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Nickel(II) Closododecaborates

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The reaction of nickel complexes of the general formula NiL_2X_2 *(L = Ph₃P; X = Cl, Br, I, SCN) with closododecaborates* $M_2B_{12}X_{12}$ *(M = Ph₄P, Na, K, Cs; X = H, Cl, Br) have been studied, using the molar ratio method, in acetone and acetonitrile and their mixtures with water at 20 °C. Compounds* $NiB_{12}Cl_{12}\cdot 6CH_3CN$ *and* $NiB_{12}Br_{12}\cdot 7CH_3CN$ *have been isolated and characterized.*

The magnetic, spectroscopic and thermal characteristics of these compounds have been examined. It is shown that the molecules of acetonitrile are bonded to the nickel ion via the nitrogen atom and that complex cation $Ni(CH_3CN)_6^{2+}$ *is present in both compounds, its interaction with the borane anion being ionic.*

Introduction

The compounds of polyhedral closoborane anions $B_{12}X_{12}^{2-}$ (X = H, Cl, Br, I), known at present, are primarily confined to salts of elements of groups I–III or organic cations $[R_4N]^+$, $[R_4P]^+$, $[R_4As]^+$ [1, 2]. Very little is known about compounds of transition metals with the above anions. It is known, for example, that $[Ni(H_2O)_6]B_{12}Cl$ [1] and $[Ni(H_2O)_6]B_{12}H_{12}$ [2] were isolated through interaction of nickel carbonate with an aqueous solution of the appropriate acid. The physicochemical characteristics of these compounds are virtually unknown.

This paper is concerned with a study of the interaction of complexes NiL_2X_2 (L = Ph_3P; X = Cl, Br, I, SCN) with closododecaborates $M_2B_{12}X_{12}$ (M = Ph_4P, Na, K, Cs; X = H, Cl, Br).

Experimental

The starting compounds, namely NiL_2X_2 [3], $M_2B_{12}X_{12}$ [1, 2] and organic solvents [4], were synthesized and purified by conventional techniques. The degree of purity of the solvents was checked by refractive indices, while that of acetonitrile was checked by a UV spectrum.

IR spectra in the region 400–4000 cm^{-1} were taken with the compounds being suspended in Nujol and pressed into KBr pellets on UR-20 spectrophotometer. Spectra in the region 400–33 cm^{-1} were taken in Nujol on a Hitachi FIS-3 instrument.

Electron absorption spectra of the solutions in the region 300–750 nm were taken on a "Specord UV–Vis" spectrophotometer, while those of the compounds pressed into KBr pellets were taken on an SF-26 spectrophotometer in the region 300–1100 nm.

Thermogravigrams were obtained on a Paulik–Erdei derivatograph (Hungary) at a heating rate of 10 °C/min.

The magnetic susceptibility was measured by the Gouy method.

ESCA spectra were taken on a VIEE-15 spectrometer. The reproducibility of energies was ±0.1 eV.

Since absorption in the visible region is exhibited only by nickel complexes, the solvent spectra were studied by the "saturation method": the concentration of NiL_2X_2 was maintained constant throughout, whereas the concentration ratio $C_M^{M_2B_{12}X_{12}}/C_M^{NiL_2X_2}$ was varied from 0.5 to 2.5. The concentration of the absorbing compound was selected such that the optical density of the solutions ranged from 0.4 to 0.7. The working solutions were prepared immediately prior to photometry, and repeated recording was taken after an hour.

Results and Discussion

Studies of NiL_2X_2 (X = Br, I)–$M_2B_{12}X_{12}$ (M = K, Cs; X = Cl, Br)–acetonitrile systems in working solutions involved precipitation of a colored residue insoluble in ether and in benzene. In the rest of the systems, no perceptible interaction between the compound was observed.

IR spectra and X-ray diffraction patterns of the colored residue powder have shown that it contained a potassium or cesium halide, as well as an unknown compound. The resulting complex was synthesized as follows:

A solution of NiL_2I_2 (1.02 g; 1.22 mmol) in 100 ml of anhydrous acetonitrile was added, with continuous stirring, to a solution of $Cs_2B_{12}Cl_{12}$ (2.00 g; 2.44 mmol) in 75 ml of acetonitrile. The reddish

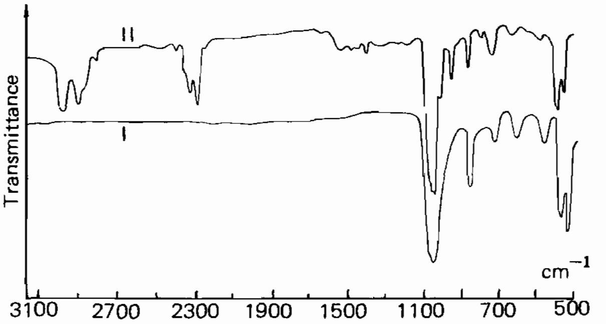

Figure 1. Infrared spectra of $NiB_{12}Cl_{12}\cdot 6CH_3CN$ (II) and $Cs_2B_{12}Cl_{12}$ (I).

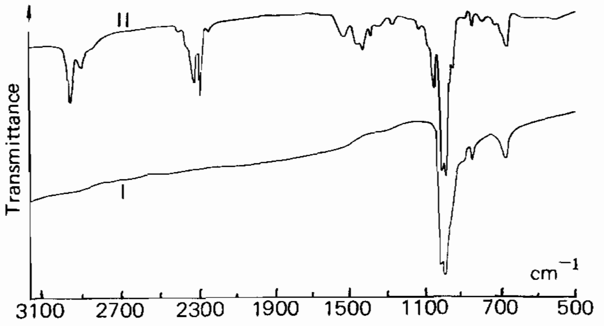

Figure 2. Infrared spectra of $NiB_{12}Br_{12}\cdot 7CH_3CN$ (II) and $Cs_2B_{12}B_{12}$ (I).

brown color of the NiL_2I_2 solution changed to pale yellow, which was followed by precipitation of a lilac-colored finely crystalline residue. The reaction was over after 25 to 30 minutes. The residue was washed several times on a glass filter with small amounts of slightly heated acetonitrile, then with absolute ether and finally dried in air at 105–110 °C. The yield was 98%, as calculated with respect to $(Ph_3P)_2NiI_2$. *Anal.* Calculated for $C_{12}N_6H_{18}NiB_{12}Cl_{12}$: C 16.8; N 9.8; H 2.1; Ni 6.8; $B_{12}Cl_{12}$ 64.6. Found: C 16.7; N 9.8; H 2.3; Ni 6.8; $B_{12}Cl_{12}$ 65.0%. A similar method was used to synthesize the compound $NiB_{12}Br_{12}7CH_3CN$.

Calculated for $C_{14}N_7H_{21}NiB_{12}Br_{12}$: C 11.7; N 6.8; H 1.5; Ni 4.1; $B_{12}Br_{12}$ 75.9. Found: C 12.0; N 6.9; H 1.8; Ni 4.1; $B_{12}Br_{12}$ 76.0%.

The compounds form as follows

$$(Ph_3P)_2NiI_2 + Cs_2B_{12}X_{12} \xrightarrow{CH_3CN} NiB_{12}X_{12}\cdot nCH_3CN + Ph_3P + CsI$$

Attempts to conduct synthesis from binary nickel halides and their hexahydrates have failed.

Both compounds are lilac-colored, finely crystalline powders stable on air. They are insoluble in benzene, toluene, chloroform, dioxane, nitrobenzene, cyclohexane, methylene chloride and ether. The compounds are not isostructural.

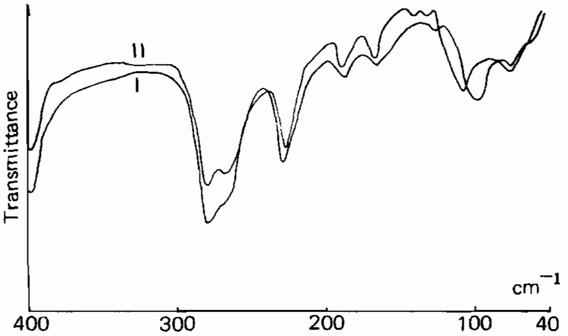

Figure 3. Far-infrared spectra of complexes $NiB_{12}Br_{12}\cdot 7CH_3CN$ (I) and $NiB_{12}Cl_{12}\cdot 6CH_3CN$ (II) in Nujol mull.

The IR spectra (Fig. 1, 2) in the region 400–4000 cm^{-1} reveal absorption bands of both polyhedral ions and acetonitrile. The shape and position of the absorption bands related to vibrations of B–B and B–Hal bonds are similar to those observed in the case of starting salts $Cs_2B_{12}X_{12}$ (X = Cl, Br). The absorption band associated with the valence vibrations of the cyano group is shifted 56 cm^{-1} towards the high-frequency region, while the combined (ν_3 + ν_4) band is shifted by 47 cm^{-1} as compared with the free nitrile [5], which is due to the coordination metal–nitrogen bond, just as in the case of $NiHal_2\cdot nCH_3CN$ [6].

The IR spectra in the region 400–33 cm^{-1} (Fig. 3) are very similar and also reveal absorption bands of polyhedral anions, invariable as compared with the starting salts. The absorption band at 396 cm^{-1} is associated with the deformation vibrations of δ(CCN), the composite band at 280 to 266 cm^{-1} is associated with the valence vibrations of ν(Ni–N) and the absorption band at 230 cm^{-1} is associated with the wagging vibration of Ni–NCC [7]. The absorption band at 189 cm^{-1} seems to be related to the deformation vibrations of N–Ni–N.

The values of effective magnetic moments coincide with those of the magnetic moments known for nickel complexes featuring an octahedral structure of inner coordination shell.

The absorption bands in the electron spectra (Table I) also corroborate the octahedral environment of the nickel ion and are indicative of the presence of cation $Ni(CH_3CN)_6^{2+}$ [8].

The binding energie $Ni_{2p}{}^{3/2}$ (Table II) are consistent with the electron and vibrational spectroscopy data. The ESCA data suggest that the acetonitrile molecules are equivalent with the donor nitrogen atoms in both complexes. The electron characteristic of the central atom appreciably varies from the starting NiL_2I_2 to the complex with the closoborane anion. The change of binding energy $Ni_{2p}{}^{3/2}$ of 3 eV is connected with withdrawing of electron density from the central atom despite the presence of molecules of the ligand-donor in the inner coordination

TABLE I. Electronic Spectra and Magnetic Data of Nickel–Borane–Acetonitrile Complexes.

Compound	Transitions (cm^{-1})				
	$^3A_{1g} \rightarrow {}^3T_{2g}$	$^3A_{1g} \rightarrow {}^3T_{1g}(F)$	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$	Dq	μ_{eff} B.M.
$NiB_{12}Cl_{12} \cdot 6CH_3CN$	11000	17500	28000	1100	3,29
$NiB_{12}Br_{12} \cdot 7CH_3CN$	11000	17400	27300	1100	3,18

TABLE II. X-ray Photoelectron Spectra of Complexes and Starting Compounds.[a]

Compound	Ni $2p^{3/2}$	B 1s	Cl 2p[b]	N 1s
$NiB_{12}Cl_{12} \cdot 6CH_3CN$	857.7	190.3	200.1	400.3
$NiB_{12}Br_{12} \cdot 7CH_3CN$	857.9	190.3	70.1[b]	400.4
$Cs_2B_{12}Cl_{12}$	–	190.8	199.8	–
$Cs_2B_{12}Br_{12}$	–	190.3	70.5[b]	–
$(Ph_3P)_2NiI_2$	854.8	–	–	–

[a] Binding energy in eV. [b] Br3p level.

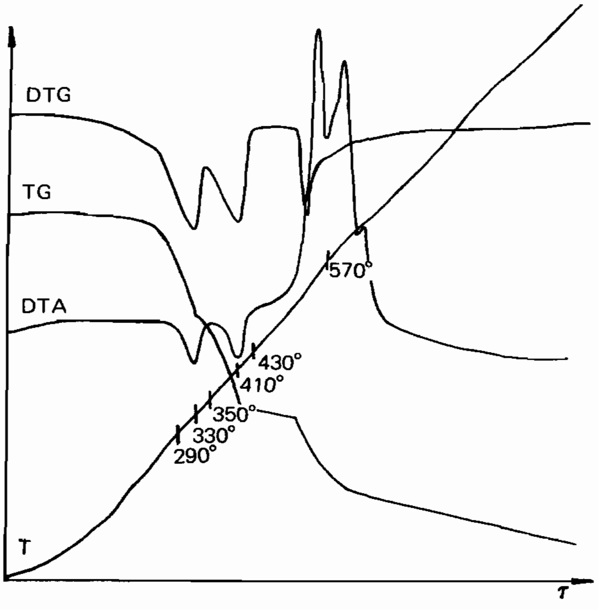

Fig. 4. Thermal decomposition of $NiB_{12}Cl_{12} \cdot 6CH_3CN$.

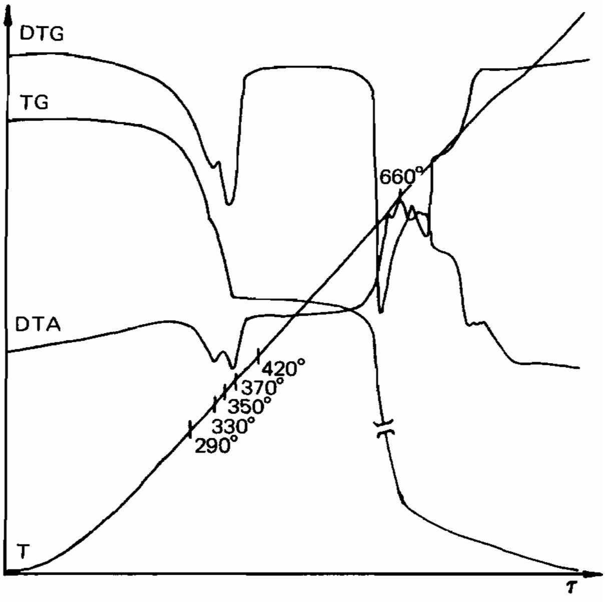

Figure 5. Thermal decomposition of $NiB_{12}Br_{12} \cdot 7CH_3CN$.

shell. In the borane anion, in contrast with the starting salts, the boron and halide atoms practically retain their energy characteristics.

Examination of the thermal properties has shown that the synthesized compounds differ drastically in thermal stability from the known nitrile complexes $NiHal_2 \cdot nCH_3CN$ [9]. The thermogravigrams (Figs. 4, 5) show two endothermal effects starting at 290 and 350 °C, respectively. The mass loss at each stage of decomposition of $NiB_{12}Cl_{12} \cdot 6CH_3CN$ corresponds to the detachment of three acetonitrile molecules. In the case $NiB_{12}Br_{12} \cdot 7CH_3CN$ four CH_3CN molecules are detached at the first stage and three molecules at the second stage. The total mass loss at two decomposition stages agrees well with the chemical analysis data and coresponds to the detachment of six and seven acetonitrile molecules, respectively. The complex exothermal effect within the range of 510–640 °C is most likely to be due to the decomposition of $NiB_{12}X_{12}$. Isolation and investigation of this compound is difficult because of its extremely high hygroscopicity.

It can be assumed that the stability of the synthesized compounds is a consequence of the similar sizes of the complex cation and polyhedral anions. This is also corroborated by the fact that no interaction takes place, under the same conditions, between the NiL_2X_2 and anion $B_{12}H_{12}^{2-}$ which is smaller in size than its halogenated derivatives.

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