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Aqueous solutions of unipositive cadmium; reactions of $(Cd^{I})_2^{2+}(aq)$†

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Aqueous solutions 10^{-3} mol dm^{-3} in $(Cd^{I})_2$, prepared by treating O_2-free solutions of $Cd(ClO_4)_2$ or $Cd(O_3SCF_3)_2$ with Cd powder at 65 °C, can be handled by conventional methods; the comproportionation constant ($Cd^{2+} + Cd \rightleftharpoons Cd_2^{2+}$) 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_3^-, $IrCl_6^{2-}$, pyridine complexes of $(NH_3)_5Ru^{III}$, and superoxo derivatives of $(NH_3)_5Co^{III}$.

The atypical oxidation state cadmium(I) has been prepared and identified in the dimeric cation, $(Cd^{I})_2^{2+}$, in aluminium chloride melts by Corbett *et al.*,[2–4] and has been further studied in the crystalline state.[5] Moreover, a highly reactive species, thought to be $Cd^{+}(aq)$, has been generated *via* pulse radiolysis of aqueous Cd^{2+} solutions by several workers.[6–8]

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(I), 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%)[9] was dissolved in a 5% molar excess of concentrated $HClO_4$ 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_3 (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 ($t_{1/2}$ = 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^{+}. The comproportionation constant [eqn. (1)] corresponds to a $\Delta E°$ value of

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

−0.10 V, which, in combination with the standard potential for Cd(II,0) (−0.403 V),[10] yields potentials −0.45 V for Cd(II,I) and −0.35 V for Cd(I,0). Dimeric Cd(I) is then a reductant thermodynamically comparable to U(III) ($E°$ −0.52 V).

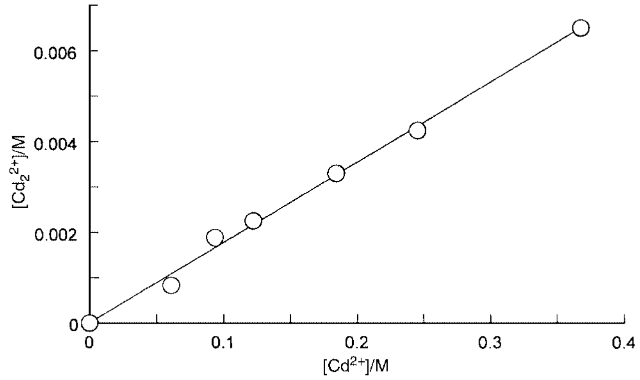

Fig. 1 Variation of concentrations of unipositive cadmium $(Cd_2)^{2+}$ with Cd(II) taken. Reactions with Cd metal powder were initiated at 65 °C and were equilibrated at 24 °C. The slope of the regression line, 0.0177 ± 0.0003, is taken as the equilibrium quotient for the comproportionation reaction: $Cd^{2+} + Cd \rightleftharpoons Cd_2^{2+}$, corresponding to a $\Delta E°$ value −0.10 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(VI) in 2-ethyl-2-hydroxybutanoate buffer (pH 3.6) is inconveniently slow.

Reactions with the 1e⁻ oxidants, $IrCl_6^{2-}$, Ru(III) and the $[(NH_3)_5Co^{III}]_2$–superoxo cation almost certainly involve an odd-electron species related to monomeric Cd(I). Formation of this from the dimer in a preequilibrium homolysis ($Cd_2^{2+} \rightleftharpoons 2\,Cd^{+}$) 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 1e⁻ 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).

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

Table 1 Reductions with aqueous cadmium(I), 24 °C[a]

Oxidant	Product	I/M	λ/nm	k/dm^3 mol^{-1} s^{-1}
I_3^- [b]	I^-	0.075	352	(1.00 ± 0.04) × 10^5
$[(4\text{-AcPy})(NH_3)_5Ru]^{3+}$	$[(4\text{-AcPy})(NH_3)_5Ru]^{2+}$	0.030	520	68 ± 3
$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$	$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ [c,d]	0.060	295	(3.8 ± 0.1) × 10^2
$IrCl_6^{2-}$ [c]	$IrCl_6^{3-}$	0.28	489	(1.41 ± 0.04) × 10^3

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

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

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

The relative rates for the two steps imply a much more negative 1e$^-$ 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)][11] to the oxidation by $IrCl_6^{2-}$, for which the outer-sphere rate constant,

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

$k_{Cd,Ir}$, is ⩽1400 M^{-1} s^{-1} (Table 1). The self-exchange rate, k_{Ir}, for Ir(IV,III) and its standard potential have been documented[12] as $10^{5.4}$ M^{-1} s^{-1} 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^{-1} s^{-1}, the minimum rate recorded for single electron self-exchanges involving simpler aquated metal ions.[11] We then calculate that $\Delta E°$ for the initiation step, eqn. (2), falls below 0.76 V, with $E°$ for $(Cd_2)^{3+/2+}$ thus more positive than +0.11 V, and the formal potential for $(Cd_2)^{3+} \longrightarrow 2Cd^{2+}$ 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[13] for In(I,II,III) (0.4 V) and that for Tl(I,II,III) (1.92 V).[14]

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Notes and references

1 S. Swavey and E. S. Gould, *Chem. Commun.*, 2000, 2159.

2 J. D. Corbett, W. J. Burkhard and L. F. Druding, *J. Am. Chem. Soc.*, 1961, **83**, 76.

3 J. D. Corbett, *Inorg. Chem.*, 1962, **1**, 700.

4 R. A. Potts, R. D. Barnes and J. D. Corbett, *Inorg. Chem.*, 1968, **7**, 2558.

5 R. Faggiani, R. J. Gillespie and J. E. Vekris, *J. Chem. Soc., Chem. Commun.*, 1986, 517.

6 D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 1968, **72**, 784; D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, 1969, **73**, 1091.

7 G. Navon and D. Meyerstein, *J. Phys. Chem.*, 1970, **74**, 4067.

8 B. H. Ershov, E. Janata and A. Henglein, *J. Phys. Chem.*, 1994, **98**, 7619.

9 Yields of Cd^{I}(aq) are extraordinarily sensitive to the purity of the $CdCO_3$ employed. With less pure (98%) material, concentrations of the reduced species fall to 20–25% those obtained with the purer carbonate.

10 Y. Okinata, in *Standard Potentials in Aqueous Solution*, ed. A. J. Bard, Marcel Dekker, New York, 1985, p. 257.

11 G. Lappin, *Redox Mechanisms in Inorganic Chemistry*, Ellis Horwood, New York, 1994, ch. 2.

12 P. Hurwitz and K. Kustin, *Trans. Faraday Soc.*, 1966, **62**, 427; P. George, I. H. Hanania and G. H. Irvine, *J. Chem. Soc.*, 1957, 3048.

13 A. M. Al-Ajlouni and E. S. Gould, *Res. Chem. Intermed.*, 1998, **6**, 653.

14 H. A. Schwarz, D. Comstock, J. K. Yandell and R. W. Dodson, *J. Phys. Chem.*, 1974, **78**, 488.