and the metal acetate in hot DMF was added. The product crystallised out when the solution was cooled.

Specific comments apply to some of the compounds as follows:

[Co(apen)]

The red-brown product from MeOH had quite a strong OH stretching frequency in the i.r., and that from DMF had significant DMF peaks; but both gave identical X-ray powder diffraction patterns. Thus occlusion of the solvent appears to occur readily here.

[Ni(captn)]

Either of two different red crystalline forms was obtained from the reaction mixtures or on recrystallisation from DMF.

[Ni(3'-NO₂-abph)]

The first crop (~20%) contained paramagnetic impurity (not identified); but later crops of the black crystals which formed slowly (days), were pure.

[Co(4'-NO₂-abph)]

The reaction mixtures were heated under reflux (4-6 hr). The dark-brown products were always mixtures, in different proportions, of the two crystalline forms. Typical analytical figures for such a mixture are listed in Table I. Two crystalline forms of the DMF solvate also were obtained, and either solvate was

obtained at various times from either the α or the β parent.

[Ni(abbn)] and [Ni₂(abbnH)₂]X₂ (X = OAc, ClO₄)

One preparation mixture for [Ni(abbn)] did not immediately deposit crystals. This was evaporated to a red oil, which was dissolved in acetone and the solution set aside in a beaker. Crystals of brown [Ni₂(abbnH)₂](OAc)₂ separated out overnight. They were water-soluble, and the α -form of the perchlorate was obtained by adding NaClO₄ to such a solution. Recrystallisation from ethanol gave the β -perchlorate.

[Ni(apen)]

All products obtained for this compound were contaminated to a greater or lesser extent by another species, which may be an analogue of [Ni₂(abbnH)₂]X₂. The second compound had a characteristic i.r. spectrum in the NH/OH region with sharp bands at 3450, 3375, 3350, 3320 and 3220 cm⁻¹. Two forms of it appear to be represented in the X-ray powder diffraction patterns – the product from MeOH being different from that in the products recrystallised from DMF.

[Ni(capen)]

Preparations from MeOH {method (iii)} were of variable composition. In one case, a fairly pure sample of [Ni(capen)] (monitored by its i.r. spectrum) was obtained, and this could be recrystallised from DMF – usually resulting in a mixture of the unsolvated material and a DMF solvate. A second brown material found here is characterised by its i.r. spectrum in the NH/OH region {3460(s), 3380(m,sp), 3315(m) and 3220(m) cm⁻¹}. It, also, has been obtained almost pure. For example, in one preparation, the mixture deposited crystals of [Ni(capen)] after a few hours; then the filtrate, when set aside overnight, deposited brown crystals of what may be another analogue of [Ni₂(abbnH)₂]X₂, but it is not water soluble.

Physical Measurements

The methods and instruments used were the same as in ref. 1.

Results and Discussion

All solids (Table I) were characterised by their X-ray powder diffraction patterns (details of which are available from the authors) and i.r. spectra (Table II). Different crystalline forms of some of the compounds were obtained as well as some DMF solvates.

The cobalt(II) and nickel(II) compounds of the same ligand generally were isomorphous – that is, they had virtually indistinguishable X-ray powder diffraction patterns. The exceptions are noted in Table II.

TABLE II. Some of the Physicochemical Data.

Compound	Magnetic Moment (B.M.)	$\nu_{\text{NH}}(\text{cm}^{-1})^c$	Structure Correlations ^a	Electronic Spectra (10^3 cm^{-1}) ^b
[Ni(abbn)]		3360m, 3321s	~i	26.8, (21.1), 20.2 27.3[7000], (21.1)[4500], 20.5[5400] 27.5[5500], (21.1)[3800], 20.3[4200]
[Ni(amen)]		(3315)m, 3308s	i	26.4, (21.1), 20.5, (19.4) 27.0[6900], 21.1[4500], 20.8[4500] (27.1)[6800], (20.8)[4400], 20.4[4500], (18.6)[2300]
[Ni(maben)]		3378w, 3342s	i	25(br), (22.2), (20.7), 20.0, (18.6) (27.4)[7200], (22.2)[3300], 20.5[4300], (18.6)[1700]
[Ni(apen)]		3361s, 3344s	i	26.3, (20.6), 19.8, (18.7)
[Ni(appn)]		3341s	i	27.0[7000], (20.8)[4000], 20.0[4500], (18.5)[2000]
[Ni(apin)]		3315m, 3300s 3327s, 3285s 3345s	i n i	26.5, (25.9), 19.3, (18.2) 26.9, (25.8), (21.0), 19.4
[Ni(capen)]		3340s (3345)m, 3340s	n n	(28.7), 25.4, (20.1), 19.3, (17.8) 26.4[5300], (20.4)[3300], 19.8[3500], (18.1)[1700] 29.3[12000], (26.8)[5100], (20.1)[5100], 19.7[3300], (18.0)[1800]
α -[Ni(capin)] β -[Ni(capin)]		3364m, 3320s	n	26.2, (25), 18.9, (17.7) 26.4[3700], 25.7[3600], 19.4[2800], (17)[400] 29.3[13000], 26.2[4100], (20.4)[2100], 18.9[2800]
[Ni(3'-NO ₂ -abph)]		3357m, (3320)m, 3275s	i(α -Co)	24.8[9700], 22.0br[10000], (18.0)[10000], 17.3[10600], 15.3sp[11800] 24.8[10000], 22.2[11700], (18.2)[10200], 17.4[10800], 15.2sp[12700] 24.6[10700], 22.0[13000], (18.0)[10600], 17.1[11300], 15.1sp[13200]
[Ni(3'-NO ₂ -abph)]DMF		3340m, 3323m	i	(27.0)[12000], 23.8br[22000], (20.0)br[10000], 15.9[6400], (15.2)[6000] (27)[13000], 24.0br[21600], (20.7)[10300], 16.1[6600], (15.3)[6100]
[Ni(4'-NO ₂ -abph)]		3305w, 3280s	i	(27)[13000], 23.8br[23600], (20.1)[11000], 15.9[7300], (15.1)[6600] 26, 23, 18.4, 9.7, 5 26.4[10900], 22.8[11100], 18.6[3400], (11.2)[56], 5[20]
[Co(abtn)]	2.0	3315m, 3298m	~i	26.2[11100], 22.5[11900], 18.8[3600], (11.3)[50], 5[30]
[Co(abbn)]	2.1			25.7, 22.8, (21.6), 18.4, (15.8), 11.1, 6 26.1[16500], 22.7[21800], (19.8)[4600], 18.6[5700], (16.0)[600], 10.7[67], 6[20]

[Co(amen)]	2.8	3291w, 3283s	i	[Solid] [CH ₂ Cl ₂]	26, (23), 18.3, 10.5, 5 26.7[10600], 22.8[12300], 18.6[2300], (16.0)[250], 10.9[150]
[Co(maben)]			i	[γ -picoline]	26.2[18200], 22.8[21000], 18.2[6800], (16.0)[620], 10.8[70], 6[30]
[Co(apen)]	2.1	3336m, 3322s	~i	[Solid] [DMF]	25.3, (22.7), 22.1, (21.1), (19.4), 18.1, (16.1), 10.4, 6 26.2[18300], 22.6[23300], (19.6)[4500], 18.3[7200], (16.0)[340], 10.8[77], 6[40]
[Co(appn)]	2.2	3352w, 3312m	i	[Solid] [DMF]	25.8, 22.6, (21.4), (19.3), 18.2, (16.1), 10.7, 6 26.2[15500], 22.7[19400], (19.3)[4000], 18.2[6600], (15.8)[330], 10.7[70], 6[30]
[Co(apm)]	2.4	3308m, (3290)m	i	[Solid] [DMF]	26.0, 22.2, 18.2, (17.0), 10.1, 5 26.1[13000], 22.4[10100], 18.6[4000], (17.3)[3600], (11.8)[80], 5[80]
[Co(capen)]	2.0	3289w, 3264m, (3240)m	i	[Solid]	26.5, 22, (20), (18), 17.8, (15.3), 10.7, 6
[Co(capen)]DMF		3301s, 3282s, 3240m	n	[γ -picoline]	25.4[20700], 22.2[25100], 19.1[5600], 17.9[8200], (15.5)[600], 10.8[84], 6.3[20]
[Co(cappn)]	2.2	(3332)m, 3320ms, 3235w	i	[Solid] [γ -picoline]	23.5, 20.5, (19.0), 17.9, 15.3, 10.9, 6 25.5[22900], 22.1[26500], 19.1[5700], 17.9[8800], (15.2)[530], 10.8[80], 6[30]
[Co(capm)]	2.1	3332m, 3322m	n	[Solid] [γ -picoline]	25, (23), 18.0, 16.7, (14.9), (12), 5 25.5[15000], 22.0[13000], 18.4[4600], (17.1)[4000], (11.4)[60]
α -[Co(4'-NO ₂ -abph)]	2.8	3300m, 3280m	i	[Solid] [DMF]	c (23.1)[23000], 22.4br[25500], (16.8)[3500], (15.1)[3400], (13.1)[1500], (10.1)[60], <5[w]
β -[Co(4'-NO ₂ -abph)]		3307m, 3292s		[DMSO]	(24.2)[23000], 22.3[26000], 16.7[3400], 14.9[3300], (13)[1400], 10.2[50], <5[150]
α -[Co(4'-NO ₂ -abph)]DMF		3270br		[γ -picoline]	(24.0)[23500], 22.3br[28400], (17.0)[3800], (15.7)[3500], (13.0)[1400], (10.5)[200], <5[w]
β -[Co(4'-NO ₂ -abph)]DMF		3300s, 3278ms		[Solid] [H ₂ O]	27.0, 20.3, (18.0)
[Ni ₂ (abbnH) ₂](OAc) ₂		3239m, 3130s,br		[CHCl ₃]	28.3, 20.6, (18.2)
α -[Ni ₂ (abbnH) ₂](ClO ₄) ₂		3355s.sp, 3277s		Solid	d 26.7[6100], (21.1)[3900], 19.7[9000], (17.4)[3900]
β -[Ni ₂ (abbnH) ₂](ClO ₄) ₂		3238s.sp, 3161s.sp 3344s.sp, 3263s, 3232s, 3155s.sp		DMF Solid DMF	d 27.3[8600], 20.2[9600], (18.1)[4300]

^a The letter "i" (isomorphous) here indicates that the X-ray powder diffraction patterns of the nickel and cobalt compounds were essentially the same; "~i" indicates a close correlation, with the differences being explicable as arising from the same molecular structure in closely related space groups; and "n" indicates a lack of correlation between the patterns. ^b Bands appearing as shoulders are given in parentheses, and extinction coefficients are given in square brackets.

^c All the main features of the solution spectra were detectable in the diffuse reflectance spectra, but this was poorly resolved. ^d The diffuse reflectance spectrum was indistinguishable from that of the acetate. ^e The spectrum was indistinguishable from that of the α -form. 'br = broad, s = strong, m = medium, w = weak, sp = sharp.

A striking feature of the X-ray patterns is the relationship between the compounds of the different ligands, especially in the positions of the stronger lines. The majority of the patterns can be divided (Figure) into two distinct classes A and B. Within these classes basic structure, conformation and crystal packing must be essentially the same. This is already proven for three members of group A – [M(abtn)]⁴, [Co(caben)]⁵ and [M(abcn)]^{1,5}. The other known structure in the series is that of [M(abpn)] (where M = Co, Ni^{1,6} and Cu⁷). From the powder data, it lies outside the two main classes, and indeed the crystal (but not molecular) structure is different from that of the class A species. Crystal structure determinations of compounds within the Class B will be attempted.

The expected four-co-planar geometry is found in all of the X-ray analyses so far⁴⁻⁷, and all molecules have an oblique-puckered conformation. The latter appears to be imposed by crystal-packing forces⁴. As in the other reports on compounds of this type, there is nothing in the present data to suggest any co-ordination geometry other than the four-co-planar. The electronic spectra are the same in non-donor and donor solvents and the magnetic moments show low-spin configurations (Table II). We had hoped to use the ¹H nmr spectra in donor and non-donor solvents to check if small amounts of paramagnetic five- or six-co-ordinate species were formed in the former (contact shifts can

give a very sensitive detection method⁸); but the compounds generally were not sufficiently soluble.

The cobalt(II) electronic spectra have quite low intensity bands at $5 \rightarrow 6 \times 10^3 \text{ cm}^{-1}$ and at $10 \rightarrow 11 \times 10^3 \text{ cm}^{-1}$. The latter sometimes change position between solution and the solid state. This is especially true for [Co(abtn)] where a well-resolved band at $9.7 \times 10^3 \text{ cm}^{-1}$ in the diffuse reflectance spectrum shifts into the higher energy allowed transition envelope when the compound is dissolved, so that it is seen only as a shoulder at $\sim 11.2 \times 10^3 \text{ cm}^{-1}$. The molecule has an apparently unstable conformation in the solid⁴, so we associate the spectral change with a change to a more planar conformation in solution.

These changes suggest that the low intensity bands should be regarded as arising from transitions between molecular orbital levels which have considerable ligand character and not just as *d-d* bands.

The compounds of the *o*-phenylene ligands all have rather intense absorption across the visible region, but the spectra are so rich that no bands are resolved. Thus, they are of no use in defining the stereochemistry of the metal species, although we have no reason to suspect that it might be different from the general four-co-planar one here.

Redox Data

Half-wave potentials for the oxidation of the compounds are listed in Table III. The majority of those for the first stage $0 \rightarrow +1$ are reversible processes under the conditions studied and so are directly comparable. They supplement those previously reported¹ and further show the marked dependence of the oxidation process on the metal.

The effects of ligand substitution are more dependent on the electron-withdrawing or donating nature of the substituent than its position on the *o*-iminobenzaldiminato moiety. Substitution of Me or Ph at the azomethine carbon (am, ap and cap ligands) lowers $E_{1/2}$ in the order $\text{H} < \text{Ph} \leq \text{Me}$; whereas the electron-withdrawing chloro at the 5-position (cap vs. ap ligands) raises $E_{1/2}$.

There appears to be little systematic variation between dimethylene and trimethylene chelate rings (and methyl substituents on them); but *o*-phenylene bridges have a marked effect. Unfortunately the electrode processes for these are generally irreversible and so observed values are not directly comparable.

Dimeric Protonated Species

In addition to the expected monomeric species, a few of the ligands gave other nickel(II) products. In one case, the new species is fully characterised as a mono-deprotonated species of empirical type [Ni(abnH)]X (where X = OAc⁻ or ClO₄⁻).

The molecular structure of this diamagnetic cationic species is not at all clear, although it appears to be

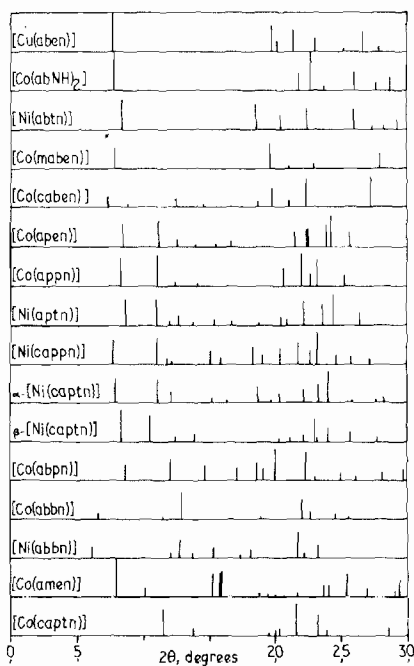


Figure. The X-ray powder diffraction patterns of the compounds, showing the classification into groups A (first five) and B (next six).

TABLE III. The Electrochemical Data^a

Compound	$E_{1/2}$ (V)	$E_{3/4}-E_{1/4}$ (mV) ^b	I_p/c ($\mu A \text{ mmol}^{-1}$)	PS ^c	Process
[Ni(abtn)]	+0.24	70	4.2	i	0 \rightarrow +1
[Ni(amen)]	+0.08	75	8.3	230	0 \rightarrow +1
	+0.6	poorly defined			+1 \rightarrow +2
[Ni(appn)]	+0.11	80	5.5	130	0 \rightarrow +1
	+0.70	130	2.9	i	+1 \rightarrow +2
[Ni(aptn)]	+0.13	70	2.5	i	0 \rightarrow +1
[Ni(capen)]	+0.21	75	10.7	105	0 \rightarrow +1
	+0.95	90	8.0	150	+1 \rightarrow +2
[Ni(cappn)]	+0.22	80	7.0	140	0 \rightarrow +1
	+1.02	90	6.9	170	+1 \rightarrow +2
[Ni(3'-NO ₂ -abph)]	+0.62	80	6.7	i	0 \rightarrow +1
[Co(abtn)]	+0.02	85	6.9	i	0 \rightarrow +1
[Co(abbn)]	+0.04	80	3.3	195	0 \rightarrow +1
[Co(amen)]	-0.13	80	4.2	i	0 \rightarrow +1
[Co(apen)]	-0.02	100	2.5	160	0 \rightarrow +1
[Co(appn)]	+0.03	70	5.0	100	0 \rightarrow +1
[Co(aptn)]	-0.01	90	6.9	135	0 \rightarrow +1
[Co(capen)]	+0.12	76	5.0	125	0 \rightarrow +1
[Co(cappn)]	+0.11	65	4.2	110	0 \rightarrow +1
	+0.84	65	2.8	105	+1 \rightarrow +2
[Co(captm)]	+0.08	80	6.7	120	0 \rightarrow +1
	+0.83	poorly defined			+1 \rightarrow +2

^a All measurements were made in CH₂Cl₂. ^b Values of ~ 70 mV usually indicate a reversible process in this solvent.

^c PS = peak separation in the cyclic voltammograms ($E_{\text{cathodic}}-E_{\text{anodic}}$). The "i" in this column means that no peak was observed on the reduction run (probably because of electrode coating).

TABLE IV. The ¹H nmr Data for [Ni(abbnH)₂]₂X₂ (τ values).

X	Solvent	Observed Signals ^a						
		CH=N	Aromatic	NH	NH ₂	CH ₂	Me(acetate)	C(Me) ₂
Acetate	D ₂ O	2.09(s,1)	2.4 \rightarrow 3.4(m,7)	c	c	6.67(s,2)	7.91(s,1)	8.67(s,6)
		b	3.64(t,1)					
Perchlorate	(CD ₃) ₂ SO	1.37(s,1.3) ^d	2.1 \rightarrow 2.65(m,5) ^e	4.32(s,1)	5.38(s,2)	6.30(s,2)		8.57(s,6)
		1.41(s,0.7)	2.85(t,1)					
			3.14(d,1)					
			3.52(t,1)					

^a Multiplicities and relative intensities are given in parentheses. Many of the aromatic proton signals also had fine structure from longer range coupling, but no attempt has been made to analyse it. ^b There are two very different azo-methine protons. The second one is mixed in with the aromatic signals above 2.4 τ . ^c Not observed, because of fast exchange with D₂O. ^d The observed separation of these signals varied between different solutions from 0.02 to 0.04.

^e Marked changes occur in this region, but not for the other three aromatic signals, when first the NH and then the NH₂ is deuterated (by adding D₂O).

dimeric. Addition of base to an aqueous solution does not give any [Ni(abbn)], so the brown product is almost certainly not a simple monomeric half-deprotonated species.

The ¹H nmr spectra (Table IV) also give evidence for a dimeric structure. The two phenylene moieties are non-equivalent, and the differences between the resonances are much greater than one could expect

from an unsymmetrical ligand in a planar monomeric species. Indeed it seems that the upfield shifts of some of these aromatic proton resonances must result from ring current effects. This could be explained if the cation had a structure similar to the one we recently reported⁹ for a nickel(II) dimer of a quadridentate dianionic hydrazone. However, there seems to be no reason why the ligands here should adopt such a structure, and it is not consistent with the observed singlets for the CH₂ and CMe₂ resonances.

The NH and NH₂ protons retain their separate identities in solution, giving separate resonances (Table IV) and exchanging with D₂O at different rates – the NII exchanging fastest.

There is also a marked variation of the spectra of the different salts in different solvents (Table IV), which suggests that the cation may exist in two distinct conformational forms (*e.g.*, the spectrum of the acetate in CDCl₃ is close to that of the perchlorate in DMSO, but different from that of the acetate in D₂O).

An X-ray structural investigation of at least one of these salts is planned.

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