

# Strong Medium and Counterion Effects upon the Redox Potential of the 12-Tungstocobaltate(III/II) Couple

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The 12-tungstocobaltate(III/II) redox couple, both oxidation states being highly negatively charged (5–/6–), is strongly influenced by the nature of the counterion present. In particular, tetraalkylammonium ions decrease  $E^\circ[\text{Co(III)/(II)}]$  significantly, relative to that measured in the presence of alkali-metal ions in an organic solvent such as acetonitrile, thus causing large decreases in redox reactivity with respect to oxidation. An increasing proportion of water in the solvent increases  $E^\circ$ . The redox properties of the hexachloroiridate(IV)/(III) couple are affected by cations in a similar way.

A new high-potential couple at ca. 1.8 V vs. the Ag/AgCl electrode was detected in the 12-tungstocobaltate system, presumably due to the 12-tungstocobaltate(IV/III) couple.

Certain heteropoly anions, e.g. the [12-tungstocobaltate(III)]<sup>5-</sup> ion [to be abbreviated Co(III)W<sub>12</sub> in the following], are close to ideal outer-sphere redox reagents toward organic compounds by virtue of their deeply embedded central ion, surrounded by a spherical sheath of chemically inert oxygen atoms exposed to the solution.<sup>1</sup> Typical examples include the oxidation of 4-methoxytoluene<sup>2</sup> by Co(III)W<sub>12</sub> via an initial, reversible outer-sphere electron transfer (ET) step followed by a rate-determining proton transfer from the radical cation to a base (an acetate salt, MOAc), and the reduction of carbon tetrabromide<sup>3</sup> [12-tungstocobaltate(II)]<sup>7-</sup> ion in a rate-determining ET step, followed by very fast cleavage of (CBr<sub>4</sub>)<sup>-•</sup>. In both cases the nature of the counterion (supplied as the counterion of the heteropoly anion salt and/or the acetate ion source, MOAc) influenced the reaction rate, particularly for the oxidation of 4-methoxytoluene. Here an exchange of sodium acetate for tetrabutylammonium acetate at the 0.5 M concentration level *decreased* the observed rate constant by a factor of ca. 1500. For reduction of carbon tetrabromide, the same change *increased* the rate constant, although only by a maximum factor of 3.

This type of kinetic effect is by no means unknown,<sup>4</sup> although Co(III)W<sub>12</sub> oxidation of 4-methoxytoluene represents an unusually strong effect that seems to run counter to accepted behaviour (see the Discussion). Redox potentials are influenced by the nature of the solvent and the ionic components present,<sup>5</sup> and the effects are both of kinetic and thermodynamic origin.

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In the case of Co(III)W<sub>12</sub>, the rate decrease was found to be of thermodynamic origin, in that  $E^\circ[\text{Co(III)/Co(II)}]$  decreased from 1.01 to 0.76 V vs. NHE (normal hydrogen electrode) upon change from potassium to tetrabutylammonium ion as the counterion.<sup>2</sup> This is in itself enough to explain the rate decrease in terms of the kinetics of the forward step of the ET equilibrium; one can calculate a theoretical  $\Delta[\log(k_{\text{ET}})] \approx 3.0$  by the Marcus equation, to be compared with a change in  $\log(k_{\text{obs}})$  of 3.2. It must however be noted that the counterion can also exert its effect on the kinetics of an ET step, as exemplified by the following rate constants for self-exchange in the hexacyanoferrate (III)/(II) system.<sup>6</sup>

Ion (0.01 M)	None	K <sup>+</sup>	Me <sub>4</sub> N <sup>+</sup>	Et <sub>4</sub> N <sup>+</sup>	Pr <sub>4</sub> N <sup>+</sup>	Bu <sub>4</sub> N <sup>+</sup>	Pe <sub>4</sub> N <sup>+</sup>
Rate constant of Fe(III)/Fe(II) exchange/M <sup>-1</sup> s <sup>-1</sup>	6.0	230	1260	250	41	23	16

The effect upon the rate of the ET step is *positive* for all ions, in comparison with an extrapolated situation at zero cation concentration. The cation effect was attributed to reduction of the coulombic repulsion between the highly charged (3<sup>-</sup>/4<sup>-</sup>) reactants in the transition state which indeed should lead to a rate enhancement for *all* types of cations.

Since the use of tetrabutylammonium salts of heteropoly anions,<sup>7</sup> which are unusually highly charged species, is mandatory in many applications in order to solubilize these reagents in organic solvents, the above-mentioned decrease

in redox reactivity is a bothersome problem for several reasons. A practical drawback is that many reactions simply become too slow to be of any use, whereas studies of reactivity problems become complicated by the sensitivity of the redox reactivity of the heteropoly anion to even small variations in its environment. We therefore considered it important to map the redox potential of a heteropoly anion,  $\text{Co(III)/(II)W}_{12}$ , in order to obtain an empirical description of these variations.

## Results

**A new, high-potential couple in the 12-tungstocobaltate system.** The 12-tungstocobaltate system has available a number of oxidation states,<sup>8</sup> but we limited our study to the easily accessible  $\text{Co(III)/Co(II)}$  transition (see below). However, we wish to put on record that cyclic voltammetry on the tetrabutylammonium salt of  $\text{Co(III)W}_{12}$  without any supporting electrolyte present revealed the existence of a new high-potential, quasi-reversible ( $E_{\text{pa}} - E_{\text{pc}} \approx 170$  mV at a sweep rate of  $100 \text{ mV s}^{-1}$ ) couple with  $E^\circ$  around 1.6 V (Fig. 1, Table 1). Presumably, this couple has previously escaped detection by being hidden in the background oxidation curve. It was also easily seen with sodium perchlorate as the supporting electrolyte when the tetrabutylammonium salt was used (Fig. 1) and also with the potassium salt in acetonitrile/water (82.5/17.5 v/v) without supporting electrolyte. The insert in Fig. 1 demonstrates the near-reversibility of the couple,  $i_{\text{pa}}/(\nu)^{0.5}$  ( $\nu$  = sweep rate) varying between 0.23 and 0.17 over a variation in  $\nu$  from 5 to  $3200 \text{ mV s}^{-1}$ . We tentatively ascribe this quasi-reversible couple to the electron transfer between a  $\text{Co(III)}$  and  $\text{Co(IV)}$  state. Very few compounds of cobalt in the +IV state are known.<sup>9</sup>

**Electrochemistry of the  $\text{Co(III)/Co(II)}$  couple.** Cyclic voltammetry at  $50\text{--}100 \text{ mV s}^{-1}$  of 1 mM solutions of  $\text{K}_5\text{Co(III)W}_{12}\text{O}_{40}$  in media containing a supporting electrolyte (0.1 M) in general displayed the behaviour of an almost reversible redox couple with peak-to-peak separa-

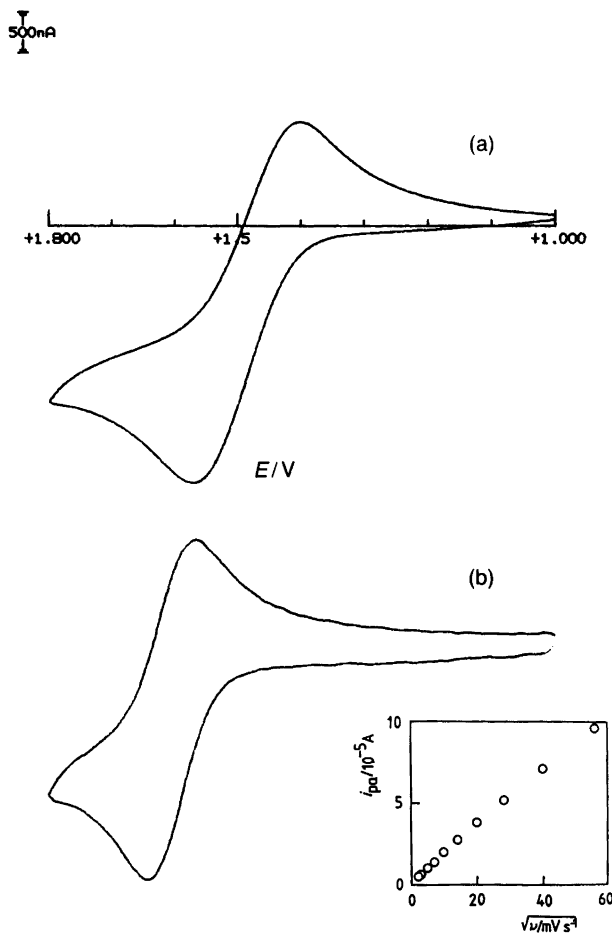


Fig. 1. Cyclic voltammograms of (a) 1 mM  $(\text{Bu}_4\text{N})_5\text{Co(III)W}_{12}$  in acetonitrile without supporting electrolyte and (b) in acetonitrile/sodium perchlorate (0.13 M) at  $100 \text{ mV s}^{-1}$ . The insert shows a plot of  $i_{\text{pa}}$  vs.  $\nu^{1/2}$  between 5 and  $3200 \text{ mV s}^{-1}$  [concentration of  $\text{Co(III)}$  salt = 4.6 mM].

tions of 60–90 mV, and reversible potentials (denoted  $E^\circ$ ) were determined as  $(E_{\text{pa}} + E_{\text{pc}})/2$ . In order to make possible a study of the effect of the solvent water contents on the two salts,  $\text{K}_5\text{Co(III)W}_{12}$  and  $(\text{Bu}_4\text{N})_5\text{Co(III)W}_{12}$ , not influenced by external counterions we chose to work without

Table 1. Electrochemical characteristics of the new, high-potential  $[\text{Co(IV)/Co(III)W}_{12}\text{O}_{40}]^{4-/-5-}$  couple, as established by cyclic voltammetry at  $100 \text{ mV s}^{-1}$ . Reference electrode,  $\text{Ag/AgCl}$ .

Salt	Medium	$E_{\text{pa}}/\text{mV}$	$E_{\text{pc}}/\text{mV}$	$\Delta E/\text{mV}$	$E^\circ/\text{mV}^a$
$\text{K}^+$	AN/ $\text{H}_2\text{O}$ (82.5/17.5), no supporting electrolyte	1870	1671	199	1771
$\text{Bu}_4\text{N}^+$	AN, no supporting electrolyte	1571	1402	169	1487
$\text{Bu}_4\text{N}^+$	AN/ $\text{NaClO}_4$ (0.13 M)	1643	1567	76	1605
$\text{Bu}_4\text{N}^+$	AN/ $\text{NaClO}_4$ (0.30 M)	1653	1570	77	1615
$\text{Bu}_4\text{N}^+$	AN/ $\text{H}_2\text{O}$ (70/30)/ $\text{Bu}_4\text{NClO}_4$ (0.1 M)	1636	Not reversible		

<sup>a</sup>  $E^\circ = (E_{\text{pa}} + E_{\text{pc}})/2$ .

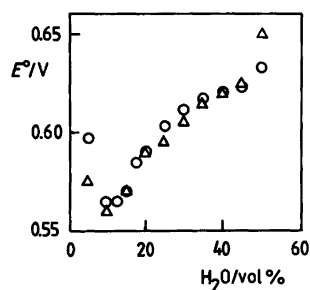


Fig. 2. Effect of water content upon  $E^\circ$  of  $K_5Co(III)/(II)W_{12}$  (1 mM) in acetonitrile without supporting electrolyte at  $v = 50 \text{ mV s}^{-1}$ :  $\circ$ , Pt electrode;  $\Delta$ , glassy carbon electrode.

any added supporting electrolyte. A 1.0 mM solution of these salts has an ionic strength of 0.015 M, enough for good voltammetric data to be obtained. Under these conditions, peak-to-peak separations were larger, of the order of 150–200 mV, which, only to a small extent, was due to an uncompensated  $iR$  term (ca. 20 mV). For solubility reasons, it was not possible to find a potassium-ion-based supporting electrolyte that was compatible with all solvent compositions. All measurements of potentials were performed with the Ag/AgCl electrode as the reference.

Fig. 2 shows the effect upon  $E^\circ$  of increasing the water content of the solvent for the potassium salt (no supporting electrolyte) on the Pt and glassy carbon electrodes. With the exception of the first point, at the lowest water concentration (5%), an increase in the water content increases  $E^\circ$ ; this is even more apparent for the tetrabutylammonium salt which displays  $E^\circ$  ca. 0.15 V in anhydrous acetonitrile with a strong increase of about 0.3 V over the first 10% of added water on both Pt and glassy C (Fig. 3). The behaviour was similar in the presence of a supporting electrolyte, except that excess tetrabutylammonium ion brought down  $E^\circ$  even further (Fig. 3).

Table 2 shows the effect upon  $E^\circ$  of different supporting electrolytes at a Pt electrode; in cases where the anion of the supporting electrolyte was varied, practically no influence was noted. Thus the effect upon  $E^\circ$  is exerted by the cation and is stronger in media of low water content.

*Effect of tetrabutylammonium ion upon the redox potential of the hexachloroiridate(IV/III) couple.* The effect of a tetraalkylammonium-ion-containing electrolyte was also briefly tested on the  $Ir(IV)Cl_6^{2-}/Ir(III)Cl_6^{3-}$  system, an often used, substitution-inert ET reagent in inorganic as well as organic chemistry.<sup>10</sup> Cyclic voltammetry of the potassium salt ( $100 \text{ mV s}^{-1}$ ) in acetonitrile/sodium perchlorate (0.1 M) demonstrated a fully reversible [peak-to-peak separation 60(2) mV]  $Ir(IV)/Ir(III)$  couple\* at 0.51 V whereas sodium hexachloroiridate under the same conditions gave  $E^\circ = 0.57 \text{ V}$  and in acetonitrile/lithium perchlorate (0.1 M)

\* In addition, the known, reversible, high-potential couple with  $E^\circ$  around 1.65 V was discernible (literature value,<sup>11</sup> 1.74 V vs. SCE in dichloromethane/tetrabutylammonium hexafluorophosphate).

Table 2. Effect of cations upon  $E^\circ[Co(III)/(II)W_{12}]^a$  (given in V vs. Ag/AgCl) in acetonitrile/water.

Salt (0.1 M)	Water (% v/v)				
	15	20	30	40	100
$LiClO_4$	0.65			0.70	
$LiNO_3$	0.66				
$NaClO_4$	0.76	0.72		0.71	0.87
$NaNO_3$	0.76				
$KClO_4$	0.73 <sup>b</sup>			0.72	
$KOAc$	0.73				
$Bu_4NClO_4$	0.49			0.53	
$Bu_4NPF_6$		0.52 <sup>c</sup>	0.53		
$Me_4NClO_4$				0.68	
$Mg(ClO_4)_2$	0.80			0.76	
$Ca(NO_3)_2$				0.78	
$Sr(NO_3)_2$				0.78	

<sup>a</sup>Measurements were made on 1 mM solutions of  $K_5Co(III)W_{12}O_{40}$  at a sweep rate of  $50 \text{ mV s}^{-1}$  and with Pt as the working electrode. <sup>b</sup>Electrolyte concentration = 0.050 M. <sup>c</sup>Sweep rate =  $100 \text{ mV s}^{-1}$ .

0.39 V. With tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte,  $E^\circ$  decreased to 0.21 V and with tetraethylammonium perchlorate (0.1 M) to  $\approx 0.2 \text{ V}$ . Thus the potential decreasing effect of tetraalkylammonium ion upon highly negatively charged redox couples is quite respectable in this system too.

## Discussion

It is well established that both solvent and counterion strongly influence the electron transfer reactivity of metal complexes, and highly charged anions seem to be especially sensitive in this respect.<sup>4-6</sup> As noted in the introduction, the kinetic effect of the cation upon the self-exchange electron transfer of the hexacyanoferrate(III/II)<sup>4-/3-</sup> couple is catalytic for all types of cation, including tetraalkylammonium

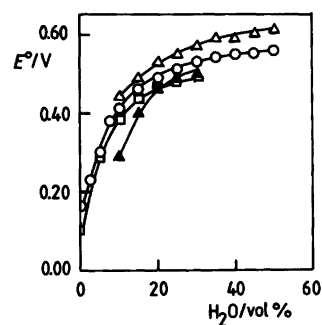


Fig. 3. Effect of water content upon  $E^\circ$  of  $(Bu_4N)_5Co(III)W_{12}$  (1 mM) in acetonitrile without supporting electrolyte ( $\circ$ , Pt;  $\Delta$ , glassy C) or acetonitrile/ $Bu_4NPF_6$  (0.1 M) ( $\square$ , Pt;  $\blacktriangle$ , glassy C) at  $v = 50 \text{ mV s}^{-1}$ .

ions.<sup>5</sup> This is logically explained by relief of coulombic repulsion between the two anions in the transition state. As for the *thermodynamic* effect of cations upon  $E^\circ$ , it is expected that the more negatively charged component of the redox couple should be stabilized, thus leading to an increase in the  $E^\circ$  value. This has been demonstrated clearly for mono-, di- and tri-valent metal cations in the hexacyanoferrate(III/II)<sup>4-/3-</sup> system where cation/anion association constants differ by a factor of ca. 10 between the two oxidation states.<sup>12</sup> Why do we then observe the very strong and at first sight somewhat paradoxical decrease of  $E^\circ$  of by tetraalkylammonium ions? The effect of such ions upon self-exchange kinetics is to increase the rate, and the thermodynamic effect should be to increase  $E^\circ$ , just as metal cations do.

This paradox is resolved by noting that the reference point for the  $E^\circ$  value also should be a hypothetical situation where no cation is present (see above). Then all cations should increase  $E^\circ$  by virtue of the stronger coulombic stabilizing effect upon the more negatively charged component; tetraalkylammonium ions are much less efficient than metal cations, most likely for steric reasons but also because of better ligand-binding properties of the more easily polarizable metal ions.

The most important consequence of the 'tetraalkylammonium effect' upon the redox reactivity of highly charged anionic reagents is of course a practical one: one can tune the redox potential simply by varying the nature of the counterion in the system. In many cases, the effect unfortunately makes reagents of this type less useful by decreasing their reactivity to very low levels.

## Experimental

Potassium 12-tungstocobaltate(III) was prepared as reported by Simmons,<sup>13</sup> except for a minor modification of the purification procedure.<sup>2</sup> The corresponding tetrabutylammonium salt was prepared by ion-pair extraction according to Ref. 7. Potassium and sodium hexachloroiridate(IV) were of commercial quality. Acetonitrile was of UVASOL® (Merck, Darmstadt) quality, and all salts used were of highest quality commercially available. CV measurements were performed under Ar protection by means of a BAS-100 instrument, using an Ag/AgCl electrode as the reference. In general, compensation for  $iR$  drop was not performed, since at the low sweep rates employed it turned out to be negligible even in electrolytes without a supporting electrolyte.

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## References

1. For an excellent treatise, see: Pope, M. T. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin and Heidelberg 1983.
2. Ebersson, L. *J. Am. Chem. Soc.* **105** (1983) 3192.
3. Ebersson, L. and Ekström, M. *Acta Chem. Scand., Ser. B* **42** (1988) 101.
4. Examples of kinetic cation effects upon the following redox systems are: manganate(VII)/(VI) Gjertsen, L. and Wahl, A. C. *J. Am. Chem. Soc.* **81** (1959) 1572; Wolfe, S. and Ingold, C. F. *J. Am. Chem. Soc.* **105** (1983) 7755; Spiccia, L. and Swaddle, T. W. *Inorg. Chem.* **26** (1987) 2265; 12-Tungstocobaltate(III/II), Nickel, U., Klein, B. and Hsin-min, J. *Ber. Bunsenges. Phys. Chem.* **91** (1987) 997. Various polycyanometalates. Shporer, M., Ron, G., Loewenstein, A. and Navon, G. *Inorg. Chem.* **4** (1965) 361; Holzwarth, J. and Strohmaier, L. *Ber. Bunsenges. Phys. Chem.* **77** (1973) 1145; Lemire, R. J. and Lister, M. W. *J. Solution Chem.* **6** (1977) 429; Ferranti, F. and Indelli, A. *Gazz. Chim. Ital.* **107** (1977) 543; Okamoto, T., Ohno, A. and Oka, S. *Inorg. Chem.* **19** (1980) 3176; Anast, J. M. and Margerum, D. W. *Inorg. Chem.* **21** (1982) 3494; Butter, K. R., Kemp, T. J., Sieklucka, B. and Samotus, A. *J. Chem. Soc., Dalton Trans.* (1986) 1217.
5. Gritzner, G., Danksagmüller, K. and Gutmann, V. *J. Electroanal. Chem.* **72** (1976) 177; **90** (1978) 203; Messina, A. and Gritzner, G. *J. Electroanal. Chem.* **101** (1979) 201; Keita, B., Bouaziz, D. and Nadjo, L. *J. Electrochem. Soc.* **135** (1988) 87.
6. Campion, R. J., Deck, C. F., King, P., Jr. and Wahl, A. C. *Inorg. Chem.* **6** (1967) 672.
7. Katsoulis, D. E. *Diss.*, Georgetown University, 1985; Katsoulis, D. E. and Pope, M. T. *J. Am. Chem. Soc.* **106** (1984) 2737.
8. Pope, M. T. and Varga, G. M., Jr. *Inorg. Chem.* **5** (1966) 1249.
9. Byrne, E. K. and Theopold, K. H. *J. Am. Chem. Soc.* **111** (1989) 3887.
10. See, e.g., Pelizzetti, E., Mentasto, E. and Pramauro, E. *Inorg. Chem.* **17** (1978) 1181; Wong, C. L. and Kochi, J. K. *J. Am. Chem. Soc.* **101** (1979) 5593; Steenken, S. and Neta, P. *J. Am. Chem. Soc.* **104** (1982) 1244; Drury, W. D. and DeKorte, J. M. *Inorg. Chem.* **22** (1983) 121.
11. Health, G. A., Moock, K. A., Sharp, D. W. A. and Yellowlees, L. J. *J. Chem. Soc., Chem. Commun.* (1985) 1503.
12. Scherer, G. and Willig, F. *J. Electroanal. Chem.* **85** (1977) 77.
13. Simmons, V. E. *Diss.*, Boston University, Boston 1963.

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