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Note

Analysis of boron-halogen derivatives of bis(1,2-dicarbollyl)cobalt(III) anions by capillary isotachopheresis

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The system nitrobenzene-cobaltocarborane of the type $[(C_2B_9H_{11-n}X_n)_2CO]^-H^-$, where $n = 1-4$ and $X = Cl (Br)$, has excellent extraction properties for mono- and divalent cations (see, e.g., refs. 1-4). Halogen atoms present in the molecule of this extraction agent (in the positions B-8 and B-8' of the dicarbollyl skeleton) remarkably improve its chemical stability⁵. High stabilities to radiation, typical of this group of compounds, make them suitable for the isolation of fission products (^{137}Cs and ^{90}Sr) from acidic solutions^{3,4}.

Mixtures of derivatives are formed on chlorination^{6,7} or bromination^{8,9} of the substrate $[(C_2B_9H_{11})_2Co]^-H^-$, (CS^-). Some of them can be obtained in a pure form by gel chromatography (Sephadex LH-20) using methanol as an eluent^{5,10}. The identity and purity of the isolated compounds is usually evaluated by ^{11}B NMR spectroscopy¹¹.

The similar physical and chemical properties of DCC {the abbreviation for $[(C_2B_9H_{11})_2Co]^-$ } and its halogen derivatives make difficult their chromatographic separation and consequently their analysis. Recently, an extensive chromatographic investigation of heteroborane anions was published by Plzák *et al.*¹². Homologous series of halogenated sandwich complexes of the above type (for structural formulae see Fig. 1) were not included in this investigation. However, the retention behaviour of this group of compounds evaluated under similar conditions¹⁰ implies hardly any separations.

The aim of this work is to show that capillary isotachopheresis (ITP) is a powerful technique for the separation of DCC and its halogen derivatives. Because of the low solubilities of cobaltocarboranes in water their ITP separations were carried out in water-methanol and water-ethanol mixtures.

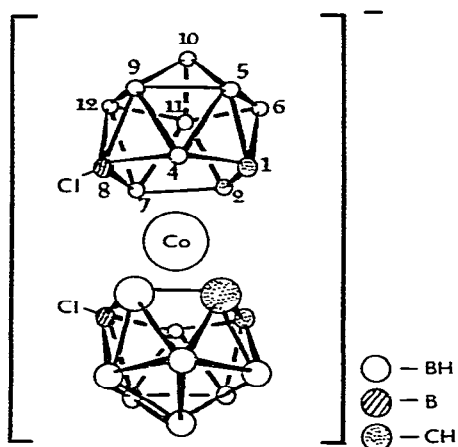


Fig. 1. Structural formula of the dichloro derivative of cobalttetracarborane anion (Cl_2DCC). The order of halogenation of DCC is as follows: 1, position 8; 2, 8'; 3, 9; 4, 9'; 5, 12; 6, 12'.

EXPERIMENTAL

Apparatus

An instrument for ITP similar to that developed by Everaerts *et al.*¹³ was used. Parts which are in contact with solutions were made of poly(tetrafluoroethylene) (PTFE). A fluorinated ethylene-propylene copolymer (FEP) capillary tube of 0.3 mm I.D. was used. Detection was performed with a conductivity detector^{13,14}. Material to be analysed was delivered with the aid of a six-way valve¹³ also made of PTFE. Stabilized current was supplied by a unit developed by Havaš¹⁵.

Reagents

Chemicals used were of pro analysi purity and if necessary were purified by conventional methods¹⁶. Trichloroacetic and benzoic acids were obtained from Lachema (Brno, Czechoslovakia), N-ethylmorpholine from Fluka (Buchs, Switzerland). Water, methanol and ethanol were doubly distilled before use. The caesium salt of DCC was prepared by Dr. J. Plešek (Institute of Inorganic Chemistry, Czechoslovak Academy of Science, Řež near Prague, Czechoslovakia). Halogen derivatives of DCC were prepared in our laboratories.

The pH values of the leading and terminating electrolytes were measured as described in the literature^{13,17}. A PHM-64 pH meter provided with a G 202 C glass electrode and a K-401 calomel electrode (all from Radiometer, Copenhagen, Denmark) was used.

RESULTS AND DISCUSSION

As mentioned above, DCC as well as its halogen derivatives are sparingly soluble in water. Therefore, ITP separations in methanol-water mixtures were studied. Small differences in the effective mobilities of the constituents to be separated were typical for this pair of solvents. Optimization of the separation according to pK

TABLE I

OPERATIONAL SYSTEM SUITABLE FOR THE SEPARATION OF DCC AND ITS HALOGEN DERIVATIVES BY ITP

Cl_3Ac^- = Trichloroacetate; $\text{C}_6\text{H}_5\text{COO}^-$ = benzoate; N-ETM = N-ethylmorpholine; MOW = Mowiol 8-88 (Hoechst, Frankfurt, M, G.F.R.).

	Leading electrolyte	Terminating electrolyte
Solvent	Ethanol-water (87:13 v/v)	Ethanol-water (95:5 v/v)
Anion	$\text{Cl}_3\text{CH}_2\text{COO}^-$	$\text{C}_6\text{H}_5\text{COO}^-$
Counter-ion	N-ETM	N-ETM
pH*	6.4	7.0
Additive**	0.01% MOW	—

* Measured as described in refs. 13 and 17.

** For the role of the additive see ref. 13.

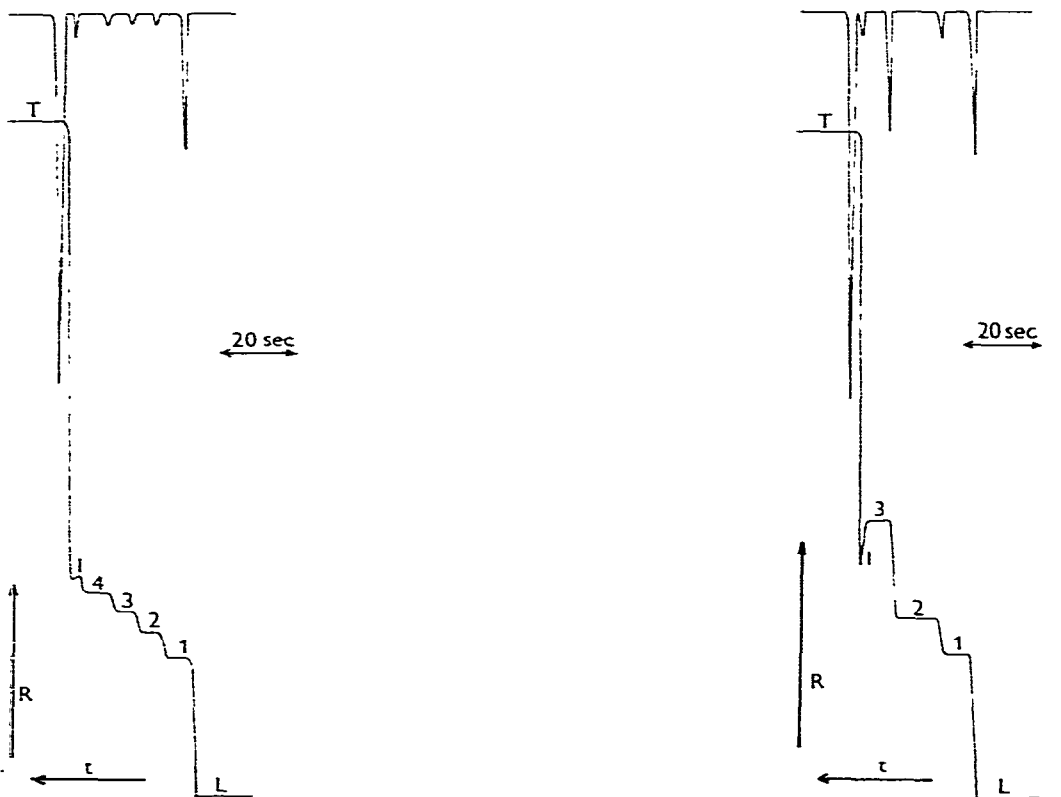


Fig. 2. An isotachopherogram of the separation of chloro derivatives of DCC. For the operating conditions see Table I. Driving current $10 \mu\text{A}$. 1 = DCC; 2 = ClDCC; 3 = Cl_2DCC ; 4 = Cl_3DCC ; L = leading anion; T = terminating anion; I = impurity; R = increasing resistance; t = increasing time.

Fig. 3. An isotachopherogram of the separation of some bromo derivatives of DCC. 1 = BrDCC; 2 = Br_2DCC ; 3 = Br_3DCC . Other symbols as in Fig. 2.

values is ineffective in this instance as these compounds are strong electrolytes in non-aqueous solvents^{10,18}. Therefore, other solvents were considered.

An unexpected improvement of the separation was obtained when ethanol-water mixtures were employed. Differences in the effective mobilities of DCC and its halogen derivatives in this solvent system were sufficient for full resolution of available members of the homologous series. Several operating systems are available for ITP separations of these compounds if the ethanol content is sufficiently high (more than 80% v/v). The one used throughout this work is given in Table I.

Isotachophorograms of the separation of chloro and bromo derivatives of DCC are given in Figs. 2 and 3, respectively. The order of migration of the derivatives indicates that their different molecular weights are responsible for the separation (strong electrolytes, same charge type, very close structural properties). However, solvation effects probably also play a rôle as insufficient resolution was found in methanol-water mixtures. A detailed investigation of the solvation effects for this group of constituents and for different solvents is the subject of current research in this laboratory.

Possible applications of ITP, *e.g.*, for control of purity and stability to radiation, are clear from the above isotachophorograms. An application to the analytical evaluation of a crude product is given in Fig. 4. We can see that the dichloro deriva-

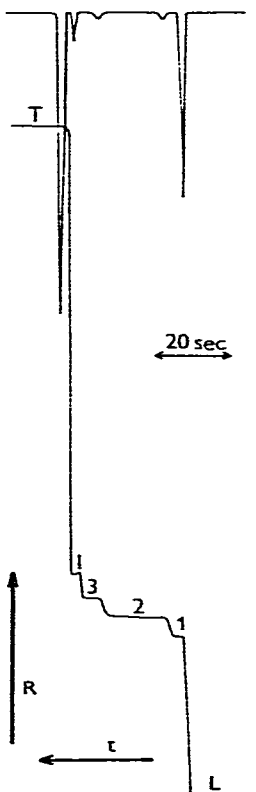


Fig. 4. Analytical evaluation of crude Cl₂DCC. 1 = ClDCC; 2 = Cl₂DCC; 3 = Cl₃DCC. Other symbols as in Fig. 2.

tive of DCC (Cl_2DCC) is accompanied by two by-products CIDCC ($\approx 16\%$) and Cl_3DCC ($\approx 27\%$).

The use of ITP for analysis of metallocarboranes, has several advantages:

(1) The analysis time was approximately 15 min in this investigation. However, modification of the apparatus, e.g., by use of coupled columns¹⁹, can decrease this substantially.

(2) The reproducibility of determination is very good (1–2% of the amount to be determined is typical).

(3) Only small amounts of material are necessary for a complete analysis, which can be of great importance when radioactive material is involved.

(4) The solvent in which the sample is dissolved was found to be of minor importance in this application²⁰.

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