Dodecatungstocuprates. A Tetrahedral Copper(I)–Copper(II) Redox System

By DALE R. WEXELL and MICHAEL T. POPE*

(*Department of Chemistry, Georgetown University, Washington, D.C.* 20007)

Summary The tetrahedral Cu^{II} complex, $CuW_{12}O_{40}^{6-}$, is reversibly reduced to the corresponding Cu^{I} species that is stable against disproportionation in aqueous solution.

ALTHOUGH the redox behaviour of certain copper-containing enzymes involves the Cu^{2+}–Cu^{+} couple, it is difficult to find simple copper complexes that can undergo repeated oxidation-reduction cycles in a chemically reversible way.

The different stereochemical and ligand preferences of the "hard" Cu^{2+} and "soft" Cu^{+} ions are given as reasons for this failure. It has been suggested that the cyclic redox ability of some copper enzymes results from a near tetrahedral co-ordination of the copper in these species,[1] but there are few suitable tetrahedral Cu^{II} complexes available for testing this idea. The heteropoly 12-tungstate ("Keggin") anions, $XW_{12}O_{40}^{n-}$, have a structure[2] that confers tetrahedral co-ordination of oxygen atoms upon the central atom X. Keggin-type tungstates with Co^{II},[3] Co^{III},[3] Fe^{III},[4] Cr^{III},[5] and Cu^{II} [6] as central atoms have been described. Brown and Mair, in their report of the last of these complexes, noted that it could not be reduced by iodide ion to a Cu^{I} species. We felt, however, that a tetrahedral environment should favour Cu^{I}, and that the anion $Cu^{I}W_{12}O_{40}^{7-}$ might well be stable against disproportionation. We have, therefore, made a more extensive investigation of the reduction of the 12-tungstocuprate(II) ion.

The potassium salt of the heteropoly anion was prepared following a slightly modified version of Brown and Mair's procedure.[6,7] A typical product analysis gave K_2O, 8·58; CuO, 2·35; WO_3, 84·11; H_2O, 5·66. $K_6CuW_{12}O_{40},10H_2O$ requires K_2O, 8·50; CuO, 2·39; WO_3, 83·69; H_2O, 5·42%. Solutions of the potassium salt appear, from spectral and polarographic measurements, to be indefinitely stable at pH 2—6. Decomposition is slow at pH 1—2 and 6—7. Polarography (dropping mercury electrode, $5·0 \times 10^{-4}$M-complex; 1·0 M-sodium sulphate; 0·2 M-buffer) shows the existence of three reduction steps corresponding to the addition of one, two, and two electrons. The first wave ($E_{\frac{1}{2}} = -0·18$ V *vs.* SCE) is independent of pH, while the half-wave potentials of the second and third waves are pH-dependent (*e.g.*, −0·50, −0·61 at pH 2·5, −0·60, −0·73 V at pH 5·1). We assign the first wave to the reduction, $Cu^{II}W_{12}O_{40}^{6-}$ to $Cu^{I}W_{12}O_{40}^{7-}$, and the subsequent waves, analogous to those seen in polarograms of other 12-tungstates,[8,9] to the formation of the heteropoly blue anions $Cu^{I}W^{V}_{2}W^{VI}_{10}O_{40}H_2^{7-}$ and $Cu^{I}W^{V}_{4}W^{VI}_{8}O_{40}H_4^{7-}$. We attach no particular significance to the apparent discrepancy between the negative shift of the Cu^{2+}–Cu^{+} reduction potential ($E^0 = -0·081$ *vs.* SCE) and the stability of Cu^{I} in the heteropoly species, since the reduction potentials of heteropoly anions are known to be strongly influenced by electrostatic factors arising from the anionic charges.[8] The 0·1 V change in reduction potential can be viewed in the context of the 0·8 V change for the corresponding 12-tungstocobaltates-(II) and -(III).[3] A better indication of the stability of Cu^{I} in the heteropoly structure is given by the absence of a polarographic wave corresponding to Cu^{I} to Cu^{0} reduction at potentials more positive than −1·0 V. Beyond this potential multiple reductions of tungsten prevent possible detection of such a process.

The 12-tungstocuprate(I) anion can be generated by controlled potential electrolysis or by Cr^{II} reduction of the Cu^{II} complex. Polarograms of the reduced solutions show the expected anodic wave, but with a markedly reduced height due to strong adsorption on the mercury. Cyclic voltammograms (see Figure) using a wax-impregnated carbon electrode[10] show that the reduction is chemically but not polarographically reversible.

Dark red solutions of the Cu^I species have been obtained by controlled potential electrolysis at pH's from 2—6. The optical spectra of these solutions show a broad band at 485 nm (20·6 kK), ϵ 2400, and another at 260 nm (38·5 kK), ϵ 7400. Beer's Law is obeyed at 485 nm at pH's 2·7 and 4·0, and no change in the spectrum is observed after 24 h. Aerial oxidation of the reduced solutions (as well as those reduced by a further two electrons) leads to virtually quantitative recovery of the Cu^{II} complex. The 485 nm band corresponds to similar absorptions, normally ascribed to "metal-to-ligand" charge transfer, observed in the spectra of several other Cu^I complexes.[11] In heteropoly anions, however, the distinction between such a description and that of an intervalence charge transfer, $Cu^IW^{VI}_{12}O_{40}{}^{7-} \longleftrightarrow Cu^{II}W^VW^{VI}_{11}O_{40}{}^{7-}$, is not clear cut. While the former description retains the language of conventional co-ordination chemistry, the latter is probably more realistic. Whatever the assignment, this anion is the only heteropoly species to show a low energy charge transfer from the central atom to the oxometallate "ligand". A band at *ca.* 38 kK is observed in the spectra of other 12-tungstates.[8]

The 12-tungstocuprate(I) anion is the first example of a heteropoly species with a univalent central atom, and the first example of a discrete Cu^I complex with ligands co-ordinated through oxygen. The electron transfer Cu^I to Cu^{II} results in only small changes† in the stereochemistry of the copper atom, and no dissociation of the "multidentate ligand" need occur in the process. These factors allow repeated oxidation–reduction cycles to be carried out, in contrast to the normal situation with copper complexes. The tungstocuprate system may thus provide a model for the electron exchange process in copper enzymes.

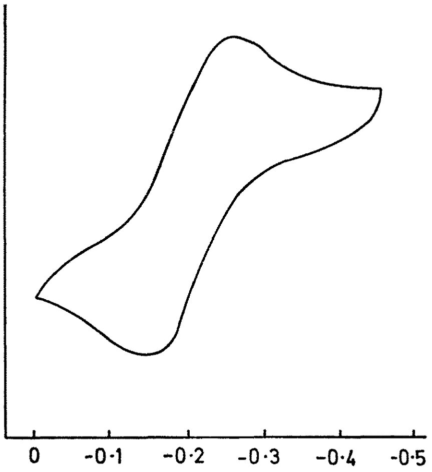

FIGURE. *Cyclic voltammogram (after* ca. *10 cycles) of the 12-tungstocuprate*(II) *anion. Wax-impregnated carbon electrode.* $5{\cdot}0 \times 10^{-4}$M-$K_6CuW_{12}O_{40}$; 1·0M-Na_2SO_4; 0·2M-*acetate buffer*, pH 4·0; *sweep rate* 0·5 V *min*$^{-1}$; *room temperature.*

This research was supported by a National Science Foundation grant and, in part, by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(*Received, December* **14*th*,** 1970; *Com.* 2160.)

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† Both e.s.r. and optical spectra show the expected axial distortions of the $Cu^{II}O_4$ tetrahedron in the oxidized anion.[7]

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