

SYNTHESIS AND SOME TRANSFORMATIONS OF COMPLEX NICKEL(II) SALTS OF BIS(3,1,2-DICARBOLLYL)NICKEL(III). PREPARATION OF 3-(2,2'-BIPYRIDYL)-*closo*-3,1,2-NICKELADICARBADODECABORANE *

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Summary

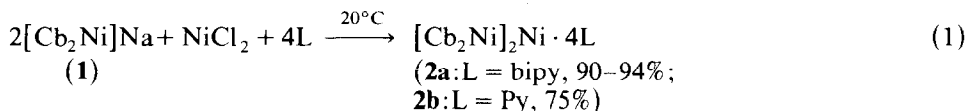
$[\text{Cb}_2\text{Ni}^{\text{III}}]_2\text{Ni}^{\text{II}} \cdot 4\text{L}$ compounds (**2a**, **b**), where Cb is π -(3)-1,2- $\text{C}_2\text{B}_9\text{H}_{11}$ and L is 2,2'-bipyridyl (**2a**) or pyridine (**2b**), have been prepared by the reaction of NiCl_2 with $[\text{Cb}_2\text{Ni}^{\text{III}}]\text{Na}$ (**1**) in the presence of the corresponding ligands L. The salt with bipyridyl (**1a**) forms the complex $[\text{Cb}_2\text{Ni}]\text{Na} \cdot 2\text{L}$ (**3**). Complexes **2a** and **3** decompose at 200-230°C to form 3-(2,2'-bipyridyl)-*closo*-3,1,2-nickeladecarborane (**4**). Compound **4** has also been prepared by thermal decomposition of bipyridyl complexes of bis-(1-*o*-carboranyl)nickel or the nickel salt of 1-*o*-carboranecarboxylic acid. In this case, the *o*-carboranic nucleus is transformed into a *closo*-nickelacarboranic one.

At present, bis-dicarbollyl derivatives of a large number of transition metals are known [1,2]. As a rule, these compounds are separated in the form of alkali, alkylammonium or thallium salts. A few examples of bis-dicarbollyl compounds containing a transition metal in the form of an organometallic cation on the external sphere have been reported (see, for example, [3]). At the same time, compounds of the $\text{M}^{\text{II}}[\text{M}^{\text{III}}\text{Cb}_2]_2$ type, where M is a transition metal and Cb is an anion, π -(3)-1,2- $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$, have not been obtained, as far as we know. Such compounds contain, both on the internal and the external spheres, the atoms of a transition metal differing only in oxidation state. They are of interest in view of their reactivity (the possibility of interaction of an external atom of the transition metal with ligands of the complex anion). In addition, these compounds are promising for applications in homogeneous catalysis.

It has been found that the sodium salt of bis-dicarbollylnickel(III) readily reacts with NiCl_2 in water in the presence of 2,2'-bipyridyl (bipy) or pyridine (Py) to form

* Dedicated to Professor O.A. Rcutov on the occasion of his 65th birthday on 5th September 1985.

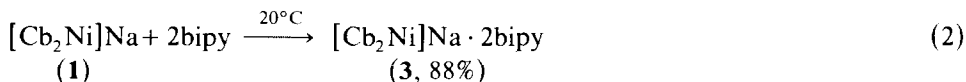
the corresponding complex nickel salts **2** in preparative yields (eq. 1).



Compounds **2** are yellow, crystalline substances which dissolve completely in acetone and acetonitrile, poorly in alcohol, and slightly in water and hydrocarbons. At room temperature they keep well in the solid state but in solutions they decompose markedly within several days. The compositions of the complex salts **2** have been confirmed by elemental analysis and IR spectral data.

The formation of compounds **2** involving four ligands L in a molecule does not depend on the ratio of the reagents in reaction 1. The above yields were obtained at stoichiometric ratios of reagents. The use of a decreased quantity of ligand L did not result in the formation of complexes containing a smaller number of ligand molecules but only reduced the yield of salt **2**. The excessive quantities of nickel chloride or ligand L introduced into the reaction remained unaffected.

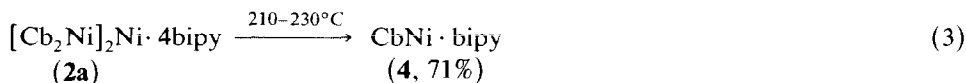
The presence of four molecules of both pyridine and bipyridyl in complexes **2** is indicative of the fact that the latter serves as a monodentate ligand. It was of interest to elucidate the distribution of the four molecules of ligand L between the nickel atoms in compounds **2**. It was thought unlikely that the nickel atom of the external sphere was capable of retaining four bipyridyl molecules. Therefore, we studied the interaction of bipyridyl with salt **1**, which was found to result in the formation of complex **3** containing two ligand molecules (eq. 2).



The composition of complex **3** was confirmed by elemental analysis and IR spectral data. The formation of complex **3** shows that in complexes **2**, at least a portion of the L ligands is coordinated near the nuclide $[\text{Cb}_2\text{Ni}]^-$.

The study of transformations in complexes **2** was exemplified by thermal decomposition of compound **2a**. The DTA * study of this compound showed that it undergoes exothermal transformation in the range of 180–300°C (maximum transformation rate at 250°C), which is practically not accompanied by loss of sample weight.

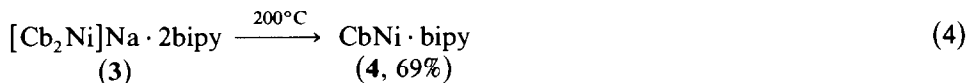
Heating compound **2a** without a solvent at 210–230°C resulted in the formation of 3-(2,2'-bipyridyl)-*closo*-3,1,2-nickeladecaborane (**4**) (eq. 3).



Compound **4** is insoluble in hexane and water. It has the form of dark needles with a metallic glitter and its solutions in acetone and DMSO are dark red in colour. Its composition was confirmed by elemental analysis and ^1H and ^{13}C NMR, mass, and IR spectral data.

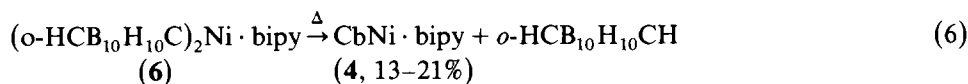
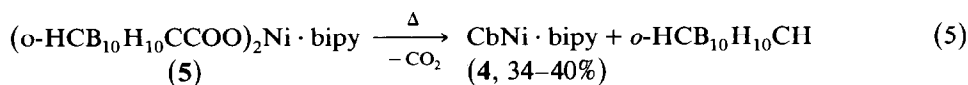
* DTA-differential thermal analysis.

Compound **4** is also formed by thermal decomposition of complex **3** (eq. 4).



The mechanism of the formation of **4** from **2a** and **3** is not known; however, it is evident that reactions 3 and 4 involve an oxidative-reductive process accompanied by the reduction of nickel(III) to nickel(II). The above yields have been calculated on the basis of the nickel content in the initial **2a** or **3** and in the prepared **4** compounds. Besides compound **4**, (eq. 3) gives a substance of variable composition which is insoluble in acetone and contains 10–12% of nickel (the yield calculated on the basis of nickel is 16–17%).

It has been found [4] that compound **4** is also formed at thermal decomposition of bipyridyl complexes of the nickel salt of 1-*o*-carboranecarboxylic acid (eq. 5) and bis(1-*o*-carboranyl)-nickel (eq. 6).



In reaction 5, the formation of the 1-*o*-carboranylnickel derivative was observed. It was not isolated in a pure form but it transformed into bis(1-*o*-carboranyl)mercury on treatment with mercuric chloride.

In reactions 5 and 6, compound **4** is formed as a result of skeleton rearrangement of the carboranic nucleus, during which fragment BH is replaced by the metal atom while the C(1) atom of the arising *closo*-metallacarboranic structure receives a hydrogen atom. This rearrangement occurs at a comparatively low temperature (140–200°C). We failed to find published examples of a similar direct thermal transformation of the carboranic nucleus into a metallacarboranic one.

To our knowledge, we are the first to obtain compound **4** [4]. It is an analogue of the *closo*-3,3-bis(triarylphosphine)-3,1,2-nickeladecaboranes described in [5,6]. The latter have been shown to rearrange under mild conditions into the isomer hydride form, in which there is a Ni–H bond. This bond is characterized by the IR absorption band at 1984 cm⁻¹ [5]. The IR spectrum of compound **4** does not contain absorption bands in the range of 1630–2400 cm⁻¹. It agrees well with published data [6], where it was stated that the formation of a hydride form is a specific reaction for 3,1,2-nickeladecaboranes containing two triarylphosphine ligands in position 3 while in complexes involving different ligands a similar rearrangement does not occur.

Experimental

The sodium salt of bis(π -(3)-1,2-dicarbollyl)nickel(III) (**1**) was synthesized by the method of Hawthorne et al. [7]; the 2,2'-bipyridyl complexes of the nickel salt of *o*-carborane-1-carboxylic acid (**5**) and bis(1-*o*-carboranyl)-nickel (**6**) were prepared by the technique given in ref. 8. IR spectra were recorded on a UR-20 spectrometer. Samples for IR spectroscopy were prepared in the form of pellets with KBr. DTA

analysis was performed on a MOM OD-103 device (Hungary). NMR spectra were taken on a Bruker WM-360 apparatus using a 20% solution of the substance in hexadeuterodimethylsulphoxide; mass spectra were recorded on a Varian MAT-311 spectrometer.

Synthesis of the nickel(II) complex salts of bis(π -(3)-1,2-dicarbollyl)nickel(III) (2a, b)

Compound 2a. An aqueous alcohol solution prepared by mixing 0.12 g (0.5 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 6 ml of water and 0.31 g (2 mmol) of 2,2'-bipyridyl in 2 ml of alcohol was added to a solution of 0.35 g (1 mmol) of salt **1** in 30 ml of water. The yellow precipitate was filtered, washed with water, and dried in vacuum over P_2O_5 . 0.6 g (0.45 mmol, 90%) of salt **2a** was obtained. On heating above 180°C the substance decomposed without melting. Found: C, 43.51; H, 5.48; N, 8.63; Ni, 12.78. $\text{C}_{48}\text{H}_{76}\text{B}_{36}\text{N}_8\text{Ni}_3$ calcd.: C, 43.33; H, 5.75; N, 8.42; Ni, 13.23%. IR spectral data: 3080w, 3040w, 2930w, 2550s, 1605m, 1570w, 1493w, 1472m, 1442s, 1313m, 1280w, 1250w, 1220w, 1173w, 1160m, 1106w, 1078m, 1045w, 1023m, 972m, 918w, 900w, 870w, 760s, 738m, 655m, 635w, 462w, 445w, 420m cm^{-1} .

Compound 2b. A solution of 0.12 g (0.5 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.158 g (2 mmol) of pyridine in 5 ml of water was added to a solution of 0.35 g (1 mmol) of salt **1** in 30 ml of water. The green-yellow precipitate was filtered, washed with a small quantity of water, and dried in vacuum over P_2O_5 . 0.38 g (0.37 mmol, 74%) of salt **2b** was obtained. The substance decomposed above 200°C. Found: C, 32.53; H, 6.74; N, 5.7; Ni, 17.17. $\text{C}_{28}\text{H}_{64}\text{B}_{36}\text{N}_4\text{Ni}_3$ calcd.: C, 32.90; H, 6.31; N, 5.48; Ni, 17.22%. IR spectral data: 3060w, 2560s, 1613m, 1583w, 1495w, 1450s, 1405w, 1360w, 1222m, 1160m, 1073m, 1046m, 1016m, 973m, 920w, 903w, 873w, 756m, 703s, 670w, 465w, 432m cm^{-1} .

Reaction of salt 1 with 2,2'-bipyridyl. Synthesis of complex 3

A solution of 0.31 g (2 mmol) of 2,2'-bipyridyl in 2 ml of alcohol was added to a solution of 0.35 g (1 mmol) of salt **1** in 30 ml of water. The mustard-coloured precipitate was filtered, washed with a small quantity of water, and dried in vacuum over P_2O_5 . 0.58 g (0.88 mmol, 88%) of complex **3** was obtained. The substance melted between 168 and 170°C. Found: C, 44.18; H, 6.04; N, 8.67; Ni, 8.91. $\text{C}_{24}\text{H}_{38}\text{B}_{18}\text{N}_4\text{NaNi}$ calcd.: C, 43.75; H, 5.81; N, 8.50; Ni 8.90%. IR spectral data: 3055w, 2550s, 1594s, 1575m, 1475m, 1437s, 1313m, 1245w, 1227w, 1180w, 1158m, 1089m, 1047w, 1005m, 977m, 875w, 758s, 656w, 637w, 623w, 465w, 420w cm^{-1} .

Thermal decomposition of salt 2a

0.67 g (0.5 mmol) of salt **2a** was heated at 210–225°C in an argon atmosphere for 300 min. On cooling, the residue was treated with acetone and filtered. The filtrate was partially concentrated by evaporation and separated on a column with alumina (acetone as eluent). A dark-red fraction was collected, acetone was removed, and 0.37 g (1.06 mmol) of compound **4** was obtained. Found: C, 41.51; H, 5.53; N, 7.89; Ni, 16.58; $\text{C}_{12}\text{H}_{19}\text{B}_9\text{N}_2\text{Ni}$ calcd.: C, 41.50; H, 5.51; N, 8.06; Ni, 16.90%. The type of spectrum and chemical shifts of the nuclides in ppm are given; groups and a number of corresponding nuclides found according to the spectral data are indicated in parentheses. ^1H NMR: 0.17–2.8 (BH, 9), 3.38 (CH, 2), 7.66–8.62 (bipy, 8). ^{13}C NMR: 43.53 ($\text{C}_2\text{B}_9\text{H}_{11}$, 2), 122.5–153.0 (bipy, 10). Mass spectrum (m/e , ions are indicated): 347, $\text{C}_{12}\text{H}_{19}\text{B}_9\text{N}_2\text{Ni}$ (molecular ion); 214, $\text{C}_{10}\text{H}_8\text{N}_2\text{Ni}$; 191, $\text{C}_2\text{H}_{11}\text{B}_9\text{Ni}$;

156, $C_{10}H_8N_2$; 132, $C_2H_{11}B_9$. IR-spectral data: 2564s, 1608m, 1472m, 1443s, 1313m, 1274w, 1158m, 1124w, 1105w, 1072m, 1019m, 972m, 869m, 762s, 745w, 727m, 682m, 650w, 427w cm^{-1} . The residue, insoluble in acetone (0.14 g), was analyzed for the nickel content. Found: Ni, 10.4%.

Thermal decomposition of complex 3

0.33 g (0.5 mmol) of complex **3** was heated at 210°C in an argon atmosphere for 300 min. The reaction mixture was treated as described above. 0.12 g (0.345 mmol) of substance **4** was obtained, identical to that described above. The yield was 69%.

Thermal decarboxylation of salt 5

(a) *In xylene.* 2.36 g (4.0 mmol) of salt **5** in 20 ml of *p*-xylene was heated at the boiling temperature for 300 min. 6.24 mmol (78%) of CO_2 was identified in the evolved gas. The reaction mixture was filtered on cooling. The precipitate was washed with hexane. The xylene and hexane solutions were combined and chromatographed on an alumina column, using hexane as eluent. 0.16 g (1.1 mmol) of *o*-carborane (27.5%) was isolated. The precipitate was washed with acetone. 0.48 g (1.38 mmol) of substance **4** was obtained from the acetone solution by the technique described and was identical with the compound given above. The yield amounted to 34.5%. The precipitate, insoluble in acetone, was boiled with a solution of 1.08 g (4 mmol) of mercuric chloride in 50 ml of alcohol for 60 min. The mixture was filtered on cooling. The addition of water to the filtrate was followed by ether extraction. The ether was removed to obtain 0.22 g (0.46 mmol, 11.5%) of bis(*o*-carboranyl)mercury (identified by TLC on Silufol in the presence of an authentic sample). In another run, salt **5** was heated in xylene for 60 min. 0.19 g (0.54 mmol, 13.6%) of compound **4** and 0.91 g (1.88 mmol, 47%) of bis(*o*-carboranyl)mercury were obtained. 4.6 mmol (57.5%) of CO_2 was identified in the evolved gas.

(b) *Without solvent.* 1.18 g (2 mmol) of salt **5** was heated at 190–210°C for 90 min. 3.2 mmol (80%) of CO_2 were identified in the evolved gas. 0.28 g (0.8 mmol, 40%) of compound **4** was isolated from the reaction mixture by the technique described above.

Thermal decomposition of compound 6

(a) *In xylene.* 0.83 g (1.66 mmol) of compound **6** was heated in 10 ml of boiling *p*-xylene for 300 min. The reaction products were isolated by the procedure described for salt **5**. 0.05 g (0.35 mmol, 20.9%) of *o*-carborane and 0.08 g (0.23 mmol, 13.6%) of compound **4** were obtained.

(b) *Without solvent.* 1.0 g (1.92 mmol) of compound **6** was heated at 190–210°C for 90 min. The reaction products were isolated by the technique described above. 0.11 g (0.76 mmol, 39.5%) of *o*-carborane and 0.14 g (0.4 mmol, 21%) of compound **4** were obtained.

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