revealed that 90% of the erythrocyte copper is bound in superoxide dismutase. Only 10% of the copper is found in the high molecular fraction following gel filtration of the haemolysate. All other copper proteins migrate in the region near $M_r = 32000$.

The yield of both superoxide dismutase and Cu_2 -(haem_b)₂-protein clearly shows that the copper of the red blood cell is distributed in these proteins. Taking into account minimal losses of intracellular copper in the course of the fractionation steps no copper proteins other than the preceding ones were detectable. It appears that Cu_2Zn_2 superoxide dismutase or cuprein is the major intracellular copper protein.

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S15

Attempts to Detect and Locate Platinum Metals in Plant Tissues by a Variety of Microscopic Techniques

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Root and leaf samples of *Eichhornia crassipes* (water hyacinth) containing the platinum metals were examined by a number of techniques.

(1) Light microscopy. This classical technique is of little use, except where the concentrations are unusually high. However, morphological changes caused by toxic elements can be studied. The palisade mesophyll of the leaf of a Pt-treated plant was found to be distorted in contrast to that in control or Rh (non-toxic) treated plants.

(2) Scanning electron microscopy with energy dispersive X-ray analysis (SEM + EDXA). Control root and leaf specimens showed high concentration of Ca and smaller amounts of P and S. Roots treated with $[PtCl_6]^{2-}$ were covered in electron dense deposits. EDXA showed Ca (K_{α} , 3.96 keV) and Pt (M_{α} , 2.05 keV; L_{α} , 9.44 keV; L_{β} , 11.07 keV). X-ray photo-electron spectra of these deposits showed a corrected Pt 4f binding energy of 76 ± 0.5 eV, indicating Pt⁴⁺ in the deposits.

(3) Electron microscope analysis (EMPA). Examination of Pt-treated roots showed clearly that platinum accumulated in the epidermal region, lesser amounts are in the cortex. Ruthenium however, was distributed more evenly.

(4) Scanning transmission electron microscopy with energy dispersive X-ray analysis (STEM + EDXA). Problems arise with Pt-treated root materials, which show widespread electron dense deposits. In order to avoid interference with Pt, sections were viewed unstained, hence cytological detail is absent. EDXA confirmed the presence of Pt.

S16

The Uptake and Accumulation of Platinum Metals by the Water Hyacinth (*Eichhornia crassipes*)

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The biological effects of the platinum group metals on plants have been studied by treating plants with chlorocomplexes of each metal at a range of concentrations. The vascular aquatic plant *Eichhornia crassipes* (water hyacinth) was selected for detailed study because of its remarkable ability to assimilate high levels of transition elements from solution. Water hyacinths are capable of recovering platinum group metals even from dilute solution though to varying degrees depending on the metal:

 $Pt^{2+} > Pd^{2+} > Os^{4+} \approx Ru^{3+} > Ir^{3+} \approx Rh^{3+}$

decreasing % recoverey at the 0.05 ppm level

When this is compared to the relative order of toxicity at the 10 ppm level for each metal, some similarities emerge:

$$Pt^{2+}(5d^8) \approx Pd^{2+}(4d^8) > Os^{4+}(5d^4) \approx Ru^{3+}(4d^5) >$$
$$> Ir^{3+}(5d^6) > Pt^{4+}(5d^6) \gg Rh^{3+}(4d^6)$$

decreasing order of toxicity at the 10.0 ppm level

The relationship between phytotoxicity and position in the periodic table is tenuous but appears to be linked with the oxidation state and hence electron configuration of the metal ion. The two least toxic ions, Ir^{3+} and Rh^{3+} , have the electron configuration (d^6) ; it is significant too that $Pt^{4+}(d^6)$ is far less toxic than $Pt^{2+}(d^8)$. A similar relationship has been found for the phytotoxicity of 1st row elements:

$$Cd^{2+}(4d^{10}) \ge Zn^{2+}(3d^{10}) > Ni^{2+}(3d^8) > Co^{2+}(3d^7)$$

decreasing relative toxicity, decreasing softness

Included in the soft acid classification is Pt^{2+} and Pd^{2+} whilst Rh^{3+} and Ir^{3+} are considered borderline between hard and soft, along with Fe^{2+} , Co^{2+} , Cu^{2+} and Zn^{2+} . This approach goes some way to explaining