Complexes of 2-Aminobenzimidazole with Cobalt(II) and Nickel(II)

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2-Aminobenzimidazole (abi) has been used to prepare (*i*) pseudotetrahedral complexes with cobalt or nickel of the types $M(abi)_2X_2$ (M = Co, X = Cl, Br, I, NCS, and MeCOO; M = Ni, X = Br), $[Et_4N][M(abi)X_3]$ (M = Co, X = Cl, Br, and I; M = Ni, X = Br), $Co(abi)_2I_2,2Me_2CO$, $Co(abi)SO_4,Me_2CO$, $Ni(abi)_2Cl_2,2H_2O$, $Ni(abi)_2I_2,3H_2O$, and $Co(abi - H)_2$; (*ii*) square-planar complexes of nickel of the type $Ni(abi)_4X_2$ (X = Cl, Br, I, NO_3, ClO_4, and $\frac{1}{2}SO_4$); and (*iii*) distorted octahedral complexes $Ni(abi)Br_2,H_2O$, $Ni(abi)_4(NCS)_2$, $Ni(abi)_3(NCS)_2$, and $Ni(abi)_2(MeCOO)_2$. The complex $Ni(abi)_4(BF_4)_2$ appears to have metal atoms in both square-planar and tetrahedral environments. These conclusions are based on electronic and i.r. spectral data and on magnetic moments of the complexes.

It has been reported[1] that substituents in the 2-, 4-, or 5-positions of imidazole and thiazole derivatives modify the stoicheiometry and stereochemistry of the complexes formed with cobalt(II) and nickel(II). In

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[1] (*a*) M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, 1962, **84**, 1543; (*b*) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 1964, 5194; (*c*) M. Goodgame and M. J. Weeks, *J. Chem. Soc.* (*A*), 1966, 1156; (*d*) M. Goodgame and L. I. B. Haines, *ibid.*, 1966, 174; (*e*) W. J. Eilbeck, F. Holmes, and A. E. Underhill, *ibid.*, 1967, 757; (*f*) E. J. Duff, M. N. Hughes, and K. J. Rutt, *ibid.*, 1968, 2354; (*g*) R. A. Ford, J. Halkyard, and A. E. Underhill, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 507.

our previous investigations[2,3] of the complexes formed by these metal ions with 2-aminobenzothiazole (abt) and 2-aminobenzoxazole (abox), we found that the provision of an alternative co-ordination site had surprisingly little effect, and only in one case, $Ni(abt)_2Cl_2$ (yellow isomer) was there evidence[2] for co-ordination through the amino-group. In general, the properties of the nickel compounds were more sensitive to the nature of the ligand than those of the cobalt compounds, and the main effect of the 2-amino-substituent was to change the basicity of the ring nitrogen. We now report our findings on the behaviour of 2-aminobenzimidazole (abi) with the same metal ions.

EXPERIMENTAL

2-Aminobenzimidazole was prepared by reaction of *o*-phenylenediamine with cyanogen bromide.[4] The product was recrystallised from ethanol as white needles, m.p. 122 °C.

Tetrakis(2-*aminobenzimidazole*)*nickel*(II) *Chloride*.—Nickel(II) chloride hexahydrate (2·38 g, 0·01 mol) dissolved in absolute ethanol was added to an ethanolic solution of 2-aminobenzimidazole (5·32 g, 0·04 mol). The solution was reduced to half its bulk by slow evaporation, and the orange solid which crystallised out was filtered off, washed with absolute ethanol and dried *in vacuo*.

The corresponding *bromide*, *iodide*, *nitrate*, and *sulphate* were prepared by a similar method using the appropriate hydrated metal salt. In the preparation of the *tetrafluoroborate* and *perchlorate* complexes, cold concentrated ethanolic solutions were mixed and allowed to evaporate at room temperature until crystals deposited.

The *di-isothiocyanatotetrakis*(2-*aminobenzimidazole*)-*nickel*(II) complex was prepared by addition of the ligand (0·04 mol) to a well-stirred suspension of metal salt (0·01 mol) in absolute alcohol. The cloudy solution became clear on heating, and the greenish precipitate obtained on standing was filtered off and washed thoroughly with absolute alcohol, to leave a pale blue complex, which was dried *in vacuo*.

Di-isothiocyanatotris(2-*aminobenzimidazole*)*nickel*(II).— A well-stirred suspension of nickel(II) thiocyanate dihydrate (2·11 g, 0·01 mol) in absolute ethanol was treated with an ethanolic solution of 2-aminobenzimidazole (4·0 g, 0·03 mol). The green solid obtained on evaporating the solution to dryness was triturated with acetone to yield the complex, which was filtered off and dried *in vacuo*.

Dichlorobis(2-*aminobenzimidazole*)*nickel*(II) *Dihydrate*.—A solution of 2-aminobenzimidazole (2·66 g, 0·02 mol) and nickel(II) chloride hexahydrate (2·38 g, 0·01 mol) in absolute ethanol (10 ml) was evaporated to dryness. The resulting green solid was dissolved in acetone (5 ml) and the solution heated to boiling. Hot carbon tetrachloride (8 ml) was added, and the solvent decanted to leave a green oil which was triturated with several portions of carbon tetrachloride until it solidified. The green complex was dried *in vacuo*.

The *bromide* and *iodide* analogues were prepared in a similar manner, but in the case of the *acetate* the solution required heating under reflux for 2 h.

Dibromo(2-*aminobenzimidazole*)*nickel*(II) *Hydrate*.—This was the only complex with metal : ligand ratio of 1 : 1 which could be positively characterised. It was obtained by evaporating to dryness an ethanolic solution of metal salt and the ligand, and triturating the resulting solid with carbon tetrachloride. The deliquescent compound was dried *in vacuo*.

Bis(2-*aminobenzimidazole*)*cobalt*(II) *Complexes*.—These were generally prepared by treating the metal salt with the ligand in acetone and precipitating the complexes out by addition of diethyl ether or carbon tetrachloride.

In the case of the *sulphate*, the ligand dissolved in acetone was added to aqueous cobalt sulphate. The royal blue complex which precipitated was filtered off, washed with ethanol, then with acetone, and dried *in vacuo*.

The *dicyano*- and *diacetato*-complexes were obtained from aqueous solution. From strongly alkaline solution the bis(2-aminobenzimidazolato)cobalt(II) complex was isolated.

The colours and analytical data of the complexes investigated are given in Table 1. Physical measurements were carried out as described previously.[2]

RESULTS AND DISCUSSION

Cobalt(II) *Complexes*.—Only complexes having metal : ligand ratio 1 : 2 could be isolated (Table 1). The diffuse reflectance electronic spectra of all these complexes are typical of pseudotetrahedral species (Table 2). The expected splitting of the ν_3 band is obtained in most cases, but the ν_2 band is less well-defined and in the majority of these compounds it is broad and asymmetric rather than split. Consideration of the band maxima indicates a weakening of the ligand field strength in the order NCS $>$ CH_3COO $>$ Cl $>$ Br $>$ I, as expected from the spectrochemical series.

The far-i.r. spectra of all these compounds show strong X-sensitive bands (Table 4) in regions diagnostic[2,3,5,6] of $\nu(MX)$ modes of tetrahedrally co-ordinated metal atoms, supporting the structures deduced from electronic spectra. Assignments of $\delta(MX)$ modes are less certain, but are in agreement with previous suggestions.[2,3,6]

The mid-i.r. vibrational frequencies due to the polyatomic anions also support co-ordination of these to the central ions. Thus $\nu(NCS)$ in $Co(abi)_2(NCS)_2$ occurs at 2090vs and 2080vs cm^{-1}; similarly for $Co(abi)_2SO_4,Me_2CO$ the bands at 1120m, 1030s, 920m, 645m and 630 mbr cm^{-1} are compatible with C_{2v} symmetry of the sulphate group.

The room temperature magnetic moments fall in the range 4·40—4·60 B.M. (Table 2) as expected for this stereochemistry. $Co(abi - H)_2$ Has an exceptionally low moment (3·98 B.M.) which is still compatible with pseudotetrahedral symmetry in view of the value[1a] for the benzimidazolato analogue (4·27 B.M.).

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[2] M. J. M. Campbell, D. W. Card, M. Goldstein, and R. Grzeskowiak, *J. Chem. Soc.* (*A*), 1970, 672.

[3] M. J. M. Campbell, D. W. Card, M. Goldstein, and R. Grzeskowiak, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3843.

[4] B. Biddle, E. S. Lane, and J. L. Williams, *J. Chem. Soc.*, 1960, 2369.

[5] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.

[6] M. Brierley, W. J. Geary, and M. Goldstein, *J. Chem. Soc.* (*A*), 1969, 2923.

Nickel(II) *Complexes*.—Nickel(II) salts afforded a wider range of complexes with the abi ligand, and examples of compounds having metal : ligand ratios 1 : 1 to 1 : 4 have been characterised.

TABLE 1

Colours and analyses [a]

Complex	Colour	Metal (%)	Carbon (%)	Nitrogen (%)	Anion (%)
$Co(abi)_2Cl_2$	Dark blue	14·8 (14·5)	42·5 (42·4)	21·3 (21·2)	17·8 (17·9)
$Co(abi)_2Br_2$	Dark blue	12·1 (12·1)	34·6 (34·7)	17·4 (17·3)	32·8 (33·0)
$Co(abi)_2I_2$	Dark blue	10·1 (10·2)	29·0 (29·0)	14·5 (14·5)	43·6 (43·9)
$Co(abi)_2I_2,2Me_2CO$	Dark blue	8·6 (8·5)	34·3 (34·5)	12·0 (12·1)	36·3 (36·5)
$Co(abi)_2SO_4,Me_2CO$	Blue-black	12·4 (12·1)	42·4 (42·6)	17·3 (17·5)	20·1 (20·1)
$Co(abi)_2(NCS)_2$	Deep blue	13·2 (12·4)	43·4 (43·5)	25·3 (25·4)	26·0 (26·3)
$Co(abi)_2(CH_3CO_2)_2$	Mauve	13·4 (13·3)	48·6 (48·8)	19·1 (19·0)	
$Co(abi - H)_2$	Blue	18·1 (18·2)	52·1 (52·0)	26·2 (26·0)	
$[Et_4N][Co(abi)Cl_3]$	Blue	13·6 (13·7)	42·4 (42·0)	12·9 (13·1)	24·7 (24·8)
$[Et_4N][Co(abi)Br_3]$	Light blue	10·2 (10·5)	32·1 (32·1)	9·9 (10·0)	42·5 (42·7)
$[Et_4N][Co(abi)I_3]$	Green	9·1 (8·4)	25·4 (25·6)	7·8 (8·0)	54·0 (54·2)
$Ni(abi)_4Cl_2$	Orange	8·7 (8·9)	50·6 (50·8)	25·3 (25·4)	10·5 (10·7)
$Ni(abi)_4Br_2$	Orange	7·6 (7·8)	44·7 (44·8)	22·4 (22·4)	21·2 (21·3)
$Ni(abi)_4I_2$	Orange	6·8 (6·9)	39·9 (39·8)	20·0 (19·9)	30·0 (30·1)
$Ni(abi)_4(NO_3)_2$	Orange	8·0 (8·2)	47·0 (47·0)	27·2 (27·4)	
$Ni(abi)_4SO_4$	Orange	8·5 (8·5)	48·7 (48·9)	24·3 (24·4)	13·8 (14·0)
$Ni(abi)_4(BF_4)_2$	Buff	7·2 (7·7)	43·6 (44·0)	21·7 (22·0)	
$Ni(abi)_4(ClO_4)_2$	Orange-brown	7·2 (7·4)	42·8 (42·6)	21·5 (21·3)	25·0 (25·2)
$Ni(abi)_2Cl_2,2H_2O$	Green	13·7 (13·6)	39·1 (38·9)	20·0 (19·5)	16·5 (16·4)
$Ni(abi)_2Br_2$	Dark green	12·3 (12·1)	34·8 (34·7)	17·3 (17·3)	30·8 (33·0)
$Ni(abi)_2I_2,3H_2O$	Light brown	9·0 (9·3)	26·5 (26·5)	13·3 (13·3)	40·0 (40·1)
$[Et_4N][Ni(abi)Br_3]$	Turquoise	10·7 (10·5)	32·3 (32·1)	10·0 (10·0)	42·5 (42·7)
$Ni(abi)Br_2,H_2O$	Light brown	15·8 (15·9)	22·9 (22·8)	11·5 (11·4)	42·6 (43·0)
$Ni(abi)_2(CH_3CO_2)_2$	Apple green	13·5 (13·3)	48·6 (48·8)	18·6 (18·9)	
$Ni(abi)_3(NCS)_2$	Light green	10·2 (10·2)	48·1 (48·1)	26·9 (26·8)	20·2 (20·2)
$Ni(abi)_4(NCS)_2$	Pale blue	8·2 (8·3)	50·9 (50·9)	27·8 (27·7)	16·5 (16·4)

[a] Calculated values in parentheses.

TABLE 2

Diffuse reflectance electronic spectra and room-temperature magnetic moments of the cobalt complexes

		$\nu_{max.}$ ($cm^{-1} \times 10^{-3}$)		
Complex	μ_{eff} (B.M.)		$\nu_3[^4T_1(P) \longleftarrow {}^4A_2(F)]$	$\nu_2[^4T_1(F) \longleftarrow {}^4A_2(F)]$
$Co(abi)_2Cl_2$	4·52	29·5, 21·5vw	17·5sh, 16·1, 15·1	8·3, 7·1, 6·3
$Co(abi)_2Br_2$	4·41	27·8	17·1, 15·9, 14·5	7·7, 6·8, 6·3
$Co(abi)_2I_2$	4·38	27·8	16·4, 15·2, 13·7	7·4sh, 6·6, 6·1sh
$Co(abi)_2I_2,2Me_2CO$	4·40	27·8	16·4, 15·2, 14·1	8·3, 6·7, 5·7
$Co(abi)_2SO_4,Me_2CO$	4·38	28·3	18·2, 16·4	8·7sh, 7·4
$Co(abi)_2(NCS)_2$	4·75	29·4vbr	17·9sh, 17·0	9·1, 8·0, 5·9sh
$Co(abi)_2(MeCO_2)_2$	4·61	29·4, 28·6sh	18·9sh, 17·2, 16·4sh	9·1sh, 8·0
$Co(abi - H)_2$	3·97	29·4	17·9, 17·0, 16·4	9·1sh, 8·0
$[Et_4N][Co(abi)Cl_3]$	4·35	29·4	16·7, 15·6, 14·7	6·9as
$[Et_4N][Co(abi)Br_3]$	4·54	29·4	16·1, 14·9, 14·3	6·6as
$[Et_4N][Co(abi)I_3]$	4·57	25·0vbr, 18·2sh	15·4, 14·3, 13·2	6·5as

The diffuse reflectance spectra of the tetrakis-complexes $Ni(abi)_4X_2$ (X = Cl, Br, I, NO_3, ClO_4, $\frac{1}{2}SO_4$) are readily interpreted in terms of a square-planar nickel(II) chromophore with nitrogen donor atoms. There are one or two weak bands below 10,000 cm^{-1} (Table 3) which can be assigned to spin-forbidden transitions (singlet–triplet), whilst at higher energies more intense bands are assigned as the $^1B_{1g} \longleftarrow {}^1A_{1g}$ and $^1A_{2g} \longleftarrow {}^1A_{1g}$ transitions in D_{4h} symmetry. With the exception of the perchlorate, where the observed magnetic moment is 1·84 B.M., these complexes show only weak paramagnetism, with room temperature moments *ca.* 1 B.M. probably due to t.i.p. Their far-i.r. spectra are closely similar, with no observable ν(MX) modes. In the complexes containing oxyanions, it is clear from the number and frequencies of the bands in the mid-i.r. spectra that these groups are not co-ordinated. The complexes can therefore be formulated as $[Ni(abi)_4]X_2$ (X = Cl, Br, I, NO_3, ClO_4 or $\frac{1}{2}SO_4$), with a planar geometry for the cation.

The complex $Ni(abi)_4(BF_4)_2$ is unusual. The diffuse reflectance electronic spectrum suggests the presence of both tetrahedral and square-planar species, and the value of the room-temperature magnetic moment (2·45 B.M.) can be rationalised with this view. In the far-i.r., in addition to $\nu_2(BF_4^-)$ at 357 cm^{-1} and bands corresponding to those in the planar complexes $[Ni(abi)_4]X_2$ (X = Cl, Br, I, NO_3, ClO_4 or $\frac{1}{2}SO_4$), a strong band is observed at 224 cm^{-1} which is consistent with ν(Ni–abi) of a tetrahedral species (*cf.* 238—210 cm^{-1} in $Ni(abi)_2X_2,nH_2O$, Table 4). Further structural deductions cannot be made at present.

The complexes $Ni(abi)_4(NCS)_2$, $Ni(abi)_3(NCS)_2$, $Ni(abi)_2I_2,3H_2O$, $Ni(abi)_2(CH_3COO)_2$, and $Ni(abi)Br_2,H_2O$ have diffuse reflectance electronic spectra and magnetic moments (Table 3) characteristic of essentially octahedral nickel(II) compounds. In $Ni(abi)_4(NCS)_2$, the symmetry of the electronic absorption bands suggests

TABLE 3

Diffuse reflectance electronic spectra and room temperature magnetic moments of the nickel complexes

Complex	μ_{eff} (B.M.)	$\nu_{max.}$ ($cm^{-1} \times 10^{-3}$)
$Ni(abi)_4(BF_4)_2$	2·45	27·6, 21·3, 15·2, 11·6, 9·5, 6·8
Square-planar:		
$Ni(abi)_4Cl_2$	1·04	29·4, 21·3, 16·4sh, 6·0
$Ni(abi)_4Br_2$	1·04	29·4, 21·3, *ca.* 9·0
$Ni(abi)_4I_2$	1·06	29·4, 21·3, 15·4vwsh, *ca.* 9·0w
$Ni(abi)_4(NO_3)_2$	0·91	29·4, 21·7, 14·6wsh, 10·0
$Ni(abi)_4SO_4$	0·91	29·4, 21·3, 18·5sh, *ca.* 9·0w
$Ni(abi)_4(ClO_4)_2$	1·84	28·6, 22·0, 15·4sh, 8·7
Tetrahedral:		
$Ni(abi)_2Cl_2,2H_2O$	3·52	*ca.* 29·4, 23·3sh, 15·9as, 9·9, 7·9br
$Ni(abi)_2Br_2$	3·40	24·3, 17·1, 15·4as, 9·9, 7·9, 7·3
$Ni(abi)_2I_2,3H_2O$	2·84	27·8, 22·2, 14·9, 12·2sh, 8·6, 7·1
$[Et_4N][Ni(abi)Br_3]$	3·53	*ca.* 29·4, 16·1, 14·3, 10·0, 8·5, 5·7br
Octahedral		
$Ni(abi)Br_2,H_2O$	3·17	29·5, 24·3sh, 19·8, 13·5, 14·5, 9·1, 6·6
$Ni(abi)_4(NCS)_2$	3·32	26·5, 22·2sh, 16·3, 13·3w, 9·9, 6·6
$Ni(abi)_3(NCS)_2$	3·10	25·1, 15·4, 13·3sh, 9·5, 6·8
$Ni(abi)_2(MeCO_2)_2$	3·27	25·4sh, 23·5, 14·7, 8·2, 6·5

that the chromophore is NiN_6, while in $Ni(abi)Br_2,H_2O$ the bands are asymmetric, indicating considerable distortion. For the latter compound strong bands are found in the far-i.r. region at 175 and 139 cm^{-1}, close to values observed for in-plane vibrations of octahedrally co-ordinated $[NiBr_2]_n$ halogen-bridged chains as in $NiBr_2(pyridine)_2$ and $NiBr_2(pyrazine)$.[7]

In the case of $Ni(abi)_3(NCS)_2$ and $Ni(abi)_4(NCS)_2$, comparison of the far-i.r. spectra with those of $CoL_2(NCS)_2$ [L = abt,[2] abox,[3] and abi (Table 4)] places ν(Ni–NCS) at *ca.* 230 cm^{-1}. The electronic spectra show a slight decrease in the ligand field strength from the tetrakis- to the tris-complex, suggesting the chromophore NiN_5S for the latter.

Complexes $Ni(abi)_2Cl_2,2H_2O$, $Ni(abi)_2Br_2$, $Ni(abi)_2I_2,3H_2O$ and $[Et_4N][Ni(abi)Br_3]$ have both electronic spectra and magnetic moments indicative of tetrahedral stereochemistry (Table 3). The far-i.r. spectrum of $[Et_4N][Ni(abi)Br_3]$ is analogous to that of the corresponding cobalt complex, and contains a strong ν(NiBr) band in the region diagnostic [2,3,5,6] of tetrahedrally co-ordinated nickel(II). However, for the other three complexes the spectra show at the most only weak bands in regions where strong ν(MX) modes of tetrahedral structures are usually found. This suggests that in these cases the halogen atoms are not involved in the primary co-ordination sphere. The close similarity of the spectrum of $Ni(abi)_2Cl_2,2H_2O$ to that of $Ni(abi)_2Br_2$ suggests that the water molecules are also not co-ordinated, but this may not be true for $Ni(abi)_2I_2,3H_2O$.

TABLE 4

Far-i.r. spectra (450—80 cm^{-1})

Compound	Internal modes of abi	ν(MX)	ν(M–abi)	Others
abi	342sh, 329s, 262s, 176vw			108s [a]
$Co(abi)_2Cl_2$	340sh, 332s, 275m, 168sh	310s, 300s,[b]	238m, 215w	425w, 358vw, 148ms,[c] 140sh
$Co(abi)_2Br_2$	370m,br, 335s, $\left\{\begin{matrix}290\text{m}\\276\text{sh}\end{matrix}\right\}$ 172mw	232s	249w	128ms,[c] 109mw, 94w
$Co(abi)_2I_2$	363m,br $\left\{\begin{matrix}335\text{s}\\316\text{sh}\end{matrix}\right\}$ $\left\{\begin{matrix}290\text{sh}\\278\text{s}\end{matrix}\right\}$ 163mw	216s, 206s	248mw	118m,[c] 92w
$Co(abi)_2(NCS)_2$	352w, 336s, $\left\{\begin{matrix}280\text{m}\\272\text{m}\end{matrix}\right\}$ 156w	307ms	250msh	182s,[c] 143w, 118w, 112sh, 92w
$[Et_4N][Co(abi)Cl_3]$	348s, 267s	325m, 317m, 305s	232m	432m, 384w, 162s,[c] 135w, 96w
$[Et_4N][Co(abi)Br_3]$	342s, 276ms, 179m	253ms, 226ms	240ms	423w, 376w, 160w, 132m,[c] 98mw
$[Et_4N][Co(abi)I_3]$	343sh, 336s, 276m	205s	237w	140mw, 132w, 110vw
$[Et_4N][Ni(abi)Br_3]$	342s, 277m, 177mw	253sh, 230s	245sh	
$Ni(abi)Br_2,H_2O$	312m, 262mw	175s, 139s	212m	*d*, 293w, 252sh, 238m [e]
$Ni(abi)_2Cl_2,2H_2O$	$\left\{\begin{matrix}318\text{m}\\310\text{sh}\end{matrix}\right\}$ 262w, 180sh		230m	*d*, 165sh, 138sbr, 112br,sh
$Ni(abi)_2Br_2$	$\left\{\begin{matrix}335\text{ms}\\315\text{sh}\end{matrix}\right\}$ 260w, 180br,sh		238mw	*d*, 287sh, 130s,br
$Ni(abi)_2I_2,3H_2O$	310ms, 173m		217m, 210sh	*d*, 118s, 111sh
$Ni(abi)_3(NCS)_2$	363w, 330s,br $\left\{\begin{matrix}284\text{mw}\\264\text{m}\end{matrix}\right\}$	231s	208m	
$Ni(abi)_4(NCS)_2$	$\left\{\begin{matrix}332\text{s}\\316\text{sh}\end{matrix}\right\}$ 283m, 182vw	228ms	212sh	*d*, 260vw, 140w,vbr
$Ni(abi)_4Cl_2$	350m,br, 289m		313m	*d*, 189s,br
$Ni(abi)_4Br_2$	350ms,br, 288m		308m	*d*, 182s, 158w, 149sh, 124m
$Ni(abi)_4I_2$	340s,br, 287m		307sh	*d*, 182m, 120w
$Ni(abi)_4(NO_3)_2$	350s,br, 290w		310sh	*d*, 260w, 188ms,vbr
$Ni(abi)_4(ClO_4)_2$	346s,br, 286ms, 174mw		313m	*d*, 258sh, 155m, 128br,sh, 100m,br
$Ni(abi)_4SO_4$	$\left\{\begin{matrix}350\text{s}\\333\text{sh}\end{matrix}\right\}$ 282mw		315sh	*d*, 190s,br

[a] External mode. [b] Resolved by cooling sample to *ca.* 100 K; 303s,br at ambient temperature. [c] δ(MX) mode. [d] Broad diffuse absorption above *ca.* 360 cm^{-1}, unresolved on cooling sample to 100 K. [e] Possibly δ(Ni–OH_2) mode.

Site of Co-ordination.—The 329 cm^{-1} band of the ligand abi, assigned to δ(C–NH_2), appears in the spectra of all the complexes (although of variable position and

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[7] M. Goldstein and W. D. Unsworth, *Inorg. Chim. Acta*, 1970, **4**, 342.

intensity) suggesting (*cf.* refs. 2 and 3) that the exocyclic amino-group remains unco-ordinated in all cases. The assignment of ν(M–abi) modes, made in the same manner as described for the abt and abox complexes,[2,3] must be regarded as tentative, since internal modes of the abi ligand occur in the same regions (Table 4). However, there seems to be a general increase in frequency of ν(M–abi) as the co-ordination geometry changes from octahedral to tetrahedral to planar, as is expected by analogy with similar variations of metal–halogen stretching modes.[2,3,5,6]

Conclusions.—Cobalt(II) gives complexes with 2-aminobenzimidazole of similar type to those obtained with 2-aminobenzothiazole,[2] 2-aminobenzoxazole,[3] and benzimidazole itself.[1a] The co-ordinating centre is the ring nitrogen in position 3; there is little effect from the presence of the NH_2 group in position 2, nor from substitution of S or O for NH in position 1 in abt or abox respectively.

Nickel(II) gives a greater variety of complexes and stereochemical structures. Most of the $Ni(abi)_4X_2$ complexes are square-planar, but X may influence the final stereochemistry. Thus a strongly co-ordinating group such as NCS^- leads to an octahedral structure, while BF_4^-, without affecting the co-ordination number, causes some of the complex cations to adopt pseudotetrahedral geometry.

The main difference between the ligands, abt, abox, and abi is found in the pseudotetrahedral complexes of the type $Ni(ligand)_2X_2$. In the case of abi there is no evidence for ν(MX) bond stretching frequencies, and therefore the organic ligand must be bidentate. Since the exocyclic amino-group is apparently not involved in co-ordination, the additional bonding of the ligand probably takes place through the –NH– nitrogen of the ring. The situation is therefore parallel to that in the benzothiazole bridging system,[1f] although no evidence was found for such bridging in the 2-aminobenzothiazole complexes.[2]

The structure of the octahedral $Ni(abi)Br_2,H_2O$ [ν(NiBr) = 175 and 139 cm^{-1}] is probably analogous to those suggested for $NiLBr_2$ (L = quinoline,[1b] pyridine [ν(Ni-Br) = 179—132 cm^{-1}],[8] or 2-aminobenzoxazole [ν(NiBr) = 189 cm^{-1}][3]).

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[8] M. Goldstein and W. D. Unsworth, to be published.