

COMPREHENSIVE INORGANIC CHEMISTRY

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COMPREHENSIVE INORGANIC CHEMISTRY

IN FIVE VOLUMES

Volume 3

Cu, Ag, Au

Zn, Cd, Hg

Sc, Y, La

Ti, Zr, Hf

V, Nb, Ta

Cr, Mo, W

Mn, Tc, Re

Fe, Co, Ni

Ru, Rh, Pd

Os, Ir, Pt

Volume 1. H, Noble Gases, Group IA, Group IIA, Group IIIB, C and Si

Volume 2. Ge, Sn, Pb, Group VB, Group VIB, Group VIIB

Volume 3. Group IB, Group IIB, Group IIIA, Group IVA, Group VA, Group VIA, Group VIIA, Group VIII

Volume 4. Lanthanides, Transition Metal Compounds

Volume 5. Actinides, Master Index

PREFACE

THE Editorial Board of Comprehensive Inorganic Chemistry planned the treatise to fill a gap in the literature. There was no work that provided more information than could be found in single volumes but was not so large as to put it out of reach of all but a few central libraries.

The Editorial Board drew up and incorporated in instructions to authors a scheme that would make the best possible use of about five thousand pages. It was envisaged that the treatise would be of service to a wide range of readers many of whom would not be professional chemists. Convenience for all classes of reader was of paramount importance so that if a conflict arose between brevity and ease of use, the latter was preferred. Nevertheless the arrangement of the treatise is so systematic that such conflicts rarely occurred. The convenience of the reader has been further ensured by the adoption of a consistent arrangement of material within the chapters on the elements. The editors have been very gratified to observe that authors have not found the imposed pattern unduly restrictive. It has certainly helped to keep the accounts coherent and to preserve the intended balance between the chapters. The editors are very sensible to the effort that authors have made to collaborate.

The section of the book devoted to the survey of topics, particularly those relating to the transition elements, was a special interest of Sir Ronald Nyholm, whose death after most chapters were in proof saddened many chemists. We hope that those chapters which bear repeated evidence of his intellectual influence will be judged to be one of the many worthy memorials that he left behind him.

A. F. TROTMAN-DICKENSON

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Master Index

27. COPPER

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1. HISTORY*

As copper occurs native in several parts of the world it is hardly surprising that it was the first metal to be harnessed by man and, being second only to iron in its usefulness down the ages, it has been called the cornerstone of civilization. Prehistoric man no doubt found that, by hammering this native copper with stones, he was able to harden it and thus to fabricate a variety of weapons; estimates have put the first such uses of copper at 5000 B.C. or even earlier. The Egyptians are thought to have obtained their copper by the reduction of the basic carbonate (Malachite, CuCO_3 , Cu(OH)_2) obtained from Sinai in charcoal fires and small cast objects dating back to 3500 B.C. have been found; estimates have given the total Ancient Egyptian output over 1500 years to be about 10,000 tons. Shortly after this, bronzes (copper-tin alloys) began to appear, the alloys apparently being formed by the deliberate mixing of tin to molten copper and not by the reduction of naturally-occurring tin-copper ores. The myth concerning the so-called lost art of hardening copper may well be unfounded because careful analysis and study of old bronzes can reveal their chemical and physical properties which furnish a complete understanding of how the Ancients treated their copper and copper alloys; in the present day, alloys can be produced which are far superior in every way. The advent of brass (copper-zinc alloys) came much later than that of bronze, the earliest known example of brass being a Roman coin minted during the reign of Augustus (27 B.C.-A.D. 14). Unlike bronze, brass was made by the smelting of copper-zinc ores and it was not until 1781 that the modern process of making brass by the direct fusion of copper and zinc was developed.

The corrosion resistance of copper appears to have been appreciated by the ancient Egyptians since they employed copper bands and nails in ship building and used copper pipes for conveying water; it is noteworthy that after the passage of centuries some of these articles still survive in good condition. The bronze age reached its peak during the Roman era when copper and bronze were used in large amounts for such things as arms, coinage, household utensils, statuary, architecture and furniture. However, with the collapse of Rome, causing a disruption in industry and trade, metallurgy fell into decline, but around the ninth century church bells were being cast in bronze and by the fourteenth century churches were being roofed in copper, and bronze cannon weighing about 18 tons could be cast. Copper played its part in the advent of electricity, being used by Volta in 1779 in his electrical batteries, by Faraday in 1831 during experiments on magneto-electricity and not least by Morse who, in 1832, relayed electrical signals over 1700 ft of copper wire constituting

* B. W. Smith, *Sixty Centuries of Copper*, Copper Development Assoc., London (1965); F. L. Wideman, *Copper*, U.S. Bureau of Mines Bulletin 630 (1965).

the first telegraph line. Today one of the major outlets of copper production is the electrical industry. Thanks largely to the alchemists' relentless quest for methods of changing the base metals into silver and gold it became apparent that the addition of other elements to copper greatly altered the characteristics of the host with the result that today the metallurgist has over a thousand alloys of copper from which to choose.

It has been estimated that during 1964 about 7.4 million short tons of copper were made available in the Western World, 4.4 million tons of which was mined, the rest being recovered from scrap. Recent calculations suggest that usable world copper reserves are of the order of 200 million tons although new and large deposits are still being discovered whilst advances in technology permit the mining of lower grades of ore; both these factors of course increase the actual potential.

2. OCCURRENCE AND METALLURGY OF COPPER

Copper is one of the trace elements essential to the healthy life of many plants¹ and animals², usually occurring as part of the prosthetic group of oxidizing enzymes^{4, 8b} (for example, ascorbic acid oxidase, tyrosinase, lactase, monoamine oxidase, cytochrome oxidase and galactose oxidase). These oxidases, high molecular weight proteins containing 0.05–0.35% of copper, play a part in life's vital oxidation and reduction processes, the copper undergoing cyclic changes between the Cu(I) and the Cu(II) states. The metal is tightly bound to ligand sites (e.g. O, S or N atoms) on the protein and cannot be removed by dialysis against water; however, treatment of the enzyme with acid or cyanide, followed by dialysis, results in the removal of copper. It is sometimes possible to reconstitute the enzyme by adding back the copper^{4c}. Field experiments have shown that copper sulphide acts as one of the main sources of copper for plant growth, a fact which Russian workers in the Middle Urals have exploited in biogeochemical prospecting for copper deposits³; by analysing plants for higher-than-average copper content, deposits of copper sulphide could be detected down to a depth of 25–30 m. Evidence has also been obtained which suggests that copper may have further rôles in the fixation of nitrogen (e.g. in vetch and clover), in photosynthesis and, possibly, in the production of chlorophyll^{1d}.

The respiratory systems of certain Crustacea and lower animals utilize the blue copper-containing pigment haemocyanin which can bind roughly 25 ml of oxygen for each 100 g of haemocyanin, about one-fifth of that bound by haemoglobin. A deficiency of copper in mammals can cause anaemia because copper apparently plays two rôles in haemoglobin synthesis, one as part of an enzyme responsible for a step in the formation of the porphyrin

^{1a} W. Stiles, *Trace Elements in Plants*, 3rd ed., Cambridge U.P. (1961).

^{1b} M. Borys, *Wiad. Bot.* 8 (1964) 205; *Biol. Abstr.* (1965) 29208.

^{1c} E. J. Hewitt, *Ann. Rev. Plant Physiol.* 2 (1951) 25.

^{1d} F. C. Steward (ed.), *Plant Physiology*, vol. III, Academic Press (1963).

^{2a} H. M. Fox and G. Ververs, *The Nature of Animal Colours*, Sidgwick & Jackson, London (1960).

^{2b} J. N. Cumings, The scientific basis of medicine, *Annual Reviews* (1965) 45.

^{2c} J. N. Cumings, *Heavy Metals and the Brain*, Blackwell, Oxford (1959).

^{2d} D. Faudin and J. H. Fellman, *Biochim. Biophys. Acta*, 141 (1967) 64.

^{3a} H. R. Marston and S. H. Allen, *Nature*, 215 (1967) 645.

^{3b} D. L. Poskotin and M. V. Lyubimova, *Geokhimiya* (1963) 603.

^{4a} H. J. Evans and G. J. Sorger, *Ann. Rev. Plant Physiol.* 17 (1966) 47.

^{4b} H. S. Mason, *Ann. Rev. Biochem.* 34 (1965) 595.

^{4c} O. Warburg, *Heavy Metal Prosthetic Groups and Enzyme Action*, Oxford U.P. (1949).

system^{1a, 2a} and the other by releasing the required iron from various storage sites in the body^{2c}. Young pigs deliberately reared on milk containing a deficiency of copper suffered, among other things, a high incidence of gross and microscopical lesions of the aorta⁵.

The diet of humans usually includes between 2 and 5 mg of copper per day^{2b} which is above the normal body maintenance requirements of about 2 mg per day. The adult body contains between 100 and 150 mg of copper, the muscle mass having 64 mg, bones 23 mg and the liver 18 mg; it also occurs to a lesser extent in the blood and the brain⁶. An hereditary deficiency or absence of ceruloplasmin, an intensely blue compound of molecular weight 151,000 and having 8 copper atoms per molecule⁷, is associated with a pathological increase in the copper content of almost all tissues, particularly the brain and liver^{2b, 2c} and is known as Wilson's disease⁸. Albino mammals lack the normal form of a copper-containing enzyme, tyrosinase, which assists in the synthesis of the pigment melanin^{2a, 2d}; interestingly no human albino has been found to have Wilson's disease. Tyrosinase produces the melanin responsible, among other things, for such diverse entities as the blackening of cut or bruised potatoes and the black areas on the wings of the cabbage white butterfly^{2a}. The only known naturally-occurring copper porphyrin system has been isolated from the red wing and tail feathers of 16 species of the African touraco bird (Musophagidae), about 8 mg of copper uroporphyrin III (turacin) being obtainable from each bird. An electron spin resonance study of turacin showed the metal to be in the Cu(II) oxidation state⁹. Copper is also found in bacteria as in the diphtheria bacillus where it is essential for the production of toxin.

Contrary to its rôle as an essential trace element, copper can be toxic in larger quantities, especially to lower organisms such as bacilli, fungi and algae, although some fungi can grow in concentrated copper sulphate solution^{1d}. Copper does not appear to be very toxic towards humans probably because it is only incompletely absorbed, the rest being excreted very readily from the system. In most cases a few milligrams of a copper salt taken as a single dose are sufficient to cause vomiting and, sometimes, diarrhoea^{6c}; one person has survived the regular ingestion of approximately 20 g samples of copper sulphate over a period of weeks! The lack of toxicity is fortunate considering the increasing use of copper tubing in household water supplies and since the average man probably consumes about 1 g of copper per year in his diet; a continued high intake of copper may cause damage to the liver, brain and nervous system.

The limits of tolerance in plants are often rather narrow, for example, tomato plants fed with nutrient solution containing 0.02 ppm were found to have an adequate supply of copper, but solutions containing 2 ppm were definitely toxic⁶. Probably the earliest commercial use of copper as a fungicide was in the form of copper sulphate solution employed as a seed dressing to destroy cereal diseases such as bunt. Later it was found that copper sulphate prevented foliage diseases, but its widespread use was restricted because it

⁵ A. Linker, W. F. Coulson and W. H. Carnes, *J. Biol. Chem.* **239** (1964) 1960.

^{6a} W. D. McElroy and B. Glass (eds.), *Copper Metabolism*, The Johns Hopkins Press, Baltimore (1950).

^{6b} H. I. Scheinberg, *Federation Proceedings*, **20** (1961) 179.

^{6c} H. I. Scheinberg and I. Sternlieb, *Pharmacological Rev.* **12** (1960) 355.

⁷ W. E. Blumberg, J. Eisinger, P. Aisen, A. G. Morell and I. H. Scheinberg, *J. Biol. Chem.* **238** (1963) 1675; C. B. Kasper, H. F. Deutsch and H. Beinert, *J. Biol. Chem.* **238** (1963) 2338; C. B. Kasper and H. F. Deutsch, *J. Biol. Chem.* **238** (1963) 2325.

^{8a} H. I. Scheinberg and I. Sternlieb, *Ann. Rev. Med.* **16** (1965) 119.

^{8b} J. Peisach, P. Aisen and W. E. Blumberg (eds.), *Biochemistry of Copper*, Academic Press, New York and London (1966).

⁹ W. E. Blumberg and J. Peisach, *J. Biol. Chem.* **240** (1965) 870.