

COBALTACARBORANYLACETYLENE 8,8'-(μ -CH \equiv C-CH $_2$ S)-(1,2-C $_2$ B $_9$ H $_{10}$) $_2$ -3-Co(III): SYNTHESIS, CHARACTERIZATION AND POLYMERIZATION OF NEW SUBSTITUTED ACETYLENE

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Synthesis, structure and properties of 8,8'-(μ -propargylthio)bis(1,2-dicarbollido)cobaltate, 8,8'-(μ -CH \equiv C-CH $_2$ S)-(1,2-C $_2$ B $_9$ H $_{10}$) $_2$ -3-Co(III), are described (NMR, IR, and UV spectra, mass spectrum, X-ray structure, dipole moment) and transformation of this acetylenic monomer into a π -conjugated homopolymer is reported.

Key words: Bridged metallocarborane; Substituted acetylenes; Metathesis; π -Conjugated polymers.

Molecules of boranes and heteroboranes involve multicenter (mostly three-center) two-electron bonds¹⁻⁴ that are delocalized in the molecular skeletons³⁻⁷. Thus, they can be regarded as formally electron-deficient conjugated systems – a counterpart of the electron-balanced σ -conjugated (polysilanes) and electron-rich π -conjugated systems (aromatics, conjugated polyenes).

Molecules in which electron-deficient and electron-rich conjugated systems are linked together can possess interesting physical properties. Some low-molecular-weight compounds involving metallocarborane skeleton linked with aromatic rings have already been described (e.g. 8,8'-(μ -*o*-phenylene)- and 4,8'-8,4'-(bis- μ -*o*-phenylene)bis(dicarbollido)cobalt(1-)-ate ions⁸⁻¹⁰). However, no polymer involving carborane and/or metallocarborane groups linked with π -conjugated chain has been reported in the literature although great attention has been devoted to π -conjugated polymers due to their potential use as advanced materials in construction of organic material-based electronic and optoelectronic devices¹¹⁻¹⁵.

Synthesis and characterization of a hitherto unreported functional metallocarborane bearing acetylenic group and its transformation into π -conjugated polymer with metallocarborane substituents is the subject of the present communication.

EXPERIMENTAL

Chemicals

Decaborane $B_{10}H_{14}$ (Katchem Inc., Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic), propargyl bromide (Aldrich), inorganic bases (KOH, NaH), acids, salts, auxiliary compounds and solvents were of analytical or reagent grade and were used as supplied. $WOCl_4$, $(C_6H_5)_4Sn$ (both Aldrich) and benzene (Lachema) were purified as described earlier^{16,17}.

Synthesis of 8,8'-(μ -Propargylthio)-(1,2- $C_2B_9H_{10}$)₂-3-Co(III) (A)

Freshly distilled propargyl bromide (1.80 g, 15 mmol) was added to a deep blue-green solution of $[8,8'-\mu-S(1,2-C_2B_9H_{10})_2-Co(III)]^- Cs^+$ (4.8 g, 10 mmol; for preparation see ref.¹⁸) in acetone (50 ml). The colour changed gradually to a permanent deep red within 30 min at ambient temperature. After all the starting anion had disappeared (according to TLC), the solution was filtered and the acetone evaporated in vacuo. The solid residue was dissolved in methylene chloride (50 ml) and filtered through a short column of silica gel to remove ionic impurities. The eluate was concentrated to 30 ml and then carefully layered with hexane (70 ml). Deep red prisms of **A** separated after three days (4.52 g, 91%). Well developed crystals were picked up for X-ray diffraction. An additional crop was obtained from the mother liquors by stripping off the solvents in vacuo.

Polymerization of A

Polymerization was carried out at room temperature using the vacuum break-seal technique¹⁶. Saturated benzene solution of $WOCl_4$ catalyst (3.4 mg, 10 μ mol in 1 ml) was mixed with solid Ph_4Sn cocatalyst (8.5 mg, 20 μ mol) and the stirred mixture was allowed to ripen for 15 min. Then a benzene solution (1 ml) of **A** (1 mmol, 393 mg) was added and the resulting mixture was allowed to react for 72 h (the polymer precipitated from the reaction mixture). The reaction was quenched with methanol (5 ml), the suspension was filtered and the solid polymer was washed with methanol and dried in vacuum to constant weight. Yield 390 mg (100%) of orange-red solid polymer, insoluble in aromatic solvents, tetrahydrofuran (THF), 1,4-dioxane, dimethylformamide, acetone, methyl ethyl ketone and acetates. The polymer was partly soluble in dimethyl sulfoxide, mainly at temperatures above ca 50 °C.

Methods

NMR spectra were taken on Varian Unity 500 (¹H at 499.84 MHz; ¹¹B at 160.36 MHz) and Varian Unity 200 (¹H at 200.06 MHz; ¹¹B at 64.16 MHz; ¹³C at 50.31 MHz) spectrometers. The ¹H and ¹³C spectra were referenced to the solvent (deuterioacetone), the ¹¹B spectra to trimethoxyborane.

IR spectra of non-diluted powdered samples were measured by means of the diffuse reflectance technique in the range 7 500–400 cm^{-1} using an FTIR Nicolet 210 instrument (128 scans, resolution 4 cm^{-1}). The spectra were collected in the log (1/R) (R is reflectance) format and then transformed to Kubelka–Munk units.

UV spectra were recorded using a Hewlett–Packard 8452 diode-array spectrometer, quartz cuvette (optical path 0.2 mm) using dimethyl sulfoxide and THF as solvents.

X-Ray diffraction. A red crystal of the dimensions $0.29 \times 0.4 \times 0.4$ mm was measured at 22 °C on a CAD4-MACHIII diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.71069$ Å). Absorption was neglected ($\mu = 0.978$ mm $^{-1}$). The lattice parameters were determined from 25 reflections in the 16–17° θ -range. Intensities of the reflections were measured using the θ – 2θ scan between h $\langle -15, 13 \rangle$, k $\langle 0, 13 \rangle$, l $\langle 0, 17 \rangle$, $(\sin\theta/\lambda)_{\max} = 0.59$ Å. Three standard reflections, monitored every 1 h, showed 3% variation during measurement. From 3 529 measured reflections, 3 400 were unique ($R_{\text{int}} = 0.019$) and 2 769 of them were regarded as “observed” using the $I \geq 2\sigma(I)$ criterion.

X-Ray data treatment. The Co atom coordinates were determined from Patterson synthesis (SHELXS86). The structure was developed by successive Fourier synthesis and all non-hydrogen atoms were anisotropically refined (SHELXL93). Positions of hydrogen atoms were found on difference Fourier map and atoms were refined isotropically. The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ where $w = 1/[\sigma^2(F_o^2)(0.0592 P^2 + 0.39P)]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$. Convergence for 336 refined parameters was achieved at $R = 0.03$ for the observed reflections and $wR_2 = 0.085$, $S = 1.04$ with $(\Delta/\sigma)_{\max} = 0.001$ for all reflections. The final difference electron map showed no peaks of chemical significance (extreme values of ± 0.41 e/Å 3). The final fraction coordinates are given in Table I, the selected bond distances and bond angles in Table II.

Mass spectrum of **A** was obtained with an INCOS 50 (Finnigan-MAT Corp.) quadrupole spectrometer operating in the EI mode, using the method of direct exposure probe and heating rate 15 mA s $^{-1}$.

Thin-layer chromatography was performed using commercial Silufol sheets (Kavalier, Votice; silica gel on aluminium foil, 3% of starch as binder).

Dipole moment was determined by Guggenheim–Smith method in benzene. Relative permittivities were measured on an instrument with direct frequency reading¹⁹. Refractive indices were measured on an Aerograph RI detector (Varian).

RESULTS AND DISCUSSION

Basic Characteristics of **A**

Molecular weight. Relative molecular mass calculated for C $_7$ H $_{23}$ B $_{18}$ CoS is 392.82. Relative intensities of molecular peaks as determined by mass spectrometry were found to be in good agreement with the theoretical values. Molecular ion mass (measured/calculated relative intensity): 388 (4.5/4.4), 389 (13.4/13.3), 390 (32.0/32.0), 391 (60.7/60.6), 392 (89.7/89.6), 393 (100/100), 394 (80.4/80.4), 395 (43.1/43.3), 396 (13.8/13.8), 397 (2.5/2.4).

X-Ray crystal data: monoclinic, space group $P2_1/c$ (No. 14), $a = 13.186(1)$ Å, $b = 11.721(1)$ Å, $c = 15.082(2)$ Å, $\beta = 123.470(8)^\circ$, unit cell volume $V = 1 944.4(3)$ Å 3 , $Z = 4$, calculated density $D_c = 1.342$ g cm $^{-3}$, $F(000) = 792$. Geometric parameters of the borane cages, i.e. bond distances, bond angles as well as the angle between the planes C1,C2,B4,B7,B8 and C1',C2',B4',B7',B8', which is equal to 16.5(1)°, are similar to those in the related compound 8,8'-(μ -CH $_3$ OCOCH $_2$ S)-(1,2-C $_2$ B $_9$ H $_{10}$) $_2$ -3-Co(III) (ref.²⁰). The acetylenic group is inclined towards the cage C1–B11 as indicated by differences in: (i) the distances C4-to-B8 and C4-to-B8' which are equal to 3.550(4) Å and 4.275(4) Å, respectively; and (ii) the dihedral angles B8–S–C3–C4 and B8'–S–C3–C4 equal to $-84.3(2)^\circ$ and $171.0(2)^\circ$. View of the 8,8'-(μ -HC \equiv C–CH $_2$ S)-(1,2-C $_2$ B $_9$ H $_{10}$) $_2$ Co

TABLE I

Atomic coordinates ($1 \cdot 10^{-4}$) and equivalent isotropic displacement parameters, U_{eq} (10^{-3} \AA^2), for **A**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Co	2985(1)	86(1)	2250(1)	31(1)
S	1203(1)	-1877(1)	1509(1)	36(1)
C1	3579(2)	566(2)	1277(2)	44(1)
C2	4584(2)	-117(2)	2309(2)	45(1)
B4	2220(3)	-98(2)	613(2)	38(1)
B5	3189(3)	-141(3)	137(3)	50(1)
B6	4705(3)	-118(3)	1222(3)	58(1)
B7	4041(2)	-1354(2)	2480(2)	39(1)
B8	2492(2)	-1371(2)	1372(2)	32(1)
B9	2485(3)	-1411(2)	186(2)	42(1)
B10	4020(3)	-1420(3)	563(3)	51(1)
B11	4962(3)	-1354(3)	1964(3)	51(1)
B12	3608(3)	-2181(2)	1333(2)	42(1)
C1'	2500(2)	1600(2)	2632(2)	46(1)
C2'	3522(2)	918(2)	3655(2)	46(1)
B4'	1291(2)	786(2)	1778(2)	38(1)
B5'	1211(3)	1777(3)	2629(3)	52(1)
B6'	2641(3)	1880(3)	3818(3)	59(1)
B7'	3137(2)	-464(2)	3641(2)	40(1)
B8'	1671(2)	-574(2)	2426(2)	34(1)
B9'	666(3)	363(3)	2509(2)	42(1)
B10'	1506(3)	1046(3)	3768(3)	50(1)
B11'	3017(3)	549(3)	4448(3)	53(1)
B12'	1793(3)	-414(3)	3652(2)	43(1)
C3	1848(3)	-3115(2)	2399(2)	45(1)
C4	1714(3)	-4124(2)	1797(2)	54(1)
C5	1587(5)	-4912(3)	1291(4)	89(1)

TABLE II
Selected atom distances (Å) and bond angles (°) with e.s.d's in parentheses for **A**

Atoms	Distances	Atoms	Distances
S-B8	1.916(2)	S-B8'	1.920(3)
Co-B8	2.035(2)	Co-B8'	2.044(3)
Co-B7	2.091(3)	Co-B7'	2.097(3)
Co-B4	2.099(3)	Co-B4'	2.101(3)
Co-C2	2.075(2)	Co-C2'	2.072(2)
Co-C1	2.085(2)	Co-C1'	2.073(2)
C1-C2	1.595(4)	C1'-C2'	1.594(4)
C1-B4	1.685(4)	C1'-B4'	1.687(4)
C1-B5	1.712(4)	C1'-B5'	1.709(4)
C1-B6	1.731(4)	C1'-B6'	1.726(4)
C2-B7	1.699(4)	2'-B7'	1.695(4)
C2-B11	1.705(4)	C2'-B11'	1.714(4)
C2-B6	1.733(4)	C2'-B6'	1.731(4)
B4-B9	1.776(4)	B4'-B9'	1.773(4)
B4-B5	1.778(4)	B4'-B5'	1.777(4)
B4-B8	1.792(3)	B4'-B8'	1.790(4)
B5-B6	1.751(5)	B5'-B6'	1.748(5)
B5-B10	1.757(4)	B5'-B10'	1.761(5)
B5-B9	1.777(4)	B5'-B9'	1.777(4)
B6-B11	1.746(5)	B6'-B11'	1.750(5)
B6-B10	1.772(5)	B6'-B10'	1.754(5)
B7-B11	1.767(4)	B7'-B11'	1.768(4)
B7-B12	1.780(4)	B7'-B12'	1.781(4)
B7-B8	1.788(4)	B7'-B8'	1.790(4)
B8-B12	1.778(4)	B8'-B12'	1.776(4)
B8-B9	1.784(3)	B8'-B9'	1.777(4)
B9-B10	1.775(4)	B9'-B10'	1.776(4)
B9-B12	1.782(4)	B9'-B12'	1.784(4)
B10-B11	1.766(5)	B10'-B11'	1.762(5)
B10-B12	1.771(4)	B10'-B12'	1.782(4)
B11-B12	1.777(4)	B11'-B12'	1.783(4)
S-C3	1.836(3)	C3-C4	1.442(4)
C3-H31	0.97(3)	C3-H32	0.89(3)
C4-C5	1.150(5)	C5-H5	0.81(4)

TABLE II
(Continued)

Atoms	Angles	Atoms	Angles
B8-S-B8'	83.10(11)	C3-S-B8'	105.48(12)
C3-S-B8	104.09(12)	S-C3-H32	103(2)
S-C3-H31	106(2)	H31-C3-H32	111(2)
S-C3-C4	109.9(2)	C4-C3-H32	113(2)
C4-C3-H31	113(2)	C4-C5-H51	168(3)
C3-C4-C5	178.1(4)		

molecule with the atom numbering is shown in Fig. 1 and packing of the molecules in the unit cell in Fig. 2.

Dipole moment. The measured value of dipole moment, $(17.7 \pm 0.3) \cdot 10^{-30}$ C m (i.e. 5.3 ± 0.1 D), proves an extremely high polarity of the $S^{\delta+}$ -to-cobaltacarbollide $^{\delta-}$ bonds.

UV/VIS spectrum of A is shown in Fig. 3 (curve 1). The molar absorption coefficient of the main band at 290 nm, characteristic of cobaltacarbollides, was determined to be $\epsilon_{290} = 31\,800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. There is a satellite band with two maxima at 442 nm and about 500 nm in the visible region with equivalent values of molar absorption coefficient: $\epsilon_{442} = \epsilon_{500} = 520 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

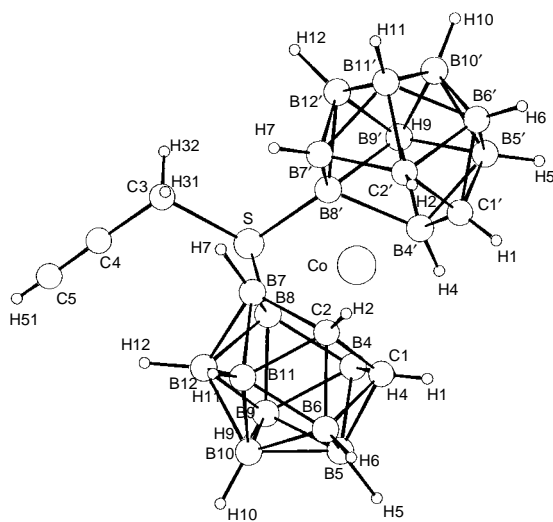


FIG. 1
Structure of 8,8'-(μ -CH \equiv C-CH $_2$ S)-(1,2-C $_2$ B $_9$ H $_{10}$) $_2$ -3-Co(III) as determined by X-ray diffraction

NMR Spectra of **A**

The ^{11}B NMR (160.36 MHz) spectrum of the propargyl cobaltacarborane **A** consists of 7 signals which can be assigned to the following boron atoms (numbering in accordance with Fig. 1); [δ in ppm, (intensity), $J(^{11}\text{B}^1\text{H})$]: B10 1.22 d (1) 146.5; B8 -4.49 s (1); B4 -6.60 d (1) 149.5; B7 -7.93 d (1) not determined; B9 and B12 -8.54 d (2) ca

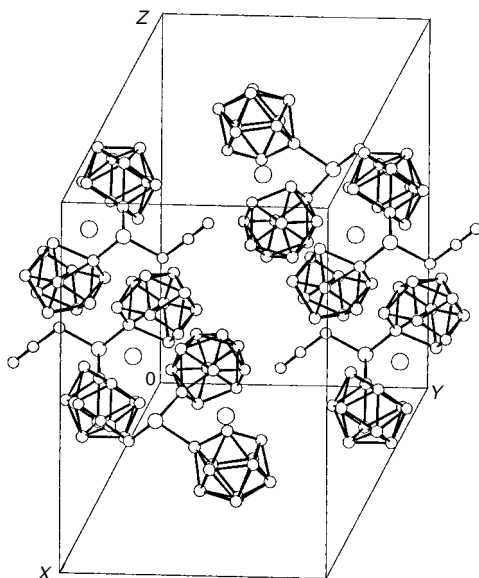


FIG. 2
Packing of the molecules of 8,8'-($\mu\text{-CH}\equiv\text{C-CH}_2\text{S}$)-(1,2- $\text{C}_2\text{B}_9\text{H}_{10}$) $_2$ -3-Co(III) in the cell unit

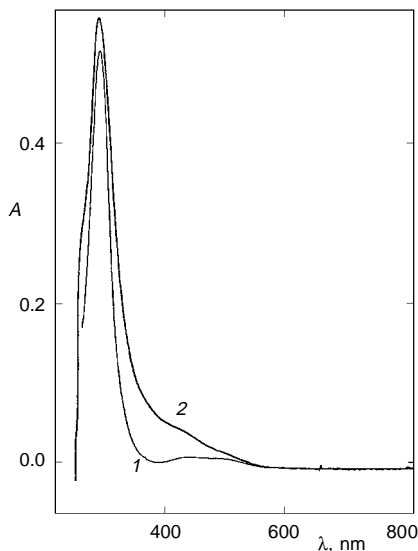


FIG. 3
UV/VIS spectra of 8,8'-($\mu\text{-CH}\equiv\text{C-CH}_2\text{S}$)-(1,2- $\text{C}_2\text{B}_9\text{H}_{10}$) $_2$ -3-Co(III) in THF (1) and soluble fraction of poly[8,8'-($\mu\text{-CH}\equiv\text{C-CH}_2\text{S}$)-(1,2- $\text{C}_2\text{B}_9\text{H}_{10}$) $_2$ -3-Co(III)] in DMSO (2)

146; B5 and B11 -14.65 d (2) 161.7; B6 -22.02 d (1) 170.9. The assignment was made on the basis of a comparison with ^{11}B NMR spectrum of the methyl analog of **A** (B10 1.22; B8 -4.19 s; B4 and B7 -6.82 ; B9 and B12 -8.45 ; B5 and B11 -14.65 ; B6 -22.04 , ref.⁸) and the analysis of ^{11}B - $^{11}\text{B}(^1\text{H})$ 2D COSY NMR spectrum. The found diversity in the shifts of the B4 and B7 atoms can be explained as the result of an additional shielding of the B7 atom by the ring current of the acetylenic bond. Due to tetrahedral arrangement of the sulfur bridge (the lone electron pair forms the fourth vertex), the propargyl group is declined to one side of the B8-S-B8' plane, shielding thus preferentially two analogous BH-vertices B7 and B7' (see the structure in Fig. 1).

The appropriate ^1H signals exhibit the following chemical shifts: H10 2.98; H4 2.21; H7 3.72; H9 and H12 2.26; H5 and H11 1.92; H6 1.81. These were assigned using selective ^{11}B - ^1H decoupling. Also here, the acetylenic group shows an important shielding of the H7 atom. The ^1H signals of hydrogens linked with carbons exhibit the following shifts: 3.14 t (H51, acetylene); 4.10 d (H31 and H32, CH_2); 4.29 s (H1 and H2, skeleton). The ^{13}C signals were assigned as follows: 29.42 (C3); 51.86 and 51.92 (C1 and C2, skeletal); 75.80 (C4); 77.20 (C5).

IR Spectrum of **A**

The IR spectrum of **A** (Fig. 4, curve 1) has been interpreted on the basis of the characteristic group frequencies^{21,22} (propargylthio group) and ref.²³ (cobaltacarborane skeleton).

The following bands attributable to cobaltacarborane skeleton were observed: (i) the strongest band in the spectrum at $2\,622\text{ cm}^{-1}$ (with overtone at $5\,186\text{ cm}^{-1}$), attributable to $\nu(\text{B-H})$ fundamental vibrations in the skeleton; (ii) band at $3\,042\text{ cm}^{-1}$ and satellite

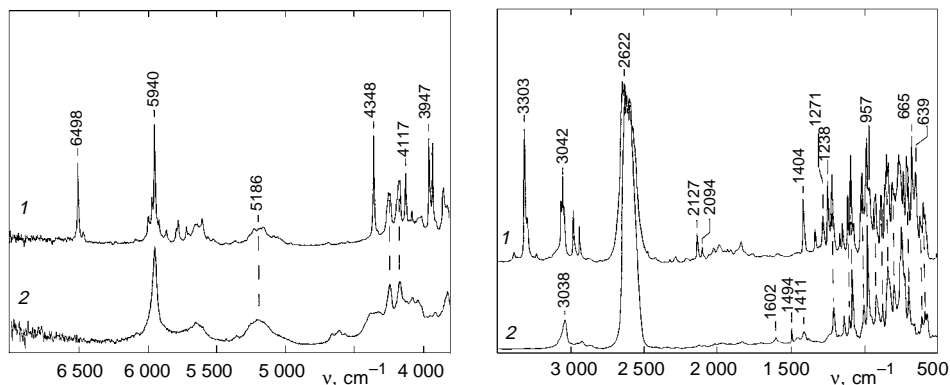


FIG. 4

Diffuse reflectance IR spectra (Kubelka-Munk units) of 8,8'-($\mu\text{-CH}\equiv\text{C-CH}_2\text{S}$)-(1,2- $\text{C}_2\text{B}_9\text{H}_{10}$) $_2$ -3-Co(III) (1) and poly[8,8'-($\mu\text{-CH}\equiv\text{C-CH}_2\text{S}$)-(1,2- $\text{C}_2\text{B}_9\text{H}_{10}$) $_2$ -3-Co(III)] (2)

bands at 3 053 and 3 031 cm^{-1} which are attributable to various $\nu(\text{C-H})$ modes of the skeleton CH groups with non-equivalent environment (the $\nu(\text{C-H})$ modes of carborane skeleton are usually observed in the region 3 100–3 000 cm^{-1} and they are known to be very sensitive to both inter- and intramolecular interactions²³); (iii) band at 1 210 cm^{-1} which can be assigned to $\delta(\text{CH})$ mode; and (iv) bands at 1 083, 975, 838 and 700 cm^{-1} which can be assigned to skeletal vibrational modes of the cages.

Bands characteristic of vibrations in the propargylthio group were found at the following wavenumbers: (i) at 3 303 (s) cm^{-1} (overtone at 6 498 cm^{-1}) with shoulder at 3 284 cm^{-1} (overtone 6 462 cm^{-1}) due to $\nu(\equiv\text{C-H})$ of acetylenic hydrogen; (ii) at 2 127 (w-m) cm^{-1} (overtone 4 117 cm^{-1}) and 2 094 (w) cm^{-1} (overtone 4 072 cm^{-1}) due to $\nu(\text{C}\equiv\text{C})$; (iii) at 659 (m-s) cm^{-1} and 639 (m) cm^{-1} ascribed to $\delta(\equiv\text{C-H})$; two of three possible bands (1 325?, 1 271 and 1 238? cm^{-1}) can be assigned as the corresponding overtones. The IR spectra suggest that there are two non-equivalent $\text{C}\equiv\text{C-H}$ groups from the vibrational point of view. The differences can originate from the different orientation of the propargyl group with respect to the cobaltacarborane skeleton.

Some of the other bands can be interpreted very tentatively. The 2 970 (m) cm^{-1} and 2 929 (m) cm^{-1} bands may be ascribed to $\nu(\text{C-H})$ vibrational modes of CH_2 in the propargylthio group. However, the wavenumbers of these two bands are higher than those typical for $\nu(\text{C-H})$ modes of the $-\text{CH}_2-\text{S}-$ group²²; the effect of the neighboring groups ($\text{C}\equiv\text{C-H}$); S-cobaltacarborane) can be suggested (see the polymer spectrum). The $\delta(\text{CH}_2)$ mode of CH_2-S can be attributed to the 1 404 (m) cm^{-1} band. The band at 957 (m) cm^{-1} can be tentatively ascribed to $\nu(\text{C-C})$ mode of the $\text{CH}_2-\text{C}\equiv\text{CH}$ group.

Characterization of Poly(A)

Due to the limited solubility of the polymer (see Experimental), its molecular weight could not be determined. An evidence that polymerization took place is seen from the UV/VIS spectrum of the polymer low-molecular-weight fraction which was extracted with dimethyl sulfoxide (Fig. 3, curve 2). An increase in absorption in the visible region as compared with the monomer is evident. It proves the presence of shorter conjugated sequences in the molecules of the extracted oligomers.

An attempt to obtain structural information from the NMR spectra of the soluble fraction failed due to low yield of this fraction. Only a poorly resolved ^{11}B NMR spectrum was obtained in which some signals corresponding to those observed for **A** are detectable (at 2, -5, -7, -8, -8.5 and -15 ppm). However, no reliable ^1H and ^{13}C spectra were obtained. Thus the main evidence for a transformation of **A** into the polymer has been obtained from the polymer IR spectrum (Fig. 4, curve 2).

The measured IR spectrum of poly(**A**) multiplied by the factor of 1.25 to obtain the same baseline-corrected area of 2 622 cm^{-1} band as in the spectrum of monomer, is shown in Fig. 4, curve 2 (it is believed that $\nu(\text{B-H})$ vibrations of cobaltacarborane skeleton remain intact by the transformation of **A** into poly(**A**)). It is seen that all the

bands characteristic of the propargyl group are absent in the spectrum of poly(**A**) (bands at 3 303, 3 284, 2 127, 2 094, 665, 639 cm^{-1} and their overtones at 6 498, 6 462, 4 117, 4 072, 1 325?, 1 271, 1 238? cm^{-1}). On the other hand, new bands which were absent in the monomer IR spectrum appeared in the spectrum of poly(**A**): bands at 1 602 (w) cm^{-1} and 1 494 (w) cm^{-1} can be tentatively assigned to $\nu(\text{C}=\text{C})$ modes in the polymer π -conjugated backbone. The 738 (s) cm^{-1} band is in the region characteristic of $\delta(\text{C}=\text{C}-\text{H})$ out-of-plane vibrations in conjugated systems^{21,22}. We can thus conclude that the IR spectrum has confirmed transformation of the $-\text{C}\equiv\text{C}-\text{H}$ functional group into π -conjugated main-chain units, i.e. that the polymerization of **A** by metathesis catalyst was successful.

Some other bands have little changed positions after the polymerization, in the first place the bands of $\nu(\text{C}-\text{H})$ modes of CH_2 groups which shift from 2 970 (m) to 2 921 (w) cm^{-1} and from 2 921 (m) to 2 869 (w) cm^{-1} . Also the $\delta(\text{CH}_2)$ modes of methylene groups are shifted for about 7 cm^{-1} . Both shifts can be regarded as the result of the change in the $-\text{CH}_2-$ group surrounding (conversion of $\text{RC}\equiv\text{C}-\text{H}$ into $-\text{RC}=\text{CH}-$).

The bands assigned to skeletal vibrations in the monomeric species have their counterparts in the spectrum of the homopolymer (without any significant wavenumber shifts; the corresponding bands are connected with dashed lines in Fig. 4). The bands of skeletal $\nu(\text{C}-\text{H})$ modes (at 3 038 cm^{-1}) are rather broad in the polymer IR spectrum as compared to that of the monomer, presumably due to overlap with the bands of $\nu(\text{C}-\text{H})$ modes of conjugated chain.

Due to low solubility (almost insolubility) of the homopolymer of **A** it was not possible to prepare films needed for tests of its electrical and photoelectrical properties. Orientation measurements were performed on films of poor quality prepared from the extracted low-molecular-weight fraction (see UV/VIS spectra) and no photoconductivity has been reliably detected. However, we have found that monomer **A** can be well copolymerized with phenylacetylene to a soluble copolymer of enhanced resistance against autoxidative degradation as compared with poly(phenylacetylene)²⁴⁻²⁶. It would thus be possible to study the effects of carboranyl groups on the electrical and photoelectrical properties of π -conjugated polymers using this or other similar copolymers. These copolymers can also be used for verification and/or examination of the equation describing an effect of polar additives (represented by cobaltacarboranyl side groups in case of the copolymers in question) on the charge carrier transport in organic polymers which has recently been derived²⁷. Research in this field is in progress.

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