Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Application of the cobaltbisdicarbollide anion to the development of Ion Selective PVC membrane electrode for tuberculosis drug analysis

Anca-Iulia Stoica[a,b], Clara Viñas[a] and Francesc Teixidor*[a]

[a] *Institut de Ciència de Materials de Barcelona*
CSIC Campus de la U.A.B., 08193 Bellaterra (Spain)
Fax: (+34)935805729 E-mail: teixidor@icmab.es
[b] *On leave from the Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest*

Supporting Information

Experimental procedures, FTIR, NMR, MALDI-TOF values, tables concerning electrode characteristics (Table 1) and selectivity coefficients of electrode for various compounds (Table 2)

Experimental Section

Instrumentation: IR spectra (ν, cm^{-1}; KBr pellets) were obtained on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H- and $^{1}H\{^{11}B\}$-NMR (300.13 MHz), $^{13}C\{^{1}H\}$-NMR (75.47 MHz), ^{11}B- and $^{11}B\{^{1}H\}$-NMR (96.29 MHz) spectra were recorded on a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were performed in d_6-acetone at 22ºC. The ^{11}B- and $^{11}B\{^{1}H\}$-NMR shifts were referenced to external $BF_3{\cdot}OEt_2$, while the ^{1}H, $^{1}H\{^{11}B\}$, and $^{13}C\{^{1}H\}$-NMR shifts were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)].

Synthesis of H[H-PZA]$_2$[cosane]$_3$(3). Firstly, $H^+[Co(1,2\text{-}C_2B_9H_{11})_2]^-$ was obtained from $Cs[Co(1,2\text{-}C_2B_9H_{11})_2]$ (0.3000 g) and HCl 1M (15 mL), extracting the resulted product in ether (20mL). The extraction procedure was made by 3 times (solution 1). Pyrazinamide (0.0123 g) was dissolved in 10 mL of HCl 3M under stirring (solution 2). Secondly, the ion-pair compound $[PZA]^+[cos]^-$ was prepared by mixing 10 mL of 0.01M solution 1 with 10 mL of 0.01M solution 2 under stirring resulting a yellow precipitate. The precipitate was filtered, washed with a solution of HCl and dried in vacuum atmosphere.

FTIR: 3468, 3356 (NH_2), 3117, 3094, 3078, 3040, 3028 (C_{aryl}-H, C_c-H); 2615, 2604, 2569, 2553, 2515 (B-H), 1709 (C=O), 1566, 1485, 1416 (N-C=O, N^+-H). ^{1}H NMR δ: 10.04, 10.00, 9.93 (s, 6H, C_{aryl}-H), 3.93 (s, 12H, C_c-H), 3.70-0.50 (br m, B-H). ^{1}H{^{11}B} NMR: δ: 10.04, 10.00, 9.93 (s, 6H, C_{aryl}-H), 3.93 (s, 12H, C_c-H), 3.38 (br s, 6H, B-H), 2.97 (br s, 6H, B-H), 2.70 (br s, 12H, B-H), 1.93 (br s, 12H, B-H), 1.61 (br s, 6H, B-H), 1.56 (br s, 12H, B-H). ^{13}C{^{1}H} NMR δ: 153.14 (s, C_{aryl}), 150,31 (s, C_{aryl}), 147.51 (s, C_{aryl}), 131.34 (s, C_{aryl}), 51.00 (s, C_c). ^{11}B-NMR δ: 7.3 (d, ^{1}J(B,H)= 145, 2B), 2.1 (d, ^{1}J(B,H)= 140, 2B), -4.9 (d, ^{1}J(B,H)= 148, 2B); -5.3 (d, ^{1}J(B,H)= 130, 8B), -16.6(d, ^{1}J(B,H)= 154, 2B), -22.1 (d, ^{1}J(B,H)= 167, 2B). MALDI-TOF (m/z): at the cathode, 154 (M +CH_2O; 74.23%), 132.60 (M+ ½ H_2O; 89.7%), 123.80 (M; 100%), 95.79 (M- CO_2, 83.50%). MALDI-TOF (m/z): at the anode 324.26 ([$Co(1,2\text{-}C_2B_9H_{11})_2$], 100%).

Synthesis of H[H_2INH][cosane]$_3$(3). Firstly, $H^+[Co(1,2\text{-}C_2B_9H_{11})_2]^-$ was obtained from $Cs[Co(1,2\text{-}C_2B_9H_{11})_2]$ (0.3000 g) and HCl 1M (15 mL), extracting the resulted product

in ether (20mL). The extraction procedure was made by 3 times (solution 1). Isoniazid (0.0069g) was dissolved in 0.5 mL of HCl 1M under stirring and diluted with 4.5mL distilled water (solution 2). Secondly, the ion-pair compound $[INH]^+[cos]^-$ was prepared by mixing 10 mL of 0.01M solution 1 with 5 mL of 0.01M solution 2 under stirring resulting a yellow precipitate. The precipitate was filtered, washed with a diluted solution of HCl and dried in vacuum atmosphere.

FTIR: 3626-3418 (NH_2), 3097, 3036 (C_{aryl}-H, C_c-H); 2549, 2523 (B-H), 1701 (C=O), 1604, 1496 (N-C=O, N^+-H). ^{1}H NMR ($CDCl_3$) δ: 9.41 (d, ^{3}J(H,H)= 5.8, 2H, C_{aryl}-H), 8.75 (d, ^{3}J(H,H)= 5.8, 2H, C_{aryl}-H), 3.94 (s, 12H, C_c-H), 3.5-0.5 (br m, B-H). ^{1}H{^{11}B} NMR ($CDCl_3$): δ: 9.41 (d, ^{3}J(H,H)= 5.8, 2H, C_{aryl}-H), 8.75 (d, ^{3}J(H,H)= 5.8, 2H, C_{aryl}-H), 3.94 (s, 12H, C_c-H), 3.37 (br s, 6H, B-H), 2.97 (br s, 6H, B-H), 2.70 (br s, 12H, B-H), 1.92 (s, 12H, B-H), 1.61 (br s, 6H, B-H), 1.56 (br s, 12H, B-H). ^{13}C{^{1}H} NMR δ: 163.1 (s, C=O), 146.4 (s, C_{aryl}), 143.5 (s, C_{aryl}), 143.0 (s, C_{aryl}), 127.3 (s, C_{aryl}), 126.5 (s, C_{aryl}), 51.06 (s, C_c). ^{11}B-NMR δ: 7.3 (d, ^{1}J(B,H)= 142, 2B), 2.1 (d, ^{1}J(B,H)= 140, 2B), -4.7 (d, ^{1}J(B,H)= 135, 2B), -5.7 (d, ^{1}J(B,H)= 153, 8B), -16.6 (d, ^{1}J(B,H)= 140, 2B), -22,04 (d, ^{1}J(B,H)= 140, 2B). MALDI-TOF (m/z): at the cathode 198.85 (M +CON_2H_5; 56%), 149.80 (M+12; 100%), 132.63 (M-5; 87%). MALDI-TOF (m/z): at the anode 324.25 ([$Co(1,2\text{-}C_2B_9H_{11})_2$], 100%).

Table 1. Electrode characteristics

Antibiotic	INH	PZA	INH	PZA	INH	PZA
Plasticizer	NPOE	NPOE	DOP	DOP	DBP	DBP
Slope mV/decade	52.37	56.98	47.80	46.70	44.10	46.64
Correlation coefficient	0.9973	0.9971	0.9989	0.9975	0.9991	0.9988
Concentration range (M)	$1.00\cdot10^{-4}$-$1.00\cdot10^{-1}$	$5.00\cdot10^{-4}$-$1.00\cdot10^{-1}$	$1.00\cdot10^{-1}$-$1.00\cdot10^{-4}$	$5.00\cdot10^{-5}$-$1.00\cdot10^{-1}$	$1.00\cdot10^{-4}$-$1.00\cdot10^{-1}$	$5.00\cdot10^{-5}$-$1.00\cdot10^{-1}$
Detection limit (M)	$5.00\cdot10^{-5}$	$3.00\cdot10^{-5}$	$5.80\cdot10^{-5}$	$1.00\cdot10^{-5}$	$7.00\cdot10^{-5}$	$2.00\cdot10^{-5}$
Time response/s	<5	< 5	<5	< 5	<5	< 5
Lifetime/ day	> 45	> 45	> 45	> 45	> 45	> 45
pH	1.85-9.50	2.20-9.50	1.85-9.50	2.20-9.50	1.85-9.50	2.20-9.50

Table 2 Selectivity coefficients of electrode for various compounds

Interfering species	$lgK^{pot}_{INH/B}$	$lgK^{pot}_{PZA/B}$	$lgK^{pot}_{INH/B}$	$lgK^{pot}_{PZA/B}$	$lgK^{pot}_{INH/B}$	$lgK^{pot}_{PZA/B}$
	NPOE	NPOE	DOP	DOP	DBP	DBP
Na^+	-1.54	-3.36	-1.88	-5.19	-1.86	-4.36
K^+	-2.57	-5.32	4.82	-6.39	-3.31	< -7
Ca^{2+}	-4.28	-6.34	-5.20	< -7	-5.19	< -7
Mg^{2+}	-4.47	-4.32	-4.98	< -7	4.90	< -7
INH	-	< -7	-	< -7	-	< -7
PZA	-2.87	-	-3.82	-	-2.88	-
sulfanilamide	-2.08	-6.02	-4.07	< -7	-4.02	< -7