## Aqueous solutions of unipositive cadmium; reactions of $(Cd^{I})_{2}^{2+}(aq)^{\dagger}$

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Received (in Irvine, CA, USA) 5th March 2001, Accepted 23rd April 2001 First published as an Advance Article on the web 15th May 2001

Aqueous solutions  $10^{-3}$  mol dm<sup>-3</sup> in (Cd<sup>1</sup>)<sub>2</sub>, prepared by treating O<sub>2</sub>-free solutions of Cd(ClO<sub>4</sub>)<sub>2</sub> or Cd(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> with Cd powder at 65 °C, can be handled by conventional methods; the comproportionation constant (Cd<sup>2+</sup> + Cd  $\rightleftharpoons$ Cd<sub>2</sub><sup>2+</sup>) is estimated as 0.018 (24 °C, *I* = 1.14 M) and the formal oxidation potential as -0.45 V; this atypical state readily reduces I<sub>3</sub><sup>-</sup>, IrCl<sub>6</sub><sup>2-</sup>, pyridine complexes of (NH<sub>3</sub>)<sub>5</sub>Ru<sup>III</sup>, and superoxo derivatives of (NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>.

The atypical oxidation state cadmium(t) has been prepared and identified in the dimeric cation,  $(Cd^{1})_{2}^{2+}$ , in aluminium chloride melts by Corbett *et al.*,<sup>2–4</sup> and has been further studied in the crystalline state.<sup>5</sup> Moreover, a highly reactive species, thought to be Cd<sup>+</sup>(aq), has been generated *via* pulse radiolysis of aqueous Cd<sup>2+</sup> solutions by several workers.<sup>6–8</sup>

However, we find no reports describing aqueous solutions of unipositive cadmium manipulable by conventional methods. By avoiding halide and other nucleophilic ligands which favor disproportionation of Cd(1), we have generated  $10^{-4}-10^{-3}$  molar solutions of this state, have estimated its redox potential, and have examined several of its reactions.

All preparations and reactions involving Cd(I) were carried out under argon. Typically, cadmium carbonate (0.97 g, G. F. Smith 99.995%)<sup>9</sup> was dissolved in a 5% molar excess of concentrated HClO<sub>4</sub> or triflic acid (HTf), diluted to 15 ml, heated to 60–65 °C, treated with 1.90 g of Cd powder (Aldrich 325 mesh) with stirring for 5–10 min, then cooled to 24 °C. Stirring was maintained for 20–30 min. After centrifugation, the Cd(I) content in the supernatant was estimated by reaction with KI<sub>3</sub> (352 nm). At equilibrium (24 °C), 1.7–1.8% of the Cd(II) taken is converted to Cd(I). After separation from Cd metal, it decays slowly ( $t_{V_2} = 25$  h at 24 °C).

Attempted analogous preparations of  $Zn^{I}$  (from Zn metal and  $ZnTf_{2}$ ) and  $Mg^{I}$  (from Mg metal and  $MgTf_{2}$ ) yielded no soluble reductant.

Concentrations of the reducing ion are very nearly proportional to  $[Cd^{II}]$  taken (Fig. 1), thus being consistent with the formulation  $Cd_2^{2+}$ , rather than monomeric Cd<sup>+</sup>. The comproportionation constant [eqn. (1)] corresponds to a  $\Delta E^{\circ}$  value of

$$Cd^{2+} + Cd \rightleftharpoons Cd_2^{2+}; K = 0.0177 \pm 0.0003 (24 °C, I = 1.14 M)$$
 (1)

-0.10 V, which, in combination with the standard potential for Cd(11,0) (-0.403 V),^{10} yields potentials -0.45 V for Cd(11,1) and

† Electron Transfer, part 146. For part 145, see ref. 1.



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**Fig. 1** Variation of concentrations of unipositive cadmium  $(Cd_2)^{2+}$  with  $Cd(\mathfrak{n})$  taken. Reactions with Cd metal powder were initiated at 65 °C and were equilibrated at 24 °C. The slope of the regression line, 0.0177 ± 0.0003, is taken as the equilibrium quotient for the comproportionation reaction:  $Cd^{2+} + Cd \rightleftharpoons Cd_2^{2+}$ , corresponding to a  $\Delta E^{\circ}$  value -0.10 V.

-0.35 V for Cd(1,0). Dimeric Cd(1) is then a reductant thermodynamically comparable to U(111) ( $E^{\circ}$  -0.52 V).

The sensitivity of Cd(i) to both strong acids and bases limits the number of redox reactions that can be studied. Rate constants for four such reactions are summarized in Table 1. Conversions are first order in both redox partners. Solutions of  $Cd_2^{2+}$  do not react perceptibly with  $PtCl_6^{2-}$ , vitamin  $B_{12a}$ (aquacob(III)alamin), quinoxaline, or the *N*-methylphenazonium cation, and its reaction with  $Cr(v_1)$  in 2-ethyl-2-hydroxybutanoate buffer (pH 3.6) is inconveniently slow.

Reactions with the le- oxidants, IrCl<sub>6</sub><sup>2-</sup>, Ru(III) and the [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>]<sub>2</sub>-superoxo cation almost certainly involve an odd-electron species related to monomeric Cd(1). Formation of this from the dimer in a preequilibrium homolysis ( $Cd_2^{2+} \rightleftharpoons 2$ ) Cd<sup>+</sup>) would be reflected in a half-order dependence on [reductant], contrary to our kinetic picture. Generation of this transient must then require an act of electron transfer to the oxidant. Since it is likely that this transfer precedes breakage of the Cd–Cd bond, we have designated this intermediate as  $Cd_2^{3+}$ . We have further chosen this as a reasonable candidate for the necessary follow-up step, although generation and reaction of monomeric Cd+ itself cannot be excluded. Kinetic curves obtained with each of these le- reagents show no irregularity indicative of accumulation or loss of this odd-electron species on the time scale of the principal reaction, pointing to a two-step process, eqns. (2) and (3).

$$Cd_2^{2+} + Ir^{IV} \rightarrow Cd_2^{3+} + Ir^{III}$$
 (slow, rate-determining) (2)

Table 1 Reductions with aqueous cadmium(1), 24 °Ca

Oxidant	Product	I/M	λ/nm	$k/dm^3 mol^{-1} s^{-1}$
$ \begin{array}{l} I_{3}^{-b} \\ [(4\text{-}AcPy)(NH_{3})_{5}Ru]^{3+} \\ [(NH_{3})_{5}Co(O_{2})Co(NH_{3})_{5}]^{5+} \\ IrCl_{6}^{2-c} \end{array} $	I– [(4-AcPy)(NH <sub>3</sub> ) <sub>5</sub> Ru] <sup>2+</sup> [(NH <sub>3</sub> ) <sub>5</sub> Co(O <sub>2</sub> )Co(NH <sub>3</sub> ) <sub>5</sub> ] <sup>4+ c,d</sup> IrCl <sub>6</sub> <sup>3–</sup>	0.075 0.030 0.060 0.28	352 520 295 489	$(1.00 \pm 0.04) \times 10^{5}$ $68 \pm 3$ $(3.8 \pm 0.1) \times 10^{2}$ $(1.41 \pm 0.04) \times 10^{3}$

<sup>*a*</sup>  $[Cd_2^{2+}] = 2.5 \times 10^{-6} - 2.6 \times 10^{-4} M$ ;  $[Cd^{2+}] = 1.5 \times 10^{-4} - 1.5 \times 10^{-2} M$ ;  $[oxidant] = 5.5 \times 10^{-6} - 4.2 \times 10^{-4} M$ . <sup>*b*</sup> Solution buffered with 0.025 M N-(2-acetamido)-2-aminoethanesulfonic acid (ACES); pH 6.8. <sup>*c*</sup> Reaction with  $Cd_2^{2+}$  in excess. <sup>*d*</sup> Reduction of  $(Co^{III})_2$ -superoxo to  $(Co^{III})_2$ -peroxo cation; pH 5.6.

 $Cd_2^{3+} + Ir^{IV} \rightarrow 2 Cd^{2+} + Ir^{III}$  (rapid, kinetically silent) (3)

The relative rates for the two steps imply a much more negative le<sup>-</sup> potential for the intermediate  $Cd_2^{3+}$  than for  $Cd_2^{2+}$ , with the two necessarily totaling 2(-0.45) V. A lower limit for the formal potential of the initiation step (2) can be estimated by applying the simplified Marcus relationship [eqn. (4)]<sup>11</sup> to the oxidation by  $IrCl_6^{2-}$ , for which the outer-sphere rate constant,

$$\log k_{\rm Cd, Ir} = 1/2(\log k_{\rm Cd} + \log k_{\rm Ir} + \Delta E^{\circ}/0.059)$$
(4)

 $k_{\text{Cd,Ir}}$ , is  $\leq 1400 \text{ M}^{-1} \text{ s}^{-1}$  (Table 1). The self-exchange rate,  $k_{\text{Ir}}$ , for Ir(IV,III) and its standard potential have been documented<sup>12</sup> as  $10^{5.4}$  M<sup>-1</sup> s<sup>-1</sup> and 0.87 V, and the self-exchange rate,  $k_{Cd}$ , for  $(Cd_2)^{3+/2+}$  may be assumed to lie above  $10^{-12}$  M<sup>-1</sup> s<sup>-1</sup>, the minimum rate recorded for single electron self-exchanges involving simpler aquated metal ions.<sup>11</sup> We then calculate that  $\Delta E^{\circ}$  for the initiation step, eqn. (2), falls below 0.76 V, with  $E^{\circ}$ for  $(Cd_2)^{3+/2+}$  thus more positive than +0.11 V, and the formal potential for  $(Cd_2)^{3+} \rightarrow 2Cd^{2+}$  therefore more negative than -1.01 V (vs. NHE). The wide gap in potentials separating the initial loss of an electron from a main group two-electron metal reducing center and the oxidation of the resulting odd-electron intermediate appears to be a general feature of reagents of this type. The gap in this case (>1.12 V) lies between that estimated<sup>13</sup> for In(I,II,III) (0.4 V) and that for Tl(I,II,III) (1.92 V).14

We are grateful to the National Science Foundation for support of this work, to Dr J. D. Corbett for valuable discussions, to Dr V. Manivannan for preparation of the ruthenium(III) oxidant, and to Mrs Arla McPherson for technical assistance.

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