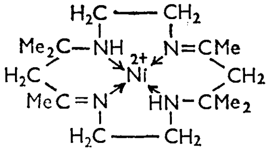
169. *Borohydride Derivatives of Some Complex Nickel*(II) *Amine Cations.*

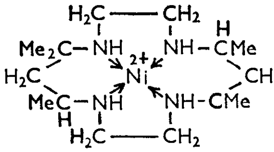
By N. F. Curtis.

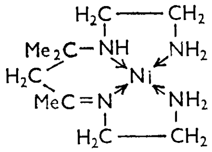
The preparation and properties of compounds of the type NiA BH_4 ClO_4 and $NiA(BH_4)_2$, where A is a cyclic tetramine or a non-cyclic tetradentate Schiff base amine, are described. The compounds are blue-violet and paramagnetic ($\mu_{eff} \sim 3$ B.M.), whereas the simple perchlorates are orange and diamagnetic, indicating considerable interaction between the nickel(II) and borohydride ions. The infrared spectra of the borohydride ion in the compounds resemble those of hydrogen-bridged compounds of the " diborane " type, with bridging and terminal B–H bonds. The BH_4^- ion in the NiA BH_4 ClO_4 compounds is considered to be acting as a chelate, filling two co-ordination positions about the nickel(II). One $NiA(BH_4)_2$ compound is considered to have two *trans* BH_4^- groups, while the other is formulated as [NiA BH_4] BH_4, with interacting and non-interacting BH_4^- ions. Some of the compounds dissolve without dissociation in polar organic solvents.

This Paper describes the preparation and properties of borohydride salts of some nickel(II) amine complex cations, for which there is evidence of three-centre bonding between the nickel ion and the borohydride ion.

The cyclic Schiff base–amine complex of nickel(II), (I), formed by condensation of nickel ethylenediamine complexes with acetone,[1] can be reduced readily to form two isomeric cyclic tetramine complexes (IIa) and (IIb).[2] Reduction can be effected by sodium borohydride in aqueous solution, by nickel–aluminium alloy in alkaline solution by catalytic hydrogenation, etc.[2]


(I)


(IIa) and (IIb)


(III)

The nickel–amine borohydride compounds were first observed when sodium borohydride in aqueous solution was used to reduce the diperchlorate of the nickel complex (I), the isomer (IIb) crystallizing as the sparingly soluble, blue-violet borohydride perchlorate of (IIb). The same compound was precipitated when sodium borohydride was added to an aqueous solution of the diperchlorate of the isomer (IIb), prepared from the complex (I) with any reducing agent. Addition of sodium borohydride to an aqueous solution of the ion (IIb) in the absence of perchlorate caused precipitation of the mauve diborohydride of the isomer (IIb).

The mauve diborohydride of the isomer (IIa) crystallized when sodium borohydride was added to a solution of the diperchlorate of the isomer (IIa) in methanol, dimethylformamide, etc., or to a solution of the chloride, nitrate, or other soluble salt of the isomer (IIa) in water. The borohydride salt is more soluble in water than the perchlorate, and hence does not crystallize when the diperchlorate of the complex (I) is reduced with sodium borohydride in aqueous solution.

When sodium borohydride was added to a cold aqueous solution of the perchlorate of the Schiff base–amine nickel complex (III) (also formed by condensation of nickel ethylenediamine complexes with acetone [1]), in an attempt to reduce the $C{:}N$ group, a mauve precipitate of the borohydride perchlorate of the complex (III) formed. If this suspension was warmed, or kept at room temperature for several hours, the complex was completely decomposed and a dark precipitate of nickel boride was formed.

Compounds analogous to those described are formed by related nickel complexes formed by the reaction of nickel di- and poly-amine complexes with carbonyl compounds.[3]

Properties.—The nickel amine borohydride salts are unaffected by heating to 120°, and kept indefinitely in a desiccator or stoppered container. They are not hygroscopic, and they decompose extremely slowly (months) on exposure to the atmosphere. The compounds are decomposed by dilute acids, hydrogen being evolved, supporting their formulation as borohydride salts (Experimental section), the ions (IIa) and (IIb) remaining in the solution. The ion (III) (which is decomposed by solutions of strong acids) remains when a solution of the borohydride perchlorate is heated with an oxidizing agent (*e.g.*, sodium chlorate). The presence of the perchlorate ion in the compounds formulated as borohydride perchlorate salts is confirmed by infrared spectra, which show strong bands at 1080 and 618 cm.$^{-1}$. The borohydride perchlorate salts explode violently when heated, as would be expected with substances containing both the borohydride and perchlorate ions. The diborohydride salts ignite when heated and burn gently, as is characteristic of borohydride salts. The analytical results for the diborohydride of the isomer (IIb) agree best with a hemihydrate formula. The infrared spectrum shows

[1] Curtis, *J.*, 1960, 4409; Curtis and House, *Chem. and Ind.*, 1961, 1708.

[2] Curtis, *J.*, 1964, 2644.

[3] Blight and Curtis, *J.*, 1962, 1204; House and Curtis, *J. Amer. Chem. Soc.*, 1962, **84**, 3248; 1964, **86**, 223, 1331.

weak bands at 3600, 3470, and 1630 cm.$^{-1}$ after prolonged drying, supporting this formulation.

Properties in Solution.—The compounds are sparingly soluble in water, forming orange-coloured solutions, which show the absorption spectra of the complex nickel cations. The diborohydride of the isomer (IIa) is insoluble in organic solvents. The other compounds dissolve in many polar organic solvents, forming blue-violet solutions. Most of these solutions are unstable, the colour changing to orange as the borohydride ion decomposes. Solutions of the compounds of the isomer (IIb) in dimethylformamide and dimethyl sulphoxide are stable. The absorption spectrum of the solution of the borohydride perchlorate of the isomer (IIb) in dimethylformamide shows three bands, characteristic of the spectra of triplet nickel(II) complexes at 10,800 cm.$^{-1}$ (ε 13·3), 18,200 cm.$^{-1}$ (ε 27·5), and 27,800 cm.$^{-1}$ (ε 47·7) together with weak absorption at 22,100 cm.$^{-1}$, characteristic of the ion (IIb) in square planar, singlet compounds [*e.g.*, a solution of the diperchlorate of the isomer in methanol]. Addition of sodium borohydride to this solution causes an increase in the bands of the triplet spectrum and a corresponding decrease in the absorption of the singlet band, suggesting partial and reversible dissociation of the borohydride adduct. In the presence of excess of borohydride, the molar extinction coefficients are $\varepsilon_{10,800\text{cm.}^{-1}} = 14{\cdot}5$, $\varepsilon_{18,200\text{cm.}^{-1}} = 32$, and $\varepsilon_{27,800\text{cm.}^{-1}} = 55$. The infrared spectra of the solutions in dimethylformamide, dimethyl sulphoxide and dichloromethane in the B–H stretching region show further evidence of this association (see below).

Reflectance Spectra.—Details of the reflectance spectra of the solid borohydride compounds, and some related compounds are shown in Table 1. (These were measured using a Unicam S.P. 700 spectrophotometer, with $MgCO_3$ as reference.) The spectrum of (IIa)$(BH_4)_2$ resembles that of other compounds (IIa)X_2, where $X = Cl^-$, CH_3COO^-, NO_3^-, etc.,[3a] the lowest energied band ($^3A_{2g} \longrightarrow {}^3T_{1g}$ for O_h symmetry) being split, as is characteristic of Ni(II) compounds with a tetragonally distorted " octahedral " ligand field, *e.g.*, the *trans* compound Ni py_4Cl_2 (py = pyridine).[3b] The spectra of (IIb)BH_4·ClO_4,$\frac{1}{2}H_2O$, (IIb)$(BH_4)_2$, and (III)BH_4·ClO_4 are similar to each other, and to those of analogous (IIb) compounds such as (IIb)NO_3·ClO_4,$\frac{1}{2}H_2O$ and (IIb)CH_3COO·ClO_4,$\frac{1}{2}H_2O$, and to that of the known *cis* compound [Ni_2 en_4Cl_2]Cl_2.[3c] The spectra of the borohydride compounds show a shoulder on the low energy side of the lowest energied band, not present for the other compounds. The similarity of the spectra of (IIb)BH_4·ClO_4,$\frac{1}{2}H_2O$ and (IIb)$(BH_4)_2$, and the dissimilarity of the spectra of (IIa)$(BH_4)_2$ and (IIb)$(BH_4)_2$ support the formulation as [(IIb)BH_4]BH_4, postulated from the infrared spectra (below).

X-*Ray Powder Diffraction.*—From their *X*-ray diffraction patterns it is concluded that (IIb)BH_4·ClO_4,$\frac{1}{2}H_2O$ and (IIb)NO_3·ClO_4,$\frac{1}{2}H_2O$ are isostructural. [(IIb)CH_3COO·ClO_4,$\frac{1}{2}H_2O$ has several planes in common, and if not isostructural must be structurally closely related]. Similarly, the pairs (IIb)$(BH_4)_2$ and (IIb)$(NO_3)_2$, (IIa)$(BH_4)_2$ and (IIa)$(NO_3)_2$, if not isostructural, at least have closely related structures. (From infrared and electronic spectral data these pairs are formulated as [(IIb)X]X and (IIa)X_2, respectively.)

Magnetic Susceptibilities.—The magnetic susceptibilities of three of the compounds were measured in the solid state by the Gouy method, trisethylenediaminenickel thiosulphate being used for calibration.[4] The results given in Table 2, show that the nickel ion in these compounds is in the triplet state, with two unpaired electrons.

Infrared Spectra.—The infrared spectra were measured in Nujol, Halocarbon oil, and hexachlorobutadiene mulls, with a Perkin-Elmer 221 spectrophotometer fitted with a sodium chloride grating and potassium bromide optics.

The spectra of the compounds show strong absorption in the B–H stretching region

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[3a] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, to be published.

[3b] Bostrup and Jorgensen, *Acta Chem. Scand.*, 1957, **11**, 1223.

[3c] Antsyshkina and Porai-Koshits, *Doklady Akad. Nauk. S.S.S.R.*, 1962, **143**, 105 (*Chem. Abs.*, 1962, **57**, 2954).

[4] Curtis, *J.*, 1961, 3147.

TABLE 1.

Reflectance spectra (cm.$^{-1}$ × 10^3).

Compound	ν_1	ν_2	ν_3
(IIa)$(BH_4)_2$	9·0, 14·0sh	19·8	29·0
(IIa)$(NO_3)_2$	8·1, 15·7	19·0	28·7
(IIa)Cl_2	8·1, 14·3	18·4	28·0
(IIb)BH_4·ClO_4,$\frac{1}{2}H_2O$	7·6sh, 10·3	18·1	27·7
(IIb)$(BH_4)_2$	8·0sh, 10·4	17·8	27·4
(III)BH_4·ClO_4	8·0sh, 10·6	18·6	28·3
(IIB)NO_3·ClO_4,$\frac{1}{2}H_2O$	10·7	17·5	27·6
[Ni en_4Cl_2]Cl_2	10·2	16·9	26·9

$\nu_1 = {}^3A_{2g} \longrightarrow {}^3T_{1g}$, $\nu_2 = {}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$, $\nu_3 = {}^3A_{2g} \longrightarrow {}^3T_{2g}(P)$ for O_h symmetry.

TABLE 2.

Magnetic susceptibilities.

Compound	T (°K)	$10^6\chi_g$	$10^6\chi_m$	Diam. corr.	$10^6\chi_m'$	$\mu_{eff.}$ (B.M.) [a]
(IIb) BH_4 ClO_4	287	8·72	3985	271	4256	3·14
(III) BH_4 ClO_4	291	10·29	3841	206	4047	3·09
(IIa) $(BH_4)_2$	291	10·19	3797	248	4045	3·08

[a] Calculated by assuming the Curie law.

TABLE 3.

Infrared spectra in the B–H stretching region (cm.$^{-1}$).

	B_2H_6	$Al(BH_4)_3$	$Be(BH_4)_2$	IIa $(BH_4)_2$	III BH_4ClO_4	IIb BH_4 ClO_4	IIb $(BH_4)_2$, $\frac{1}{2}H_2O$	Ph_4AsBH_4,$2H_2O$
Bridging B–H ↑	1604				1602 NH_2 def.			
	1850				1663 C:N str.			
	1984		1985		2037s	2040s	1990s	
		2031	2060	2073m		(2070sh)?		
				2118s	2110s	2117s	2080m	
		2154	2165	2190m	2180w	2200w	2170sh	2150s
Terminal B–H ↓				2290sh	2270s	2295s	2240vs	2220vs
				2320s			2300s	2280s
	2522	2493	2480	2370sh	2353s	2370s	2380s	
	2614	2559	2553		2393s	2410s	2430s	

(Table 3 and Figure), the bands falling into two groups. The first, at 2200—2400 cm.$^{-1}$, are in the same region as the bands of the borohydride ion in ionic compounds,[5-7] and are attributed to "terminal" B–H bonds. The second group, at 2000—2200 cm.$^{-1}$ are in the same region as bands of the borohydride ion in aluminium and beryllium borohydrides, which have bridged structures related to diborane, and attributed to B–H bonds weakened by multicentre interactions.[7,8]

The spectra in the B–H stretching region of the two borohydride–perchlorate compounds are very similar, and differ from those of both of the two diborohydride compounds, which have dissimilar spectra. The spectra of solutions in organic solvents closely resemble the spectra of solid mulls of the same compounds. The spectra of the complex nickel cations in the 1400—800 cm.$^{-1}$ region are very complex and mask the B–H deformation absorptions.

The compound tetraphenylarsonium borohydride hydrate was prepared and its spectrum measured, as an example of an "ionic" borohydride salt with minimal polarization of the borohydride ion. The spectra reported for alkali-metal borohydrides [5] are very variable, probably because of the difficulty in obtaining satisfactory mulls with these compounds, and because of their hygroscopic nature. The tetraphenylarsonium salt gave a satisfactory mull spectrum. (Related "onium" borohydride salts have previously been reported.[9])

The borohydride perchlorate of the complex (III) shows strong C⁚N absorption at 1663 cm.$^{-1}$ and strong NH_2 deformation absorption at 1600 cm.$^{-1}$, the spectrum in this

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[5] Price, *J. Chem. Phys.*, 1949, **17**, 1044; Ketelaar and Schutte, *Spectrochim. Acta*, 1960, **16**, 1054; 1961, **17**, 815; Goubeau and Kallfass, *Z. anorg. Chem.*, 1959, **299**, 160.

[6] Waddington, *J.*, 1958, 4783.

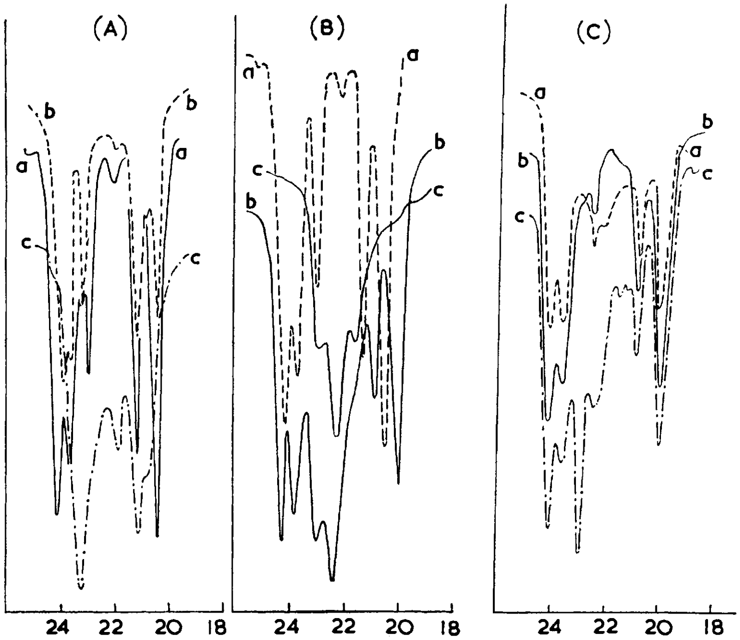
[7] Price, Longuet-Higgins, Rice, and Young, *J. Chem. Phys.*, 1949, **17**, 217; Price, *ibid.*, p. 1044.

[8] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2142.

[9] Heal, *J. Inorg. Nuclear Chem.*, 1960, **12**, 255.

region being very similar to that of other salts of the ion (III), and indicating that the $\mathrm{C{\vdots}N}$ group has not been reduced.

Discussion.—The ions (IIa), (IIb), and (III) form orange diamagnetic salts with anions that have little tendency to co-ordinate, *e.g.*, ClO_4^-, $ZnCl_4^{2-}$, $PtCl_6^{2-}$, etc., and form blue-violet paramagnetic salts with other anions.[10,11] In these cases, the infrared spectrum of the anion frequently shows evidence of interaction with the nickel ion.[10,11] The paramagnetism, $\mu_{\mathrm{eff}} \sim 3$ B.M., observed for the nickel(II) ion in the borohydride derivatives (Table 1) indicates sufficient interaction between the nickel and borohydride ions to give a triplet ground state, with (probably) pseudo-octahedral co-ordination about the nickel ion.



Infrared spectra in the B–H stretching region ($cm.^{-1} \times 10^2$).

(A) Mulls.	(B) Mulls.	(C) Solutions (freshly prepared).
(a) (IIb) $BH_4{\cdot}ClO_4$.	(a) (IIb) $BH_4{\cdot}ClO_4$.	(a) (IIb) $BH_4{\cdot}ClO_4$ in dimethylformamide.
(b) (III) $BH_4{\cdot}ClO_4$	(b) (IIb) $(BH_4)_2,\frac{1}{2}H_2O$.	(b) (IIb) $BH_4{\cdot}ClO_4$ in dichloromethane.
(c) (IIa) $(BH_4)_2$.	(c) $(C_6H_5)_4AsBH_4,2H_2O$.	(c) (IIb) $(BH_4)_2,\frac{1}{2}H_2O$ in dichloromethane.

The ions (IIb) and (III) form ethylenediamine adducts (*e.g.*, [(IIb) en]$(ClO_4)_2$), in which the four nitrogens of the (IIb) or (III) ions must be *cis* to accommodate the chelate.[10] They also form derivatives of the type (IIb) X$\cdot$ ClO_4 where X = NO_3^-, $CH_3{\cdot}COO^-$, $\frac{1}{2}C_2O_4^{2-}$, (and BH_4^-), etc., which are considered, on the basis of the infrared spectra of the anion X, to have related structures, with the anion acting as a chelate.[10,11] The ion (IIa) forms paramagnetic salts of type (IIa)X_2, where X = Cl^-, NO_3^-, CH_3COO^-, (and BH_4^-), etc., and shows no tendency to form adducts with chelates such as ethylenediamine, or salts of the type (IIa) X$\cdot$ ClO_4, as above.[8,10] The cobalt(III) analogue of the isomer (IIb) readily forms a chelated oxalato-derivative [(Co-IIb) C_2O_4] ClO_4, whereas attempts to form a similar compound with the analogue of the isomer (IIa) have been unsuccessful.[10] It is concluded that the isomer (IIa) is constrained from adopting the buckled *cis*-configuration, and that the derivatives, including the diborohydride, have the *trans*-configuration.

The borohydride ion forms " ionic " salts with cations of low polarizing power, *e.g.*, $NaBH_4$, with tetrahedral BH_4^- ions.[5,6] With the cation Tl^+ the infrared spectrum indicates

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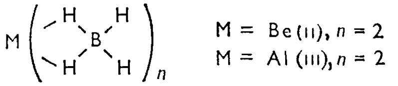
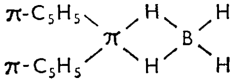
[10] Curtis, unpublished work.

[11] Curtis, *J.*, 1963, 4109.

polarization of the BH_4^- ion. With highly polarizing ions, molecular compounds are obtained, *e.g.*, $Be(BH_4)_2$,[7] $Al(BH_4)_3$,[7] $U(BH_4)_4$,[12] $Ti(BH_4)_4$,[13] $Sn(BH_4)_2$,[14] $Zn(BH_4)_2$,[15] etc.[13] Bridged structures, (IV), related to diborane have been suggested for $Be(BH_4)_2$ and $Al(BH_4)_3$ as a result of electron diffraction studies.[16] The infrared spectra of $Be(BH_4)_2$ and $Al(BH_4)_3$ have also been interpreted as supporting the bridged structures.[7] Similar bridged structures have been suggested for a variety of hydride, alkyl- and aryl-substituted borohydride derivatives,[13,17] *e.g.*, $(\pi\text{-}C_5H_5)_2TiBH_4$ [18] (V).



(IV)



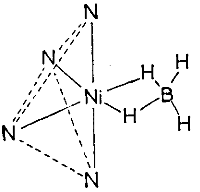
(V)

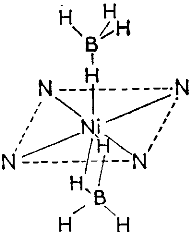
The compound $K_2Zn_3(BH_4)_8$ has been formulated [19] as a borohydride zinc complex $K_2Zn[Zn(BH_4)_4]_2$, but the infrared spectrum in the B–H stretching region is similar to that of " ionic " borohydride, with bands at 2223, 2293, and 2392 cm.$^{-1}$, and no bands in the bridging region, 2000—2200 cm.$^{-1}$.

The infrared spectra of the nickel amine borohydride derivatives, $Be(BH_4)_2$, $Al(BH_4)_3$,[6] $(\pi\text{-}C_5H_5)_2Ti\ BH_4$[18] and the hydrido-aluminium borohydride derivatives,[17] show two groups of bands in the B–H stretching region, one group in the range 2400—2200 cm.$^{-1}$, attributed to the stretching of terminal B–H bonds, and a group in the range 2200—2000 cm.$^{-1}$, attributed to the stretching of B–H bonds weakened by multicentre interactions, *i.e.*, bridging groups [5] (Table 2 and Figure).

In view of the ability of the BH_4^- group to form hydrogen-bridging compounds and the tendency of the ions (IIb) and (III) to form compounds with an oxyanion acting as a chelate, it seems reasonable to formulate the borohydride perchlorate compounds with chelating borohydride as in (VI). In this structure, the bonding between the nickel and borohydride ions can be considered as largely electrostatic, the covalent component arising from the occupancy of two sets of tricentric Ni–H–B orbitals, involving two of the octahedral hybrid orbitals of the nickel ion. An alternate, six-co-ordinate structure for these compounds with the BH_4^- group linking nickel ions to form a chain polymer (as in $Ni\ en_2\ NO_2\ ClO_4$) [20] is considered improbable since, (*a*) they dissolve readily, to form violet solutions in solvents of such relatively low co-ordinating power as acetone and dichloromethane, and (*b*) on steric grounds, if the Ni–H–B–H–Ni is even approximately the tetrahedral angle of 109°.

(VI)





(VII)

(VIII)

The upper, (VII), and lower, (VIII), portions of this diagram represent *alternate* possible structures of (IIa) $(BH_4)_2$.

[12] Schlesinger and Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 219.
[13] Wiberg and Bauer, *Z. Naturforsch.*, 1950, **5**b, 397.
[14] Amberger and Kula, *Chem. Ber.*, 1963, **96**, 2556.
[15] Wiberg and Henle, *Z. Naturforsch.*, 1952, **7**b, 579.
[16] Bauer, *J. Amer. Chem. Soc.*, 1950, **72**, 622.
[17] Ruff, *Inorg. Chem.*, 1963, **2**, 515; Wiberg, Graf, Schmidt, and Usón, *Z. Naturforsch.*, 1952, **7**b, 578.
[18] Nöth and Hartwimmer, *Chem. Ber.*, 1960, **93**, 2238.
[19] Hagenmuller and Rault, *Compt. rend.*, 1959, **248**, 2758.
[20] Llewellyn and Waters, *J.*, 1962, 3845.

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The difference between the infrared spectra of the mono- and diborohydride compounds indicates some difference in the Ni–BH_4 interactions. The diborohydride of the isomer (IIa) can be most simply formulated, analogously to the dinitrate, dichloride, etc., with *trans* BH_4^- ions interacting with the nickel ion through single Ni–H–B bridges, each involving one octahedral hybrid orbital of the nickel atom (VII). An alternative structure, with two bridging hydride ions, as in the other borohydride derivatives, (VIII), is possible; in this case, both hydrogens could be considered as interacting *via* the same nickel hybrid orbital. The differences between the infrared spectra of the diborohydride of the isomer (IIa) and the borohydride perchlorate of the isomer (IIb) if both have structures with two bridging hydrogens [(VIII) and (VI)] may be due to the different constraints on the BH_4^- ion, maximum orbital overlap requiring the closing of the H–B–H angle in the first case, and spreading of it in the second.

The infrared spectra of the two diborohydride compounds in the B–H stretching region are quite dissimilar (Figure) indicating structural differences between the compounds. The spectrum of the diborohydride of the isomer (IIb) closely fits a superimposition of the spectra of the borohydride perchlorate of the isomer (IIb), and an ionic borohydride (*e.g.*, tetraphenylarsonium borohydride) (Figure) suggesting that the compound should be formulated as an analogue of the borohydride perchlorate, *i.e.*, [(IIb) BH_4] BH_4, with one interacting and one ionic borohydride ion. This is supported by the solubility in organic solvents, which resembles that of the borohydride perchlorate of the isomer (IIb), rather than that of the diborohydride of the isomer (IIa). Moreover, treatment of the diborohydride of the isomer (IIb) with cold dilute perchloric acid yields the α conformational isomer of diperchlorate of the isomer (IIb),[2] as with the borohydride perchlorate of the isomer (IIb), the diperchlorate of the complex [(IIb) en], and the members of the [(IIb) X] ClO_4 series of compounds mentioned above. This conformational isomer is considered to be derived from compounds of the isomer (IIb) with the cyclic tetramine buckled into the *cis*-configuration in pseudo-octahedral derivatives. If the diborohydride of the isomer (IIb) had a structure with both borohydride ions interacting in *trans*-positions, it is considered that treatment with perchloric acid should yield the more stable β-isomer of the diperchlorate of the isomer (IIb). (A structure with two borohydride ions interacting in a *cis*-position is considered improbable on steric grounds.) The isomerism of the compounds of the isomer (IIb) will subsequently be described in detail.

The infrared spectra, in the B–H stretching region, of the solutions of the borohydride perchlorate of the isomer (IIb) in dimethylformamide, dimethyl sulphoxide, and dichloromethane are identical (Figure) and very similar to the spectra of solid mulls, indicating retention of the chelated structure even in strongly co-ordinating solvents such as dimethyl sulphoxide. (The compounds dissociate in aqueous solution.) The spectrum of the diborohydride of the isomer (IIb) in dichloromethane (Figure) similarly resembles that of a solid mull, indicating retention of the structure of the solid, with one interacting and one ionized borohydride ion, in solution.

EXPERIMENTAL

The derivatives of the ions (IIa) and (IIb) can be prepared from the salts of the ions (IIa) and (IIb), prepared as previously described,[2] or from the perchlorate of the complex (I), by using sodium borohydride as the reducing agent. The perchlorates of the complexes (I) and (III) were prepared as previously described.[1] For convenience in naming, the *trans*-configuration is assumed for the ions (I) and (II).

5,7,7,12,14,14-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradecanenickel*(II) *Borohydride Perchlorate, Isomer b* IIb BH_4 ClO_4.—Sodium borohydride (2 g.) was added to a solution of the diperchlorate (12 g.) of the complex (I) and borax (0·5 g.) in water (250 ml.). The solution was heated at 60° for 30 min., then allowed to cool to about 30° whereupon the blue-violet product was filtered off, and washed several times with small portions of ice-water, followed by isopropyl alcohol and ether. The yield was approximately 25—30%, based on the complex (I). (If the reaction solution is set aside the product will be contaminated by the orange diperchlorate of the isomer

(IIa).) The compound is precipitated when sodium borohydride is added to an aqueous solution of the diperchlorate of the isomer (IIb) (Found: Ni, 13·0; C, 41·9; H, 9·1; N, 12·4. Calc. for $NiC_{16}H_{40}N_4B(ClO_4)$: Ni, 12·9; C, 42·0; H, 8·8; N, 12·3%).

Notes. (*a*) Hydrogen is evolved during the borohydride reduction, which is incomplete unless there is at least 1 mole of $NaBH_4$ per C:N group, suggesting that the reaction proceeds according to the equation

$$BH_4^- + {>}C{:}N{-} + 2H_2O \longrightarrow {>}CH{\cdot}NH{-} + HBO_2 + 3H_2$$

(*b*) The total yield of the isomer (IIb) when sodium borohydride is used to reduce the complex (I) is 45% (cf. 22% with nickel–aluminium alloy in alkaline solution [2]). The total yield of the isomer (IIb) (or the residue in the filtrate after the separation and washing of the borohydride perchlorate) can be recovered as the insoluble hemioxalate perchlorate [2] by the addition of sodium oxalate to the hot filtrate.

5,7,7,12,14,14-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradecanenickel*(II) *Diborohydride Hemihydrate, Isomer b* IIb $(BH_4)_2,\frac{1}{2}H_2O$.—The compound precipitated when sodium borohydride was added to a concentrated aqueous solution of the dichloride of the isomer (IIb) (or other soluble salt). The mauve product was washed with a little ice-water and isopropyl alcohol, and dried under vacuum (Found: Ni, 15·3; C, 50·0; H, 11·5; N, 14·5. Calc. for $NiC_{16}H_{44}N_4B_2,\frac{1}{2}H_2O$: Ni, 15·4; C, 50·3; H, 11·6; N, 14·7%).

Note. The diperchlorate of the isomer (IIb) crystallizes when a cold aqueous suspension of the borohydride perchlorate of the isomer (IIb) is acidified with perchloric acid. The dichloride of the isomer (IIb) crystallizes when lithium chloride is added to a hot solution of the perchlorate in dimethylformamide. The preparation of salts of the isomer (IIb) will be described later.

5,7,7,12,14,14-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradecanenickel*(II) *Diborohydride, Isomer a* IIa $(BH_4)_2$.—As for the previous preparation, substituting the dichloride of the isomer (IIa) for the dichloride of the isomer (IIb) (Found: Ni, 15·7; C, 52·0; H, 12·1; N, 15·2. Calc. for $NiC_{16}H_{44}N_4B_2$: Ni, 15·8; C, 51·6; H, 11·9; N, 15·0%).

Note. The dichloride of the isomer (IIa) crystallizes when lithium chloride is added to a solution of the diperchlorate of the isomer (IIa) in acetone.

4,6,6-*Trimethyl*-3,7-*diazanon*-3-*ene*-1,9-*diaminenickel*(II) *Borohydride Perchlorate* III BH_4ClO_4.—Excess of sodium borohydride was added to an ice-cold aqueous solution of the diperchlorate of the complex (III), the mauve product being precipitated. The product was filtered off and washed in the same way as previous preparations [Found: Ni, 15·8; C, 31·5; H, 7·6; N, 14·9. Calc. for $NiC_{10}H_{28}N_4B(ClO_4)$: Ni, 15·8; C, 32·1; H, 7·5; N, 15·0%].

Tetraphenylarsonium Borohydride Dihydrate.—The salt was precipitated when sodium borohydride was added to an aqueous solution of tetraphenylarsonium chloride. The white precipitate was washed with a little ice-water and dried under vacuum at room temperature (Found: C, 67·1; H, 5·7. Calc. for $C_{24}H_{24}AsB,2H_2O$: C, 66·5; H, 5·5%).

Analysis for Borohydride.—The compounds were treated with N-sulphuric acid and the volume of hydrogen evolved was measured. The borohydride perchlorate of the isomer (IIb) gave 193 and 187 ml. of H_2/g. at S.T.P., corresponding to 7·9 and 7·6 moles of hydrogen/mole. The borohydride perchlorate of the complex (III) gave 214 ml. of H_2/g. at S.T.P., corresponding to 7·1 moles of H/mole. A small amount of black nickel boride, which was precipitated during the reaction, explains the low result. The diborohydride of the isomer (IIa) gave 462 ml. of H_2/g. at S.T.P., corresponding to 15·6 moles of H/mole. The diborohydride hemihydrate of the isomer (IIb) gave 473 ml. of H_2/g. at S.T.P., corresponding to 15·3 moles of H/mole.

Under acid conditions the borohydride ion decomposes according to the equation

$$BH_4^- + H^+ + 2H_2O = HBO_2 + 8H.$$

The above figures therefore support the formulation of the first pair of compounds as monoborohydride salts and the second pair as diborohydride salts.

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