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### **K(18-crown-6-ether)CN: a new stationary phase material for the separation of organocyanometallates**

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Chromatography has become increasingly important as a means of separating and purifying sensitive organometallic compounds which are of interest as catalysts and synthetic reagents. Standard chromatographic methods are often not applicable when these compounds are notably basic and air or moisture sensitive, as is often the case. Research into the synthesis and chemistry of the organocyanometallates<sup>1-5</sup> has been hindered by several problems. In addition to their frequent air and water sensitivity, the known organometallates are often insoluble in unreactive aprotic solvents which should otherwise be suitable for their handling. Work in our laboratory has shown that with the use of crown ethers as solubilizing agents this problem can be alleviated<sup>6</sup>. Another serious hindrance in this work has been the lack of generally applicable purification techniques, besides crystallization, for these compounds.

Although high-performance liquid chromatography (HPLC) has for example been recently used to separate some neutral air-sensitive isomeric organocobalt complexes<sup>7</sup>, it is not a method easily adapted to preparative scale work. Some air-stable organocyanocobaltate(III) compounds were successfully purified using alumina<sup>5</sup>, but in general we have found that similar compounds in which the metal is in a lower oxidation state are bound irreversibly to alumina and decomposed by silica gels or bonded-phase silicas in which the entire surface of the absorbent is not covered, due to their extreme basicity.

Since the cyanometallates being prepared were crown-ether-complexed salts, experiments were undertaken to investigate the use of crown-ether-derived stationary phases in a liquid chromatographic system that was operated in an inert atmosphere glove box, facilitating the handling of these sensitive materials. It was decided to explore classical column chromatography as the method most easily and cheaply adapted to preparative scale work in the glove box environment. All the compounds of interest are deeply colored so there was no need for a special detection system which would have been difficult to fit in the confines of the glove box.

The last decade has seen an increasing use of crown ethers in liquid chromatography. Both cations and anions have been successfully separated using crown ethers in the mobile phase<sup>8</sup>, immobilized on silica gel<sup>9</sup>, incorporated into ion-exchange resins<sup>10,11</sup> or as a polyamide crown resin<sup>12</sup>. Elaboration of these techniques has enabled the successful accomplishment of many diverse analyses: the enantiomeric resolution of amino acids<sup>13</sup>, isolation of antibiotics from physiological fluids<sup>14</sup>,

separation of alkali metal chlorides<sup>15</sup> and sulphonic acids<sup>16</sup>. We now report the results of chromatography using (K-crown)CN coated on silica or alumina as a means of separating organocyanocobaltates using two specific reactions as models. Included also is a comparison with other chromatographic systems.

#### EXPERIMENTAL

The chromatography was performed in a Vacuum Atmospheres Dri-Lab glove box equipped with a HE493 Dritrain.

#### *Reagents*

Solvents used in column packing material preparations were HPLC grade. Tetrahydrofuran (THF) was dried using sodium benzophenone ketyl. Acetonitrile was refluxed with phosphorus pentoxide for 12 h after pre-drying with anhydrous potassium carbonate. Dimethylformamide (DMF) (Burdick & Jackson) was stirred for 3 days with freshly activated 3A molecular sieves under nitrogen and was then filtered through a fine frit.

18-Crown-6-ether (Aldrich) was recrystallized from acetonitrile and dried for 2 days *in vacuo* in the presence of P<sub>2</sub>O<sub>5</sub>. Trimethylchlorosilane (TMCS) (Kodak, technical) was used without purification. Potassium cyanide was purified by a literature method<sup>17</sup>, dried as for the crown ether and assayed spectrophotometrically<sup>18</sup>. K(crown)CN was also prepared by a literature method<sup>19</sup>, adjusting the molar ratio of potassium cyanide:18-crown-6-ether to account for potassium cyanide purity.

#### *Chromatographic materials*

Silica (100–200 μm) and neutral alumina (Brockmann reactivity 0, I) were both obtained from Woelm; Florisil (60–100 mesh) and magnesium oxide (U.S.P., heavy powder) were purchased from Aldrich and Mallinckrodt respectively. Biobeads (SX-8, 200–400 mesh) were purchased from BioRad. Cyanopropylsilane bonded to silica (50 μm) was obtained from Baker. Silica was silanized with TMCS using a standard procedure<sup>20</sup>. Crown-silica, (K-crown)CN silica and alumina packings were prepared by either of the following two methods: (A) 50 g of alumina or silica was placed in a solution containing 7.5 g (K-crown)CN in 150 ml methanol [since (K-crown)CN is hygroscopic, care should be taken to avoid undue atmospheric exposure]. The suspension was placed on a rotary evaporator and methanol removed until solidification occurred. The material was then dried *in vacuo* for 12 h under an infrared heating lamp. (B) 50 g of alumina or silica was heated to 110°C and then plunged into a solution of 7.5 g (K-crown)CN in 100 ml methanol and occasionally shaken over a period of 1 h. The solution was decanted, and the residue washed with 100 ml methanol and then placed on a medium frit and washed successively three more times with 100 ml methanol before drying as for (A).

#### *Chromatographic procedure*

Glass columns (12 × 1 cm or 20 × 2.2 cm) were packed by the slurry method and washed with 3–4 volumes of the same solvent (THF), with the exception of the cyanopropylsilane-silica where the solvent was acetonitrile-DMF (1:1, v/v). The Biobeads were allowed to swell for 12 h in THF before columns were packed. In

general, discontinuous elutions using solvents of successively higher polarity were performed, the elutropic series being THF, acetonitrile, DMF. Gel permeation and reversed-phase chromatography were performed using isocratic elution. Separation of the various complexes was monitored by color and resolution estimated usually, with additional measurements of approximate retention volumes where possible. Column flow-rates were typically 3–5 ml/min with the exception of the reversed-phase column, run at 20–30 ml/min, at 2 p.s.i. above atmospheric pressure.

## RESULTS AND DISCUSSION

The chromatography of crude products from two reactions was studied: (1) the reduction of  $(\text{K-crown})_2\text{Co}(\text{CN})_4$  in the presence of diphenylacetylene and (2) the photolysis of  $\text{CoCp}(\text{CO})_2$  in the presence of  $(\text{K-crown})\text{CN}$ . The THF fraction from the residue of reaction (1) contains hexaphenylbenzene,  $(\text{K-crown})\text{CN}$ , diphenylacetylene and smaller amounts of three alkynecyanocobaltate species (designated A, B and C) plus a variable amount of inorganic material of the type  $(\text{K-crown})_x\text{Co}(\text{CN})_y$ . The THF fraction from the residue of reaction (2) contains  $(\text{K-crown})\text{CN}$ , an anionic cobalt carbonyl cluster species, an anionic cyanocarbonyl cobaltate and  $(\text{K-crown})\text{CoCp}(\text{CO})(\text{CN})$  (the latter three compounds designated D, E and F, respectively). Details of these reactions and structures of the products will be reported elsewhere.

The stationary phases compared in the chromatographic studies are listed in Table I. All of the compounds A–F were found to bind irreversibly to stationary

TABLE I  
STATIONARY PHASES USED

Roman numerals in parentheses refer to Brockmann Activities. Capital letter in parenthesis indicates the method used to prepare stationary phase.

<i>Stationary phase</i>	<i>Designated number</i>
Basic alumina (I)	1
Neutral alumina (I, III, V)	2
Florisil	3
MgO	4
Celite	5
Silica	6
Silica-TMS	7
Biobeads SX-8	8
Cyanopropylsilane silica	9
$(\text{K-crown})\text{CN}$ alumina(I), (B)	10
$(\text{K-crown})\text{CN}$ alumina(I), (A) (15% by wt.)	11
$(\text{K-crown})\text{CN}$ alumina (O), (B)	12
$(\text{K-crown})\text{CN}$ alumina(III), (B)	13
Crown-silica, (A) (5% by wt.)	14
$(\text{K-crown})\text{CN}$ -silica, (A) (8% by wt.)	15
$(\text{K-crown})\text{CN}$ -silica, (A) (15% by wt.)	16
$(\text{K-crown})\text{CN}$ -silica-TMS, (B)*	17

\* Silica was reacted with TMCS first.

phases 1-4 and could not be eluted with DMF, suggesting extremely strong interactions. The same phenomenon was observed for phases 10-13, although to a lesser extent (recovery studies with compound F suggested typically 60% remaining on column). Extensive decomposition was seen on testing phases 6-9 and 14 (indicated by the changing of the red or brown color of the complexes to green). Elution data for the compounds separated by the remaining stationary phases is shown in Table II. While baseline resolution was obtained in many instances, unsatisfactory performance was seen for phases 5, 8 and 17 for all compounds. The separation of compounds E and F proved particularly difficult and no stationary phase resolved them completely. Average peak width for bands eluting from the larger column were of the order 20-40 ml, with typical retention volumes of 60-100 ml. Due to the lack of suitable equipment and the properties of the compounds themselves, it was not possible to determine relative concentrations of the compounds in emerging bands; thus resolution had to be judged on a visual basis rather than from intensity and retention volume data. Nevertheless, it was clear that the modified alumina phases generally gave better resolution than the silica-based ones. There seemed to be no significant differences between coated phases produced by methods A or B, although resolution was definitely poorer when the percent loading of (K-crown)CN was increased from 8 to 15% for the silica. The best phase on average was considered to be the (K-crown)CN silica (A) (8% by weight). The best resolution obtainable for modified silica columns is highly dependent on the amount of material to be separated. Although individual cases vary, the typical maximum figure for a 20 × 2.2 cm I.D. packed column would be 150-200 mg. Resolution and also capacity might be enhanced by using smaller diameter, more porous silica particles, although an increased phase loading may also be necessary. In our work we have found that using

TABLE II  
ELUTION CONDITIONS FOR SELECTED STATIONARY PHASES

The order of elution found for the eluotropic series THF, acetonitrile, DMF is A, B, C and D, E, F for all the phases listed here. MeCN = acetonitrile. All solvent compositions are in volume units.

Stationary phase	Compound					
	Reaction (1)			Reaction (2)		
	A	B	C	D	E	F
10	THF-MeCN 1:1	MeCN	DMF	THF-MeCN 1:1	MeCN-DMF 1:1	MeCN-DMF 1:1
11	THF-MeCN 2:1	MeCN	DMF	THF-MeCN 2:1	MeCN-DMF 1:1	MeCN-DMF 1:1
12	THF-MeCN 1:1	MeCN	DMF	THF-MeCN 1:1	MeCN-DMF 1:1	MeCN-DMF 1:1
13	THF-MeCN 1:1	MeCN	DMF	THF-MeCN 1:1	MeCN-DMF 1:1	MeCN-DMF 1:1
15	THF	THF-MeCN 1:1	DMF	THF-MeCN 3:1	THF-MeCN 1:1	THF-MeCN 1:1
16	THF	THF MeCN 2:1	MeCN-DMF 1:1	THFMeCN 3:1	THF-MeCN 3:1	THF-MeCN 3:1

particle diameters averaging less than 75  $\mu\text{m}$  necessitates an external pressure source which can present regulation problems for work performed in a glove box. Fine control over elution is also difficult given the limited number of solvents which are compatible with the glove box oxygen scavenging system and do not react with the compound themselves.

All coated stationary phases are subject to stripping from the support with use, and (K-crown)CN modified aluminas and silicas are no exception. Under the conditions used, column bleed has been found to be acceptable, and any crown ether which does co-elute can be separated from the product of interest by crystallizing it out from acetonitrile by cooling. Column packings can be cleaned *in situ* by DMF or by removing the packing material, washing with methanol and drying. Certain modified silicas have been used 3-4 times before discarding due to unremovable impurities. If removal of crown ether from the stationary phase is suspected to have become excessive, then chromatography of (K-crown)CoCp(CO) (CN) will provide a standard for indicating if surface coverage is insufficient.

It is not clear how the (K-crown)CN has modified the surface of the adsorbent. One possibility for silica is that cyanide deprotonates the silanol group to give HCN and ion pairing of  $\text{Si-O}^-$  (K-crown) $^+$ . Alternatively, the (K-crown)CN may orient itself specifically with the surface with the cyanide groups facing outwards and the potassium ions on the inside surrounded by the crown ether.

The use of (K-crown)CN modified alumina and silica columns has demonstrated a significant advance in the chromatography of organocyanometallates and it is clear that the potential of this method is only just being realized. With further improvements, it will be possible to separate these complexes which heretofore have been chromatographically intractable.

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