Inorganica Chimica Acta, 129 (1987) 75–80

The Direct Electrochemical Synthesis of Zinc and Cadmium Catecholates and Related Compounds

HASSAN E. MABROUK, DENNIS G. TUCK* and MASOOD A. KHAN
Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont., N9B 3P4, Canada

(Received October 10, 1986)

Abstract

The electrochemical oxidation of either zinc or cadmium (= M) in acetone solutions of $o\text{-}C_6H_4(OH)_2$ (= $R(OH)_2$) gives $M(O_2R)$ in good yield. The advantages of this method are discussed. When neutral mono- or bidentate donors are present in the solution, the products are the 1:2 or 1:1 adducts of $M(O_2R)$. Similar results are reported for 2,3-dihydroxynaphthalene and 2,2'dihydroxybiphenyl. A preliminary crystal structure determination on $Zn(O_2C_6H_4)(phen)_2\cdot 2C_6H_4(OH)_2$ (phen = 1,10-phenanthroline) shows the presence of a ZnO_2N_4 kernel; each oxygen atom of the catecholate ligand is hydrogen-bonded to both hydrogens of a neutral $C_6H_4(OH)_2$ molecule.

Introduction

The synthesis and study of metal complexes of aryl-1,2-dihydroxy compounds has long been a matter of interest to inorganic chemists, especially because of the redox properties of such systems [1, 2 and refs. therein]. The analogy between the $M(O_2R)_n$ and $M(S_2R)_n$ systems is also of importance, but progress in the latter area has been the easier because of the relatively simple synthetic routes which are available. In contrast, the obvious route from $R(OH)_2$ via RO_2^{2-} is hindered by the extreme air-sensitivity of alkaline solutions of these diols, and the complete exclusion of air is vital in such work.

We have now extended our earlier investigations of the direct electrochemical synthesis of metal derivatives of weak acids to these aromatic diols, and can report that zinc and cadmium complexes of 1,2-dihydroxybenzene, 2,3-dihydroxynaphthalene and 2,2'-dihydroxybiphenyl are readily prepared by the electrochemical oxidation of the metal anode in a non-aqueous solution of the parent $R(OH)_2$. Adducts of $M(O_2R)$ with neutral organic donors are accessible by a variant of the same technique. In this work, as in previous studies of derivatives of thiols [3–5], thiocyanates [6], phenylacetylene copper [7], β-diketonates [8, 9], and carboxylates [10], the prime advantages of the method are simplicity and high yield.

Experimental

Materials

Zinc (m2N5) and cadmium (m5N5) were in the form of rods (Alfa). Acetone (Reagent Grade) was dried over anhydrous magnesium sulphate. All other substances, including the starting materials 1,2-dihydroxybenzene (catechol), 2,3-dihydroxynaphthalene and 2,2'-dihydroxybiphenyl (Aldrich) were used as supplied.

Analysis and Spectroscopy

Metal analysis was by atomic absorption spectrophotometry. Microanalysis was carried out by Guelph Chemical Company.

Infrared spectra were recorded on a Nicolet 5DX spectrometer (KBr discs) and ^1H NMR spectra on a Bruker WP-80 instrument. Mass spectra were run on a Varian MAT CH-5DF spectrometer.

Electrochemical

The electrochemical techniques were essentially those used in previous work, with a cell consisting of a 100 ml tall-form beaker containing a non-aqueous solution of the parent dihydroxy compound, with a platinum cathode and the sacrificial anode immersed in the liquid phase. All preparative work was carried out under dry nitrogen. The solution composition, electrochemical conditions and yield are given in Table I. Some typical procedures are described in detail below. Analytical results are given in Table II.

Zinc and Cadmium Catecholates

After the appropriate period of electrolysis (see Table I), the colourless product was collected by filtration, washed with acetone and then diethylether,

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

TABLE I. Experimental Conditions for the Direct Electrochemical Synthesis of $M(O_2R)$ Compounds and Adducts (M = Zn, Cd)

Product[a]	Solution composition[b]		Initial voltage[c] (V)	Time of electrolysis (h)	M dissolved (mg)	Yield[d] (%)
	$R(OH)_2$ (g)	Ligand (g)				
$R(OH)_2$ = 1,2-dihydroxybenzene						
$Zn(O_2R)$	0.2		15	3	83	82
$Zn(O_2R)\cdot$bpy	0.2	0.28	15	3	81	84
$Zn(O_2R)\cdot$phen	0.2	0.33	10	3	75	81
$Zn(O_2R)\cdot$2py	0.2	0.3	10	4.5	113	89
$Zn(O_2R)\cdot$2dmso	0.2	0.3	10	2.5	74	80
$Zn(O_2R)(phen)_2\cdot 2R(OH)_2$	0.14	0.15	10	1	26	59
$Cd(O_2R)$	0.1		20	2	80	76
$Cd(O_2R)\cdot$bpy	0.11	0.17	20	2.5	113	90
$Cd(O_2R)\cdot$phen	0.12	0.2	20	3	125	87
$Cd(O_2R)\cdot$tmed	0.2	0.23	15	3.3	137	80
$Cd(O_2R)\cdot$2py	0.1	0.15	20	2	89	80
$Cd(O_2R)\cdot$2dmso	0.1	0.14	20	2	85	84
$Cd(O_2R)(phen)_2\cdot 2R(OH)_2$	0.05	0.08	20	1	45	40
$R(OH)_2$ = 2,3-dihydroxynaphthalene						
$Zn(O_2R)$	0.16(e)		20	2.5	60	73
$Zn(O_2R)\cdot$bpy	0.16	0.16	10	2.5	61	82
$Zn(O_2R)\cdot$phen	0.25	0.28	20	3	75	89
$Zn(O_2R)\cdot$2py	0.16	0.24	10	4	100	71
$Cd(O_2R)$	0.16[e]		15	2.5	105	87
$Cd(O_2R)\cdot$bpy	0.16	0.16	20	2	88	90
$Cd(O_2R)\cdot$phen	0.25	0.28	20	4	171	87
$Cd(O_2R)\cdot$2py	0.16	0.10	20	2.5	103	76
$R(OH)_2$ = 2,2′-dihydroxybiphenyl						
$Zn(O_2R)$	0.22		15	3	75	77
$Zn(O_2R)\cdot$bpy	0.22	0.19	20	3	73	82
$Zn(O_2R)\cdot$phen	0.22	0.22	20	3	76	80
$Zn(O_2R)\cdot$2py	0.26	0.22	20	3.5	90	72
$Cd(O_2R)$	0.15		20	2	90	76
$Cd(O_2R)\cdot$bpy	0.18	0.16	20	2.5	102	88
$Cd(O_2R)\cdot$phen	0.22	0.22	20	3	133	75
$Cd(O_2R)\cdot$2py	0.15	0.14	20	2	90	80

[a] bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; py = pyridine; dmso = dimethylsulphoxide; tmed = *N,N,N′,N′*-tetramethylethanediamine. [b] In 50 ml acetone containing *ca.* 25 mg Et_4NClO_4. [c] Voltage required to give an initial current of 20 mA. [d] Based on mass of metal dissolved. [e] Solution in 50 ml methanol containing *ca.* 25 mg Et_4NClO_4.

and dried *in vacuo*. Both zinc and cadmium compounds are air-sensitive, becoming gray and then green on standing. The compounds are insoluble in the common organic solvents, except that $Zn(O_2C_6H_4)$ is soluble in 1,4-dioxane. Similar descriptions apply to the preparation and properties of the other $M(O_2R)$ compounds.

Adducts

Adducts of the $M(O_2R)$ compounds are readily prepared by oxidizing the metal electrochemically in the presence of both $R(OH)_2$ and the ligand in question. The products precipitated during electrolysis and were collected and washed in the usual way. The dmso, py and tmed adducts of zinc and cadmium catecholates are air-sensitive, changing colour within a few hours on exposure to moist air, but the adducts of these compounds with bpy and phen show no signs of decomposition. The derivatives of 2,3-dihydroxynaphthalene are all apparently air-stable, but the adducts of M(2,2′-dihydroxybiphenylate) all change colour on exposure to air. The adducts are insoluble in solvents other than dmso. The FAB mass spectrum of $Zn(O_2C_6H_4)\cdot$bpy showed predominant ions corresponding to $Zn(O_2C_6H_4)\cdot bpy^+$ and $Zn\cdot bpy^+$, but there was no indication of higher polymeric species.

The derivatives of zinc or cadmium catecholate with 1,10-phenanthroline call for special comment.

TABLE II. Analytical Results

Compound	Colour	M (%)	
		found	calculated
$R(OH)_2$ = 1,2-dihydroxybenzene			
$Zn(O_2R)$	colourless	37.3	37.7
$Zn(O_2R)\cdot bpy$	pale yellow	19.9	19.8
$Zn(O_2R)\cdot phen$	yellow	19.1	18.5
$Zn(O_2R)\cdot 2py$	colourless	20.2	19.7
$Zn(O_2R)\cdot 2dmso$	colourless	19.6	19.8
$Zn(O_2R)(phen)_2\cdot 2R(OH)_2$	yellow	9.5^a	8.7
$Cd(O_2R)$	colourless	50.5	51.0
$Cd(O_2R)\cdot bpy$	pale yellow	29.6	29.8
$Cd(O_2R)\cdot phen$	orange	27.5	28.1
$Cd(O_2R)\cdot tmed$	colourless	34.6	33.4
$Cd(O_2R)\cdot 2py$	off-white, green	29.3	29.7
$Cd(O_2R)\cdot 2dmso$	colourless	29.3	29.8
$Cd(O_2R)(phen)_2\cdot 2R(OH)_2$	orange	13.9^b	14.0
$R(OH)_2$ = 2,3-dihydroxynaphthalene			
$Zn(O_2R)$	colourless	29.3	29.3
$Zn(O_2R)\cdot bpy$	yellow	17.1	17.2
$Zn(O_2R)\cdot phen$	deep yellow	16.1	16.2
$Zn(O_2R)\cdot 2py$	pink	17.3	17.1
$Cd(O_2R)$	colourless	41.3	41.5
$Cd(O_2R)\cdot bpy$	yellow	26.1	26.3
$Cd(O_2R)\cdot phen$	deep yellow	25.0	24.9
$Cd(O_2R)\cdot 2py$	pale green	26.4	26.2
$R(OH)_2$ = 2,2′-dihydroxybiphenyl			
$Zn(O_2R)$	colourless	26.4	26.2
$Zn(O_2R)\cdot bpy$	pale yellow	15.9	16.1
$Zn(O_2R)\cdot phen$	yellow	14.9	15.2
$Zn(O_2R)\cdot 2py$	colourless	15.9	16.1
$Cd(O_2R)$	colourless	37.5	37.9
$Cd(O_2R)\cdot bpy$	pale yellow	25.1	24.8
$Cd(O_2R)\cdot phen$	deep yellow	23.4	23.6
$Cd(O_2R)\cdot 2py$	colourless	24.8	24.7

[a] Found: C, 66.3; H, 4.62; N, 7.29. Calc.: C, 66.9; H, 4.28; N, 7.43%.
[b] Found: C, 62.8; H, 4.31; N, 6.62. Calc.: C, 63.0; H, 4.03; N, 6.99%.

When electrolysis occurred with a solution of 0.2 g of $R(OH)_2$ and 0.33 g of phen in 50 ml acetone, a deep yellow solution formed at the outset, and a small quantity of yellow crystalline material deposited in the cell. As the electrolysis proceeded, the precipitate became powdery rather than crystalline, and the quantity of this material increased with time. This powder was identified as $M(O_2R)\cdot phen$ (M = Zn, Cd). The crystalline material was subsequently obtained in experiments using lower concentrations of $R(OH)_2$ and phen; electrolysis was stopped after 1 h, and the deposited crystals collected, washed with acetone and then ether, and dried *in vacuo*. Analysis showed these crystals to have the composition $M(O_2R)(phen)_2\cdot 2R(OH)_2$, and a crystal structure study confirmed this in the case of the zinc compound.

Crystallographic Studies

Crystals of $Zn(O_2C_6H_4)(C_{10}H_8N_2)\cdot 2\ C_6H_4(OH)_2$ (**1**) were collected and a suitable crystal mounted in a Syntex $P2_1$ diffractometer. The procedures for data collection [11], and the programmes used in the refinement [12], were those described in previous publications. Details are as follows: triclinic crystals, $a = 11.837(3)$, $b = 12.629(3)$, $c = 14.449(4)$ Å, $\alpha = 101.21(2)$, $\beta = 100.20(2)^\circ$, $V = 1836$ Å, $Z = 2$, $D_c = 1.364$ g cm^{-3}, $D_{ex} = 1.37$ g cm^{-3}. Radiation Mo Kα, $\lambda = 0.71069$ Å, $\mu = 6.7$ cm^{-1}. Total reflections mea-

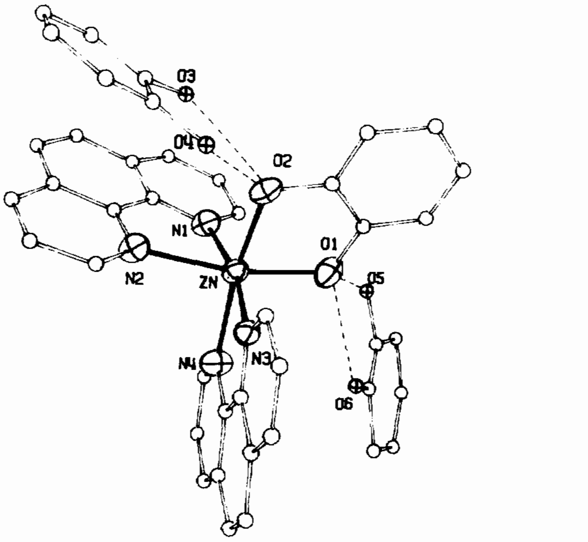

Fig. 1. ORTEP diagram of the molecular structure of $Zn(O_2C_6H_4)(C_{10}H_8N_2)_2 \cdot 2C_6H_4(OH)_2$.

sured 4767 ($-h, \pm k, \pm l$), $2\theta_{max} = 45°$, unique data ($I > 3\sigma(I)$) = 3108. $R = 0.087$, $R_w = 0.087$, $s = [\Sigma(w|F_o| - |F_c|^2/(m - n)]^{1/2} = 2.7$, max = 0.8 e $Å^{-3}$, max shift/error = 0.5.

The initial data analysis and refinement of the structure of **1** was undertaken assuming the centrosymmetric space group $P\bar{1}$, but as the refinement proceeded it became clear that the neutral catechol molecules were significantly disordered (see Fig. 1). The intensity statistics did not indicate the presence of a centric cell, and the refinement was therefore subsequently carried out in the non-centric space group $P1$ in order to resolve the disorder problem. Unfortunately these attempted refinements were neither successful nor conclusive, both because of the pseudosymmetry and the lack of a sufficiently large data set. Since our main interest was in correctly characterizing the molecular structure of **1**, which was achieved to a reasonable R-value using the $P1$ space group, the results available to date are included in this paper.

Figure 1 shows the molecular structure of **1**, and Table III the important bond lengths and atoms. See also 'Supplementary Material'.

Results and Discussion

Preparative and Spectroscopic

The electrochemical oxidation of zinc or cadmium in the presence of an aromatic dihydroxy compound is a simple and direct route to compounds which are otherwise difficult to prepare. Adducts with mono- or bidentate nitrogen donor ligands, and with dimethylsulphoxide, are also readily accessible by essentially the same technique. The yields are high in all cases, and the electrochemical method lends itself to continuous production with little attention needed. The method could no doubt be applied to metals other than those studied here.

TABLE III. Selected Bond Lengths (Å) and Angles (°) for $Zn(O_2C_6H_4)(C_{10}H_8N_2)_2 \cdot 2C_6H_4(OH)_2$

Zinc coordination			
Zn–O(1)	2.091(7)	Zn–N(2)	2.207(9)
Zn–O(2)	2.048(8)	Zn–N(3)	2.220(8)
Zn–N(1)	2.165(8)	Zn–N(4)	2.162(10)
O(1)–Zn–O(2)	81.5(3)	O(2)–Zn–N(4)	165.8(3)
O(1)–Zn–N(1)	94.1(3)	N(1)–Zn–N(2)	75.4(3)
O(1)–Zn–N(2)	166.8(3)	N(1)–Zn–N(3)	168.2(3)
O(1)–Zn–N(3)	96.8(3)	N(1)–Zn–N(4)	97.9(3)
O(1)–Zn–N(4)	94.9(3)	N(2)–Zn–N(3)	94.4(3)
O(2)–Zn–N(1)	96.0(3)	N(2)–Zn–N(4)	94.4(3)
O(2)–Zn–N(2)	91.6(3)	N(3)–Zn–N(4)	76.8(3)
O(2)–Zn–N(3)	90.0(3)		
Hydrogen bonds (O···O distances)			
O(1)···O(5)	2.62(1)	O(2)···O(3)	2.62(1)
O(1)···O(6)	2.73(1)	O(2)···O(4)	2.66(1)

The advantages of the present method in the preparation of $M(O_2R)$ species are exemplified by the case of $Zn(O_2C_6H_4)$. Two previous papers [1, 13] have reported the synthesis of this compound by the reaction of catechol and a zinc(II) salt in aqueous solution. The extreme air-sensitivity of the system is emphasized by both sets of authors, and the insoluble product is described as being either black [13] or dark green [1]. In the present work, we obtained a colourless substance, which on exposure to moist air became grey and then deep green. Similar colour changes were observed with the cadmium analogue, and with the other compounds listed in Table II. Given the facile redox reactions of catechol and other 1,2-arenediols, it is clear that aqueous solutions are best avoided in the preparation of metal derivatives of these ligands. The compounds obtained by the reaction of $M(C_2H_5)_2$ (M = Zn, Cd) with $C_6H_4(OH)_2$ [14] have almost identical properties to those observed with the substances prepared electrochemically.

In each electrochemical experiment, hydrogen gas was evolved at the cathode. The electrochemical efficiency (E_F), defined as moles of metal dissolved per Faraday, was in the range 0.48–0.53 mol F^{-1} for the whole range of syntheses reported in Table I. The reaction mechanism can therefore be simply written as:

$$\text{cathode: } R(OH)_2 + 2e \longrightarrow RO_2^{2-} + H_2(g)$$

$$\text{anode: } RO_2^{2-} + M \longrightarrow M(O_2R) + 2e$$

The constancy of the E_F values suggests that the formation of $M(O_2R)\cdot bpy$ and similar adducts occurs after the formation of $M(O_2R)$ at the anode.

The spectroscopic results confirm the general structure of these compounds (see below) but are otherwise not very informative. The infrared spectra establish that ν(O–H) of the parent dihydroxy compounds at 3410–3280 cm^{-1} is absent in the metal derivatives. The ν(C–O) mode, identified at 1255 cm^{-1} in catechol, is in the 1250–1260 cm^{-1} region for all the zinc and cadmium derivatives prepared. In the case of 2,3-dihydroxynaphthalene, the band at 1278 cm^{-1} is lowered slightly to 1260–1270 (Zn) and 1250–1275 cm^{-1} (Cd), while with 2,2′-dihydroxybiphenyl derivatives the 1250 cm^{-1} mode occurs at 1280–1310 (Zn) and 1285–1310 cm^{-1} (Cd). The infrared spectra also confirm the presence of the various neutral ligands in the adducts. None of the catechol or naphthalene derivatives are sufficiently soluble for NMR spectroscopy, but the spectra of the biphenyl analogues were recorded in d_6-dmso; the expected complex spectrum was found in the aromatic region for both the parent $M(O_2R)$ compounds and the phen, bpy and py adducts, but no attempt was made to integrate the spectra for analytical purposes.

The Structure of $Zn(O_2C_6H_4)(phen)_2\cdot 2C_6H_4(OH)_2$ (1)

Despite the space group problems discussed in 'Experimental', the structure of **1** was refined to the point at which the main features of the molecular structure are unambiguously defined. The coordination at zinc involves two bidentate 1,10-phenanthroline molecules, with Zn–N bond distances (average value 2.189 Å) slightly greater than those in $phen\cdot ZnCl_2$ [15] (2.072(7), 2.050(7) Å), corresponding to the change in coordination number from four to six. The average Zn–O bond length of 2.070 Å is also similar to the distances reported in the literature [16, 17] but any detailed discussion of the bond distances and angles must be delayed until the refinement problems are satisfactorily solved. The main conclusion at the present time is that the molecule is indeed a zinc(II) catecholate derivative.

The most unusual feature of the structure is the presence of two neutral catechol molecules which are hydrogen bonded to the oxygen atoms of the catecholate ligand. Such hydrogen bonding is rare, as is the bonding of both phenolic hydrogens of catechol to a single acceptor atom; the recently reported structures of $Bu_4N[X + \text{catechol}]$ (X = Cl, Br) [18] provide another example of this type of interaction. The level of refinement does not allow any discussion of the effect of these $RO\text{---}(HO)_2R$ interactions on the Zn–O bond lengths.

Some comment is required on the sequential formation of two related compounds, $M(O_2R)(phen)_2\cdot 2R(OH)_2$ and $M(O_2R)phen$ (M = Zn, Cd), in the electrochemical synthesis. Compound **1**, and its cadmium analogue, are clearly formed in the early stages of the synthesis when the molar ratios $R(OH)_2$:M and phen:M in solution are high. As the oxidation proceeds, these ratios fall and formation of the $M(O_2R)\cdot phen$ species will be favored, so that **1** presumably dissociates to give way to the latter. It seems reasonable to suppose that a similar sequence applies to the 2,2′-bipyridine compounds.

Structural: General

The properties of the $M(O_2R)$ compounds prepared, especially in terms of their insolubility in organic solvents, point to a cross-linked polymeric structure, and the hydrogen bonding identified in **1** emphasizes the importance of such interactions. The adducts are also for the most part insoluble, and here again cross-linking may be significant. With 2,2′-dihydroxyphenylate, the extra steric bulk of the ligand gives rise to higher solubility and here presumably mononuclear units are the dominant species.

Supplementary Material

Tables of atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and observed and calculated structure factors are available on request.

Acknowledgement

This work was supported in part by Operating Grants (to D.G.T.) from the Natural Sciences and Engineering Research Council of Canada.

References

1 F. Röhrscheid, A. L. Balch and R. H. Holm, *Inorg. Chem.*, *5*, 1542 (1966).
2 J. A. McCleverty, *Prog. Inorg. Chem.*, *10*, 49 (1969).
3 F. F. Said and D. G. Tuck, *Inorg. Chim. Acta*, *59*, 1 (1982).
4 J. L. Hencher, M. A. Khan, F. F. Said, R. Sieler and D. G. Tuck, *Inorg. Chem.*, *21*, 2787 (1982).
5 J. L. Hencher, M. A. Khan, F. F. Said and D. G. Tuck, *Polyhedron*, *4*, 1263 (1985).
6 C. Oldham, M. J. Taylor and D. G. Tuck, *Inorg. Chim. Acta*, *100*, L9 (1985).
7 R. Kumar and D. G. Tuck, *J. Organomet. Chem.*, *281*, C47 (1985).
8 J. J. Habeeb, D. G. Tuck and F. H. Walters, *J. Coord. Chem.*, *8*, 27 (1978).
9 L. Matassa, N. Kumar and D. G. Tuck, *Inorg. Chim. Acta*, *109*, 19 (1985).
10 N. Kumar, D. G. Tuck and K. D. Watson, *Can. J. Chem.*, in press.

11 M. A. Khan, R. C. Steevensz, D. G. Tuck, J. G. Noltes and P. W. R. Corfield, *Inorg. Chem., 19,* 3407 (1980).

12 M. A. Khan, C. Peppe and D. G. Tuck, *Acta Crystallogr., Sect. C, 39,* 1339 (1983).

13 J. D. Bu'lock and J. Harley-Mason, *J. Chem. Soc.,* 2248 (1951).

14 K. Andrä and H. R. Hoppe, *Z. Chem., 20,* 267 (1980).

15 M. A. Khan and D. G. Tuck, *Acta Crystallogr., Sect. C, 40,* 60 (1984).

16 G. Smith, E. J. O'Reilly, C. H. L. Kennard, K. Stadnicka and B. Oleksyn, *Inorg. Chim. Acta, 47,* 111 (1981).

17 A. Boardman, R. W. H. Small and I. J. Worrall, *Acta Crystallogr., Sect. C, 39,* 1005 (1983).

18 M. A. Khan, A. W. McCulloch and A. G. McInnes, *Can. J. Chem., 63,* 2119 (1985).