Complexes of Hydroxy-acids containing Two Different Metals

By H. M. N. H. IRVING* and W. R. TOMLINSON
(*Department of Inorganic and Structural Chemistry, The University, Leeds* 2)

WHILE determining small amounts of copper in certain alloys by liquid–liquid extraction of the bischelate of copper(I) with 2,2′-biquinolyl in the presence of citrate ions, Elwell[1] reported low recoveries of copper when chromium(III) was present. The adverse effect of chromium(III) could be overcome by adding a substantial concentration of ferrous ions.

We have now shown that the inhibiting effect of chromium(III) is attributable to the formation of a kinetically inert complex of chromium(III), copper(II), and citrate ions which contain an equal number of atoms of each metal as determined by the method of continuous variations applied to both 1-phase and 2-phase systems. The copper can be displaced from this complex by any of the transition cations whose immediate effectiveness is increased in the order $\mathrm{Zn^{2+} < Mn^{2+} < Co^{2+} < Ni^{2+} < Fe^{2+}}$ although the extraction of $\mathrm{Cu^{I}}$ could be made quantitative in every case by prolonging the equilibration for 2—3 days. As expected for chromium(III), the formation of the ternary complex with copper and citrate is slow at room temperature; but once formed it is kinetically inert to reduction *e.g.* by hydroxylamine in the cold. In addition, we have shown that ternary complexes of comparable stability are not formed by $\mathrm{Fe^{III}}$ or $\mathrm{La^{III}}$, and although $\mathrm{Al^{III}}$ can also form a ternary complex with $\mathrm{Cu^{II}}$ and citrate its stability is markedly less than that with $\mathrm{Cr^{III}}$. Copper(II) and citrate ions ($\mathrm{H_4L}$) have recently been shown[2] to form a dimer of formula $\mathrm{Cu_2(HL)_2^{2-}}$ and work on related systems is currently in progress in many laboratories.

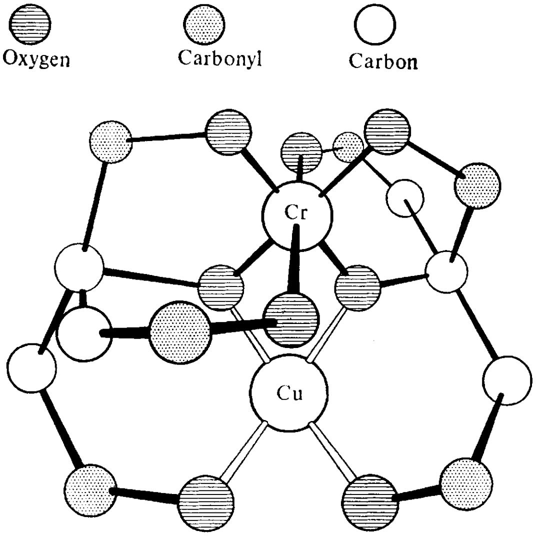

FIGURE. *A possible structure for the ternary complex* $\mathrm{CuCrL_2^{3-}}$.

Examination of scale models of a complex formed from $\mathrm{Cr^{3+}}$ and two citrate ions shows that it can itself behave as a tetradentate ligand with two free carboxyl groups. It presents a convenient 'hole' in which a divalent transition cation can fit, square-planar or octahedral co-ordination being completed, through two of the oxygen atoms already co-ordinated to the chromium. A diagram of a possible structure for the complex $\mathrm{CuCrL_2^{3-}}$ is shown.

Although complexes of a single metal with two different ligands are relatively common, the formation of a water-soluble complex involving two different metals and a common ligand is unusual. Spectral and polarographic studies of solutions containing $\mathrm{UO_2^{2+}}$, $\mathrm{Al^{3+}}$ and citrate demonstrate the existence of complexes containing one uranyl, one aluminium, and two citrate residues per molecule similar to that shown in the diagram.[3] The unsuspected formation of ternary compounds may explain a number of anomalous observations and unexplained interferences in analytical procedures. Thus Flaschka[4] observed an unexpected reduction in reaction rate when copper was titrated at pH 8 with triethylenetetramine in a tartrate medium that also contained aluminium. The explanation suggested was that a kinetically inert tartrato-complex containing both copper and aluminium in the molar ratio 1:2 was formed. It is possible that many similar examples of binuclear (or polynuclear) complex ions involving different metals remain to be discovered and some at least will prove to have significance analytically.

(*Received, March* 11*th*, 1968; *Com.* 294.)

---

[1] W. T. Elwell, *Analyst*, 1955, **80**, 508.
[2] K. S. Rajan and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1967, **29**, 463.
[3] G. L. Boorman and W. B. Holbrook, *Analyt. Chem.*, 1959, **31**, 10.
[4] H. Flaschka, J. Butcher, and R. Speights, *Talanta*, 1961, **8**, 400.