

## THE DIRECT ELECTROCHEMICAL SYNTHESIS OF ANIONIC ORGANODIHALOCADMATE(II) COMPLEXES

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### Summary

The tetra-*n*-propylammonium salts of  $\text{RCdX}_2^-$  anions ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{H}_9, \text{CF}_3, \text{C}_6\text{H}_5, \text{C}_6\text{F}_5$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) have been prepared by the electrochemical oxidation of cadmium metal. The element forms the sacrificial anode of a cell in which the solution phase is a methanol/benzene mixture containing  $(\text{C}_3\text{H}_7)_4\text{NX}$  and  $\text{RX}$ . Gram quantities of product were obtained by room temperature electrolysis for ca. 5 h.

### Introduction

In an earlier paper [1], it was shown that the electrochemical oxidation of cadmium metal in the presence of an alkyl or aryl halide provides a simple and convenient method for the synthesis of organocadmium halides. These reactive compounds, which cannot be prepared by direct thermal reaction between cadmium and an organic halide, are readily stabilised as adducts  $\text{RCdX} \cdot \text{L}_2$  or  $\text{RCdX} \cdot \text{L}^{\text{II}}$  with neutral organic monodentate (L) or bidentate ( $\text{L}^{\text{II}}$ ) ligands, and a number of such compounds were prepared and characterised ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9, \text{C}_6\text{H}_5, \text{C}_6\text{F}_5$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). The advantages of direct electrochemical synthesis in this and related organometallic systems have been rehearsed elsewhere [1,2].

A second group of derivatives in which the parent  $\text{RCdX}$  compounds are stabilised by further coordination are the anionic complexes  $\text{RCdX}_2^-$ . The first preparation of such compounds,  $\text{CH}_3\text{CdI}_2^-$  and  $\text{C}_2\text{H}_5\text{CdBr}_2^-$  (as their salts with the tetra-*n*-propylammonium cation) by electrochemical oxidation of the metal in the presence of  $(\text{C}_3\text{H}_7)_4\text{NX}$  and  $\text{RX}$  has already been briefly discussed in a preliminary communication [3]. We now report the extension of this work to the preparation of a series of these previously unknown anions with a variety of alkyl, perfluoroalkyl, aryl and pentafluoroaryl groups, and with chloride, bromide and iodide.

## Experimental

### General

Cadmium (m4N) was used in the form of a rod, 8.5 cm long, 0.25 cm diameter, or as a sheet (ca.  $2 \times 2$  cm). Solvents and neutral ligands were as described in previous work [2].

Metal analysis was by atomic absorption spectrophotometry, and halide analysis by the Volhard method. In three cases,  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$  groups were determined by decomposing the compound with acetic acid and measuring the volume of  $\text{CH}_4$  or  $\text{C}_2\text{H}_6$  released. Analytical results are given in Table 1. The presence of the tetra-*n*-propylammonium cation was established by infrared spectroscopy for each compound prepared.

### Electrochemical preparation

The preparative methods followed closely those described in previous publications [1,2], and the details of the experimental conditions are given in Table 2. In the case of  $\text{CH}_3\text{CdBr}_2^-$ , the cell was cooled to  $-10^\circ\text{C}$  to prevent excessive loss of methyl bromide from the solution. The experiment with  $\text{CF}_3\text{I}$  was carried out in a small cell used for work on nickel and palladium compounds [4], and requiring smaller quantities of material than in the standard method. All preparations and handling of products were carried out under dry nitrogen.

As the electrolysis proceeded, colourless crystals deposited in the cell; these were collected, washed with acetonitrile and dried in vacuo. This precipitate typically represented a 30–40% yield of salt, based on dissolved cadmium, but further product could be obtained by careful evaporation of the solvent, or by the addition of petroleum ether. As in the work on neutral organocadmium halides [1], care must be taken to avoid the disintegration of the surface of the cadmium anode, which causes contamination of the product with particles of cadmium metal.

TABLE 1  
ANALYTICAL RESULTS FOR SALTS OF ORGANODIHALOCADMATE(II) ANIONS

Complex anion <sup>a</sup>	Found (%)		Calculated (%)	
	Halogen	Cd	Halogen	Cd
$\text{CH}_3\text{CdBr}_2^-$	33.5	23.6	33.8	23.7
$\text{CH}_3\text{CdI}_2^-$ <sup>b</sup>	45.0	19.8	44.8	19.8
$\text{C}_2\text{H}_5\text{CdBr}_2^-$ <sup>c</sup>	32.7	23.2	32.8	23.3
$\text{C}_2\text{H}_5\text{CdI}_2^-$ <sup>d</sup>	43.7	19.2	43.6	19.3
<i>n</i> - $\text{C}_4\text{H}_9\text{CdI}_2^-$	41.5	—	41.7	—
<i>t</i> - $\text{C}_4\text{H}_9\text{CdBr}_2^-$	31.0	—	31.0	—
$\text{C}_6\text{H}_5\text{CdCl}_2^-$	15.3	25.2	15.9	25.2
$\text{C}_6\text{H}_5\text{CdBr}_2^-$	29.2	21.4	29.0	21.0
$\text{C}_6\text{H}_5\text{CdI}_2^-$	40.9	18.1	41.1	17.9
$\text{CF}_3\text{CdI}_2^-$	25.8	17.7	25.6	18.0
$\text{C}_6\text{F}_5\text{CdBr}_2^-$	42.6	17.6	41.8	18.5

<sup>a</sup> As the tetra-*n*-propylammonium salt in each case. <sup>b</sup> Acid decomposition of 0.201 g gave 8.0 cm<sup>3</sup> of gas (NTP); calcd. 7.9 cm<sup>3</sup>. <sup>c</sup> Acid decomposition of 0.183 g gave 8.4 cm<sup>3</sup> of gas (NTP); calcd. 8.4 cm<sup>3</sup>.

<sup>d</sup> Acid decomposition of 0.185 g gave 7.0 cm<sup>3</sup> of gas (NTP); calcd. 7.1 cm<sup>3</sup>.

TABLE 2

REACTION CONDITIONS FOR DIRECT ELECTROCHEMICAL SYNTHESIS OF  $(C_3H_7)_4N[RCdX_2]$  SALTS

Anion	Volume (cm <sup>3</sup> )			Mass Pr <sub>4</sub> NX (g)	Voltage (V)	Initial current (mA)	Time of electrolysis (h)	Weight of Cd dissolved (g)
	RX	CH <sub>3</sub> OH	C <sub>6</sub> H <sub>6</sub>					
CH <sub>3</sub> CdBr <sub>2</sub> <sup>-</sup>	2.0	8	20	2.7	40	25	5	0.48
CH <sub>3</sub> CdI <sub>2</sub> <sup>-</sup>	2.5	10	30	1.5	25	25	5	0.59
C <sub>2</sub> H <sub>5</sub> CdBr <sub>2</sub> <sup>-</sup>	3.5	10	30	2.7	40	25	6	0.67
C <sub>2</sub> H <sub>5</sub> CdI <sub>2</sub> <sup>-</sup>	2.5	10	30	1.5	30	25	5	0.65
n-C <sub>4</sub> H <sub>9</sub> CdI <sub>2</sub> <sup>-</sup>	3.0	8	20	2.5	35	30	4	0.45
t-C <sub>4</sub> H <sub>9</sub> CdBr <sub>2</sub> <sup>-</sup>	3.5	8	20	2.7	35	25	5	0.38
C <sub>6</sub> H <sub>5</sub> CdCl <sub>2</sub> <sup>-</sup>	3.0	10	30	1.5	50	25	6	0.43
C <sub>6</sub> H <sub>5</sub> CdBr <sub>2</sub> <sup>-</sup>	3.0	10	30	1.3	40	25	6	0.40
C <sub>6</sub> H <sub>5</sub> CdI <sub>2</sub> <sup>-</sup>	3.0	10	30	1.5	30	25	5	0.55
CF <sub>3</sub> CdI <sub>2</sub> <sup>-</sup>	1.5	3	8	1.2	10	25	4	0.35
C <sub>6</sub> F <sub>5</sub> CdBr <sub>2</sub> <sup>-</sup>	2.0	8	20	2.7	40	30	5	0.71

## Results and discussion

The series of anions prepared represent a new group of organocadmium halide complexes, clearly related to the neutral  $RCdXL_2$  compounds. There are no reports of the preparation of analogous zinc or mercury compounds, although Goggin, Goodfellow and Hurst [5] have identified  $RHgX_2^-$  species ( $R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9$ ;  $X = Cl, Br, I, SCN$ ) spectroscopically in various organic solvents. We have recently shown that the analogous zinc  $RZnX_2^-$  species can also be prepared electrochemically [6], and it therefore seems highly probable that the mercury compounds will also be accessible by this route. The method of direct electrochemical synthesis leads to the formation of  $RCdX_2^-$  salts with each of the elements chlorine, bromine and iodine, and with a variety of organic groups and the synthesis appears to be a general one for these anions. Not only are cadmium—alkyl and —aryl bonds formed in this way but the perfluoro analogues are also accessible; the anion  $CF_3CdI_2^-$  appears to be the first example of a crystalline compound containing a Cd—CF<sub>3</sub> bond.

The tetra-n-propylammonium salts of the  $RCdX_2^-$  anions are moisture-sensitive materials, and insoluble in the common organic solvents, which unfortunately prevented any investigation of their NMR spectra. The stoichiometry suggests a structural similarity to the mononuclear  $CdX_2Y^-$  anions ( $X \neq Y = Cl, Br, I$ ) reported recently and shown to involve three-coordinate cadmium [7], but a detailed structural investigation, probably at the level of X-ray crystallography, will be required to investigate this analogy. Indeed, the solubilities of the respective compounds suggest some structural differences, since the salts of the perhalogeno species  $CdX_3^-$  and  $CdX_2Y^-$  are soluble in acetone/acetonitrile or methanol/acetonitrile mixtures, whereas such solvents could not be used for recrystallising the  $RCdX_2^-$  salts. The general insolubility in organic solvents contrasts with the appreciable solubility in the electrolyte solution (see Electrochemical preparation), which may be due to the formation of  $[RCdX_2S]^-$  anions ( $S = CH_3OH$ ), or to association with halide ion to give  $RCdX_3^{2-}$ . Both these proposed species involve four-coordinate cadmium, and a similar increase in

coordination number in the solid state by halide bridging, reported for many cadmium complexes, may be responsible for the insolubility of the crystalline material.

Despite the low solubility of the salts, it was possible to dissolve sufficient material in acetonitrile to allow determination of the molar conductivities of mM solutions. The results were as follows:

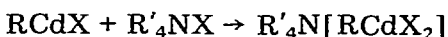
$(C_3H_7)_4N[CH_3CdBr_2]$	$\Lambda_0$ 147 ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
$(C_3H_7)_4N[CH_3CdI_2]$	$\Lambda_0$ 138 ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
$(C_3H_7)_4N[C_2H_5CdBr_2]$	$\Lambda_0$ 136 ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
$(C_3H_7)_4N[C_2H_5CdI_2]$	$\Lambda_0$ 140 ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>

The normal range of values for 1/1 electrolytes in acetonitrile is 120–160 ohm cm<sup>-2</sup> mol<sup>-1</sup> [8], which agrees with the formulation of the compounds in question as 1/1 electrolytes in solution. This agreement is not however unambiguous (cf. ref. 8), and in any case such results do not establish the solid state structure (see above). The main conclusion must be that the compounds are indeed salts of organohalocadmiate anions.

The mechanism of the reaction has not been investigated, since it seems clear that the formation of RCdX in the presence of excess Pr<sub>4</sub>NX will readily give rise to Pr<sub>4</sub>N · RCdX<sub>2</sub>. The electrochemical oxidation of cadmium to give RCdX has been discussed earlier [1], at which time it was reported that the electrochemical yield corresponds to the reaction sequence shown in eq. 1–4 with



eq. 3 and 4 providing a sequence of reactions to explain the current efficiencies (~2 mol Cd dissolved per Faraday) (c.f. ref. 2). The stabilisation of RCdX by



then yields the observed products. In the present case, as in the earlier work, the electrochemical method presents a convenient, simple and efficient synthesis of new organocadmium compounds in gram quantities.

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