Formation of the Bis(biuretato)-complex of Tervalent Copper and Its Redox Potential

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THE preparation of a stable Cu^{III}–biuret complex has been reported recently.[1] This complex was prepared by using a powerful oxidizing agent ($K_2S_2O_8$) in the presence of 5N-KOH. We report the oxidation of Cu^{II} to Cu^{III} in the presence of biuret under much milder oxidizing conditions: Na_2IrCl_6 ($E_0 = 1{\cdot}08$ v) or Fe(phenanthroline)$_3^{3+}$ ($E_0 = 1{\cdot}07$ v) were found to oxidize Cu^{II} biuret to the Cu^{III} complex under slightly alkaline conditions (pH 11·0).

Biuret (10 mmoles) and $CuSO_4,5H_2O$ (5 mmoles) were mixed in water (30 ml.) and the pH raised to 11·0 with NaOH in a pH-stat; Na_2IrCl_6 (5 mmoles) was added, resulting in rapid precipitation of the brown $NaCu^{III}bi_2$. The precipitate was washed several times with distilled water and then dried *in vacuo* at 100° over H_2SO_4.

Upon reaction with acidified potassium iodide solution, one gram atom of copper in the biuret complex yielded two equivalents of iodine, thus establishing the trivalency of the copper within the compound. It should be noted that the formation of $NaCu^{III}bi_2$, when $IrCl_6^{2-}$ and $Cu^{II}bi_2^{2-}$ are mixed, is instantaneous, while the rate of the spontaneous reduction of $IrCl_6^{2-}$ by water at this pH (11·0) is negligible. It may thus be concluded that the formation of $NaCu^{III}bi_2$ proceeds by direct electron transfer from the $Cu^{II}bi_2^{2-}$ to $IrCl_6^{2-}$ and does not involve oxidation products of water as intermediaries:

$$Cu^{2+} + IrCl_6^{2-} + 2biH_2 + 4OH^- \rightarrow Cu^{III}(bi^{2-})_2 + IrCl_6^{3-} + 4H_2O$$

$Fe^{III}(phen)_3^{3+}$ also yields $NaCu^{III}bi_2$ when mixed with $Cu^{II}bi_2^{2-}$ at pH 11·0. Since Fe^{III}-(phen)$_3^{3+}$ is reduced very rapidly by water, even in neutral solutions (pH 6), the possibility arises that in the latter case the oxidation of Cu^{II} to Cu^{III} might be carried out by OH radicals produced in the decomposition of water by the Fe^{III}(phenanthroline)$_3^{3+}$ complex.[2] However, if the reaction is carried out in the presence of a molar ratio of 10 : 1 MeOH or sodium benzoate to Cu, no diminution in the yield of the $Cu^{III}bi_2$ is observed. As these reagents are efficient OH radical scavengers[3,4] this result strongly suggests that the Fe^{III} (phen)$_3^{3+}$–$Cu^{II}bi_2^{2-}$ oxidation also proceeds by direct electron transfer. The latter conclusion further implies that the electron-transfer reaction is an extremely fast process, the rate most probably being diffusion controlled.

Under comparable conditions $OsCl_6^{2-}$ ($E_0 = 0{\cdot}85$v) does not yield $NaCu^{III}bi_2^-$ from $Cu^{II}bi_2^{2-}$. This indicates that the redox potential of the couple Cu^{II}/Cu^{III} when copper is bound in a biuret complex is between 0·85—1·07 v, one volt lower than E_0 for Cu^{II}/Cu^{III} in the aquo-complex.[5]

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