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Synthesis and Some Transformations of Complex Salts of Bis-*o*-dicarbollyliron(II), -cobalt(II), and -nickel(II)

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Abstract—The complex salts $[(o\text{-}C_2B_9H_{11})_2M^{3+}]_2M'^{2+}\cdot 4$bipy, where M = Fe, Co, or Ni, M' = Fe, Co, Ni, Cu, Mn ($M \neq M'$), and bipy is 2,2'-bipyridyl, were synthesized. The salts with M = Ni decompose to give 3-(2,2'-bipyridyl)-3,1,2-nickelacarborane, when refluxed in alcohol, and to give 2-(2,2'-bipyridyl)-2,1,7-nickelacarborane, when refluxed in dodecane (216°C).

Earlier we described complex salts of the general formula $[(o\text{-}C_2B_9H_{11})_2M^{3+}]_2M^{2+}\cdot 4L$ (**I**), where M = Fe [1], Co [2], or Ni [3, 4], L = 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), or pyridine (Py); these complex salts contained both in the inner and in the outer sphere the same transition metal M but in different oxidation degrees. Proceeding with these studies we synthesized the heterometallic complex salts $[(o\text{-}C_2B_9H_{11})_2M^{3+}]_2M'^{2+}\cdot 4$bipy (**IIa**–**IIl**) containing in the inner and outer spheres different transition metals ($M \neq M'$) [M = Fe, M' = Co (**a**); M = Fe, M' = Ni (**b**); M = Fe, M' = Mn (**c**); M = Fe, M' = Cu (**d**); M = Co, M' = Fe (**e**); M = Co, M' = Ni (**f**); M = Co, M' = Mn (**g**); M = Co, M' = Cu (**h**); M = Ni, M' = Fe (**i**); M = Ni, M' = Co (**j**); M = Ni, M' = Mn (**k**); M = Ni, M' = Cu (**l**)]. Compounds **IIa**–**IIl** were obtained in 45–78% yields by the reaction of stoichiometric amounts of the sodium salt of the corresponding bisdicarbollylmetal $[(o\text{-}C_2B_9H_{11})_2M^{3+}]Na$ (**IIIa**–**IIIc**) [M = Fe (**a**), Co (**b**), Ni (**c**)], a soluble salt (chloride, sulfate, or acetate) of the metal M', and bipy in aqueous alcohol.

Compounds **IIa**–**IIl** are crystalline substances readily soluble in acetone and acetonitrile, worse soluble in ethanol, and poorly soluble in water and hydrocarbons. The salts can be handled at room temperature. Their structure was proved by elemental analysis, IR and UV spectroscopy, and mass spectrometry.

The IR spectra of compounds **IIa**–**IIl** exhibit the same trends as those of compounds **I** [1–4]. The spectra lack bands at 3049–3043 and 1200 cm^{-1} due, respectively, to stretching and bending CH vibrations of the carborane nucleus [5, 6]. This fact suggests that in compounds **IIa**–**IIl**, like in **I**, the bipyridine ligands are coordinated via protonation of their nitrogens by the carbollyl C–H hydrogens.

Earlier [1, 2, 4] we noted that the UV spectra of complexes **III**–2L (L = bipy, phen) are simply a superposition of the spectra of salt **III** and the ligand L and concluded that the complex formation involves no interaction of the ligands with the central metal atom M^{III}. At the same time, in the spectra of complex salts **I** we observed a bathochromic shift of ligand bands, implying an interaction of the protonated ligands with M^{2+}. A similar bathochromic shift is observed in the UV spectra of complex salts **IIa**–**IIl**, i.e. here, too, M'^{2+} interacts with the protonated bipyridyl. Thus, in complex salts **IIa**–**IIl**, like in **I**, there are two types of coordination: protonation of the bipyridyl nitrogens by the carbollyl C–H hydrogens and interaction of M'^{2+} with the protonated ligands.

The mass spectra of complexes **IIi** and **IIl** with an inner-sphere Ni^{3+} show a peak at *m/e* 384 due to the nickelacarborane dimer $(C_2B_9H_{11}Ni)_2$. The same peak is observed in the mass spectrum of complex **IIb** having an outer-sphere Ni^{2+}, whereas the spectrum of complex **IIk** contains a peak at *m/e* 576 corresponding to the trimer $(C_2B_9H_{11}Ni)_3$. In the spectra of Co^{3+} complexes **IIe, IIg**, and **IIh**, there is a peak at *m/e* 386 due to the dimer $(C_2B_9H_{11}Co)_2$. The peak of dimeric metal carborane was also found in the mass spectrum of CoNi complex **IIf**, but this peak could not be assigned because of the close atomic weights of these metals. The mass spectra of complexes **IIa, IIc**, and **IId** show no peaks due to metal carboranes.

The mass spectra of complexes **II** point to the possibility of metal carborane formation on decomposition of the complexes. Earlier we showed that compounds **I** (M = Ni, L = bipy or phen) slowly decompose in ethanol (a faster reaction occurs under reflux) to give *o*-nickelacarborane 3-L-3,1,2-$NiC_2 \cdot B_9H_{11}$ (**IVa, IVb**). At a higher temperature (under reflux in dodecane, 216°C), the decomposition was accompanied by skeletal rearrangement to give the *meta* isomer of 2-L-2,1,7-$NiC_2B_9H_{11}$ (**Va, Vb**) [3, 4]. The structure of compounds **IV** and **V** was established by X-ray diffraction [7]. By contrast, the decomposition of compounds **I** (M = Fe or Co) under the same conditions gives no metal carboranes [1, 2]. In the present work we studied transformations of heterometallic complexes **IIa**–**IIl**.

In ethanol, complexes **IIi**–**IIl** with an inner-sphere Ni^{3+} began to decompose already at room temperature, while under reflux the decomposition was complete within 15 h and gave nickelacarborane **IVa**. The yield of the latter (65–70%) was almost independent of the nature of metal M' in the outer sphere of the starting complex. The decomposition of complexes **IIi**–**IIl** in boiling dodecane resulted in formation of nickelacarborane **Va**; its yield (70–80%), too, was scarcely dependent on M'. Complexes **IIb** and **IIf** with an outer-sphere nickel were stable in ethanol both at room temperature and under reflux. Complex **IIb** (but not **IIf**) in dodecane under reflux gave nickelacarborane **Va** in a low yield (~10%). With all the other complexes, no metal carboranes could be found among decomposition products.

Earlier in our thermoanalytical study of complexes **I** (M = Fe, Co) [1, 2] we showed that the complexes undergo an exothermic transformation at 250–360°C with almost no weight loss. Similar behavior was characteristic of most complexes **II**. However, with complexes **IIi** and **IIl** (M = Ni, M' = Fe and Cu, respectively) we faced an unexpected phenomenon: a 20–25% weight gain at 250–450°C under argon.

X-ray photoelectron spectra revealed in residues after thermal analysis appreciable amounts of argon, and the corresponding mass spectra contained a peak at *m/e* 40 due to argon. Thermal analysis of compound **IIi** in air showed no weight change, while in a helium atmosphere a 25–30% weight loss was observed. The ability of cluster compounds to reaction with inert gases has been reported [8]. We proposed that in our case argon reacted with the cluster nickelacarborate arising in the course of thermal analysis of complexes **IIi** and **IIl**. Actually, on thermal analysis of nickelacarborane **IVa** in argon, too, a weight gain of about ~20% was observed.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument in KBr pellets. The UV spectra were measured on a Specord UV-Vis spectrophotometer in 0.5 mM solutions in alcohol. The mass spectra were obtained on an MKh-1320 mass spectrometer at an ionizing voltage of 50 V. Thermal analysis was performed on a MOM OD-103 instrument (Hungary). Analysis for metals was performed by atomic absorption on a Varian Spectr AA-200 instrument; samples were transferred into the water-soluble form by wet combustion. Argon in samples after thermal analysis was detected by X-ray photoelectron spectroscopy on an ES-2401 spectrometer.

Sodium bis-(3)-1,2-dicarbollylferrate, -cobaltate, and -nickelate (**IIIa**–**IIIc**) were synthesized by the procedure in [9].

Complexes II *(general procedure).* To a solution of 1 mmol of salt **III** in 30 ml of water we added a solution obtained by mixing 0.5 mmol of a salt of M'^2 in 6 ml of water and of 2 mmol of 2,2'-bipyridyl in 2 ml of ethanol. The precipitate that formed was separated, washed with water, and dried in a vacuum dessicator over P_2O_5.

Complex IIa. Yield 74%. IR spectrum, ν, cm^{-1}: 2570 s, 1603 s, 1493 m, 1477 m, 1449 s, 1320 m, 1250 m, 1170 m, 1100 m, 1030 m, 980 m, 770 s, 760 m, 658 m, 630 w. UV spectrum, λ_{max}, nm: 211, 244, 295, 307. Mass spectrum, *m/e* (ion): 193 ($C_2H_{11}B_9Co^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2H_{11}B_9^+$), 59 (Co^+), 56 (Fe^+). Found, %: Co 4.20; Fe 8.44; N 8.01. $C_{48}H_{76}B_{36}CoFe_2N_8$. Calculated, %: Co 4.44; Fe 8.50; N 8.45.

Complex IIb. Yield 77%. IR spectrum, ν, cm^{-1}: 2570 s, 1600 s, 1490 m, 1470 m, 1449 s, 1310 s, 1249 m, 1163 m, 1093 m, 1020 m, 977 s, 763 s, 730 m, 650 m, 630 w. UV spectrum, λ_{max}, nm: 211, 249, 295, 308. Mass spectrum, *m/e* (ion): 384 ($C_4H_{22}B_{18}Ni_2^+$), 192 ($C_2H_{11}B_9Ni^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2H_{11}B_9^+$), 58 (Ni^+), 56 (Fe^+). Found, %: Fe 9.05; N 8.48; Ni 4.13. $C_{48}H_{76}B_{36}Fe_2N_8Ni$. Calculated, %: Fe 8.43; N 8.46; Ni 4.43.

Complex IIc. Yield 75%. IR spectrum, ν, cm^{-1}: 2560 s, 1559 s, 1490 m, 1470 m, 1442 s, 1314 m, 1245 m, 1163 m, 1093 m, 1020 s, 976 s, 760 s, 730 m, 650 m, 630 w. UV spectrum, λ_{max}, nm: 213, 236, 244, 283, 294, 307. Mass spectrum, *m/e* (ion): 210 ($C_{10}H_8MnN_2^+$), 190 ($C_2H_{11}B_9^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2H_{11}B_9^+$), 56 (Fe^+), 54 (Mn^+). Found, %: Fe 8.12; Mn 4.02; N 8.20. $C_{48}H_{76}B_{36}Fe_2MnN_8$. Calculated, %: Fe 8.45; Mn 4.16; N 8.48.

Complex IId. Yield 78%. IR spectrum, ν, cm^{-1}: 2550 s, 1614 s, 1490 m, 1470 m, 1455 s, 1321 s, 1251 m, 1170 m, 1103 m, 985 s, 773 s, 740 m, 657 m, 629 w. UV spectrum, λ_{max}, nm: 213, 236, 244, 286, 296, 1320. Mass spectrum, *m/e* (ion): 219 ($C_{10}H_8 \cdot CuN_2^+$), 190 ($C_2H_{11}B_9Fe^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2H_{11}B_9^+$), 63 (Cu^+), 56 (Fe^+). Found, %: Cu 4.79; Fe 8.63; N 8.37. $C_{48}H_{76}B_{36}CuFe_2N_8$. Calculated, %: Cu 4.78; Fe 8.40; N 8.43.

Complex IIe. Yield 70%. IR spectrum, ν, cm^{-1}: 2570 s, 1607 m, 1470 m, 1450 m, 1317 w, 1249 s, 1170 m, 1105 m, 1025 m, 990 m, 770 s, 740 m, 655 w, 620 w. UV spectrum, λ_{max}, nm: 210, 249, 260, 299, 340. Mass spectrum, *m/e* (ion): 386 ($C_4H_{22}B_{18} \cdot Co_2^+$), 215 ($C_{10}H_8N_2Co^+$), 193 ($C_2H_{11}B_9Co^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2H_{11}B_9^+$), 59 ($Co^+$), 56 ($Fe^+$). Found, %: Co 8.64; Fe 4.44; N 8.81. $C_{48}H_{76}B_{36}Co_2FeN_8$. Calculated, %: Co 8.87; Fe 4.20; N 8.43.

Complex IIf. Yield 45%. IR spectrum, ν, cm^{-1}: 2575 s, 1600 m, 1490 m, 1477 m, 1443 s, 1314 m, 1249 w, 1167 m, 1101 m, 1027 m, 990 m, 770 s, 740 m, 650 m, 630 w. UV spectrum, λ_{max}, nm: 211, 250, 296, 307, 338. Mass spectrum, *m/e* (ion): 384–386 ($C_4H_{22}B_{18}M_2^+$), 193 ($C_2H_{11}B_9Co^+$), 156 ($C_{10}H_8 \cdot N_2^+$), 134 ($C_2H_{11}B_9^+$), 59 (Co^+), 58 (Ni^+). Found, %: Co 9.08; N 8.14; Ni 4.60. $C_{48}H_{76}B_{36}Co_2N_8Ni$. Calculated, %: Co 8.86; N 8.42; Ni 4.41.

Complex IIg. Yield 47%. IR spectrum, ν, cm^{-1}: 2550 s, 1600 s, 1490 m, 1470 m, 1448 s, 1320 m, 1245 m, 1170 m, 1107 m, 1030 s, 990 m, 765 s, 730 m, 651 m, 630 w. UV spectrum, λ_{max}, nm: 210, 236, 244, 285, 338. Mass spectrum, *m/e* (ion): 386 ($C_4H_{22}B_{18}Co^+$), 215 ($C_{10}H_8N_2Co^+$), 210 ($C_{10}H_8N_2 \cdot Mn^+$), 193 ($C_2H_{11}B_9Co^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2H_{11}B_9^+$), 59 (Co^+), 54 (Mn^+). Found, %: Co 9.18; Mn 4.23; N 8.39. $C_{48}H_{76}B_{36}Co_2MnN_8$. Calculated, %: Co 8.88; Mn 4.14; N 8.42.

Complex IIh. Yield 52%. IR spectrum, ν, cm^{-1}: 2575 s, 1600 s, 1490 m, 1477 m, 1445 s, 1314 m, 1250 w, 1163 w, 1101 m, 1027 m, 990 m, 770 s, 740 m, 650 w, 625 w. UV spectrum, λ_{max}, nm: 213, 236, 244, 288, 295. Mass spectrum, *m/e* (ion): 386 ($C_4H_{22}B_{18}Co_2^+$), 349 ($C_{12}H_{19}B_9CoN_2^+$), 199 ($C_{10}H_8 \cdot N_2Cu^+$), 193 ($C_2H_{11}B_9Co^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2H_{11}B_9^+$), 63 (Cu^+), 59 (Co^+). Found, %: Co 9.58; Cu 3.2; N 8.24. $C_{48}H_{76}B_{36}Co_2CuN_8$. Calculated, %: Co 8.82; Cu 4.76; N 8.38.

Complex IIi. Yield 74%. IR spectrum, ν, cm^{-1}: 2575 s, 1605 m, 1470 m, 1450 s, 1320 m, 1250 m, 1170 m, 1080 s, 1030 w, 980 s, 770 s, 740 m, 652 w, 630 w. UV spectrum, λ_{max}, nm: 210, 249, 292, 299, 349. Mass spectrum, *m/e* (ion): 384 ($C_4H_{22}B_{18}Ni_2^+$), 324 ($C_4H_{22}B_{18}Ni^+$), 214 ($C_{10}H_8N_2Ni^+$), 192 ($C_2H_{11} \cdot B_9Ni^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2H_{11}B_9^+$), 58 (Ni^+), 56 (Fe^+). Found, %: Fe 4.15; N 8.61; Ni 8.35. $C_{48}H_{76} \cdot B_{36}FeN_8Ni_2$. Calculated, %: Fe 4.20; N 8.43; Ni 8.84.

Complex IIj. Yield 69%. IR spectrum, ν, cm^{-1}: 2570 s, 1600 s, 1490 m, 1470 m, 1443 s, 1313 m, 1243 m, 1163 m, 1080 m, 1020 m, 973 s, 763 s, 730 m, 650 m, 630 w. UV spectrum, λ_{max}, nm: 210, 250, 295. Mass spectrum, *m/e* (ion): 347 ($C_{12}H_{19}B_9 \cdot N_2Ni^+$), 324 ($C_4H_{22}B_{18}Ni^+$), 215 ($C_{10}H_8N_2Co^+$), 192 ($C_2B_9H_{11}Ni^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2B_9H_{11}{}^+$), 59 ($Co^+$), 58 ($Ni^+$). Found, %: Co 3.90; N 8.18; Ni 8.92. $C_{48}H_{76}B_{36}CoN_8Ni_2$. Calculated, %: Co 4.42; N 8.42; Ni 8.82.

Complex IIk. Yield 60%. IR spectrum, ν, cm^{-1}: 2570 s, 1600 s, 1490 m, 1470 m, 1449 s, 1320 s, 1250 m, 1170 m, 1080 m, 1020 s, 977 s, 763 s, 740 s, 651 m, 630 w. UV spectrum, λ_{max}, nm: 210, 238, 244, 284, 308, 354. Mass spectrum, *m/e* (ion): 576 ($C_6H_{33}B_{27}Ni_3^+$), 324 ($C_4H_{22}B_{18}Ni^+$), 214 ($C_{10}H_8N_2 \cdot Ni^+$), 192 ($C_2H_{11}B_9Ni^+$), 156 ($C_{10}H_8N_2^+$), 134 ($C_2B_9 \cdot H_1{}^+$), 58 (Ni^+), 54 (Mn^+). Found, %: Mn 4.15; N 7.82; Ni 8.60. $C_{48}H_{76}B_{36}MnN_8Ni_2$. Calculated, %: Mn 4.14; N 8.44; Ni 8.85.

Complex IIl. Yield 78%. IR spectrum, ν, cm^{-1}: 2530 s, 1605 s, 1490 m, 1470 m, 1449 s, 1320 s, 1250 m, 1166 m, 1093 w, 1030 m, 973 m, 766 s, 730 m, 651 m, 630 w. UV spectrum, λ_{max}, nm: 211, 244, 289. Mass spectrum, *m/e* (ion): 384 ($C_4H_{22}B_{18} \cdot Ni_2^+$), 347 ($C_{12}H_{19}B_9N_2Ni^+$), 324 ($C_4H_{22}B_{18}Ni^+$), 214 ($C_{10}H_8N_2Ni^+$), 156 ($C_{10}H_8N_2^+$), 192 ($C_2H_{11}B_9Ni^+$), 134 ($C_2H_{11}B_9^+$), 63 ($Cu^+$), 58 ($Ni^+$). Found, %: Cu 4.89; N 8.39; Ni 9.30. $C_{48}H_{76}B_{36}CuN_8Ni_2$. Calculated, %: Cu 4.76; N 8.39; Ni 8.79.

Decomposition of complexes IIi–IIl. *a. In ethanol.* A mixture of 0.2 mmol of complex **II** and 50 ml of absolute ethanol was heated under reflux under argon for 15 h. After cooling, the precipitate was separated, washed with ethanol, and dissolved in acetone. The solution was chromatographed on a column of Al_2O_3 (eluent acetone–hexane, 1:1). A dark rose fraction was separated, the solvent was removed, and the residue was dried in a vacuum over P_2O_5 to obtain *o*-nickelacarborane **IVa**. The product is identical to that reported in [7]. Yield 65–70%.

b. In dodecane. A mixture of 0.2 mmol of complex **II** and 30 ml of dodecane was heated under reflux under argon for 5 h and then treated as described above to obtain *m*-nickelaborane **Va**. The product is identical to that reported in [7]. Yield 70–85%. Under the same conditions, from complex **IIb** we obtained *m*-nickelacarborane, yield 10%.

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