Inorganica Chimica Acta, *130* (1987) 11–12

The Reaction Between Copper Complexes and Zinc Sulphide in Aqueous Solution

JOHN HEALY*

School of Chemistry, Robert Gordon's Institute of Technology, St Andrew Street, Aberdeen AB1 1HG, U.K.

JAMES R. LUSTY*

School of Chemistry, Lancashire Polytechnic, Preston, PR1 2TQ, U.K.

and COLIN F. MILLS

Department of Inorganic Biochemistry, Rowett Research Institute, Greenburn Road, Bucksburn, Aberdeen AB2 9SB, U.K.

(Received January 20, 1987)

Studies of the reaction between zinc sulphide and aqueous copper(II) have been inconclusive, identifying either copper(I) [1] or copper(II) [2] sulphide as the product. This type of reaction has been implicated [3] as a possible cause of the conditioned copper deficiency symptom observed in ruminant species when dietary copper is not low, but when certain other trace metals exceed normal dietary requirements [4]. The reaction is also important in mining industry activation–flotation processes, used to concentrate certain sulphide minerals [2].

As part of our continuing studies on the interaction of sparingly soluble metal sulphides and aqueous copper(II) [5] we have investigated the reaction between copper complexes with ligands containing oxygen, nitrogen or sulphur donor atoms, which are possible models for dietary copper complexes, and zinc sulphide in aqueous solution.

A single batch of zinc sulphide with a specific surface area of 61 m^2 g^{-1} and mean pore diameter of 11.5 nm was used throughout because the extent of reaction was found to be dependent on SSA [6].

Portions of solid zinc sulphide were mixed with aliquots of copper complex solution (8.00×10^{-3} M) and the resultant mixture left shaking for 24 h at 25.0 °C. The quantity of zinc sulphide employed was varied and by plotting the amount of copper complex removed from solution *versus* the molar ratio of zinc sulphide to initial complex concentration ($[ZnS]/[CuLn]^{x\pm}$), the R50 value of the complex was obtained. This R50 value is characteristic of the complex and is defined as the molar ratio of zinc sulphide to initial complex concentration required to remove 50% of the complex from solution by forming an insoluble copper sulphide species.

The results obtained (Table I, Figs. 1 and 2) illustrate the influence upon the reaction of both donor atom and complex stability. The S-donor ligand complexes do not react with zinc sulphide while

TABLE I. Copper Complexes and Associated Parameters[a]

Compound	Reference for preparation	pK_n of complex[d]	R50 value
Cu–O systems			
$CuCl_2$[b]		−0.52	1.26
$[Cu(Ac)_2]$		3.30	1.38
$CuSO_4$[b]		2.35	1.50
$[Cu(Mal)]$	7a	5.60	1.73
Cu–N systems			
$[Cu(Py)_4]S_2O_8$	7b	6.54	4.40
$[Cu(Im)_4](NO_3)_2$	7c	12.84	7.7
$[Cu(en)_2](NO_3)_2$	7d	19.60	13.6
$[Cu(DMG)_2]$	7e	23.30	148
Cu–S systems			
$[(n\text{-}Bu)_4N]_2[Cu(MNT)_2]$[c]	7f	unknown	no reaction
$[(n\text{-}Bu)_4N][Cu(TDT)_2]$[c]	7g	unknown	no reaction

[a] Abbreviations used: Ac = acetate anion, Mal = malonate dianion, Py = pyridine, Im = imidazole, en = ethylene diamine, DMG = dimethylglyoximate anion, MNT = maleonitrile dithiolate dianion, TDT = toluene-3,4-dithiolate dianion. [b] For the purposes of this study, aqueous solutions of these salts are considered as copper(II) complexed by O-donor ligands. [c] Although not in aqueous solution ($[Cu(MNT)_2]^{2-}$ in ethanol–acetone mixture (1:1, *v*/*v*), $[Cu(TDT)_2]^{1-}$ in actone), the authors feel that inclusion of these complexes is essential for comparative purposes. In any case, these solvents invariably enhance the extent of reaction [10]. [d] Instability constant (K_n) values from refs. 8 and 9.

---

*Authors to whom correspondence should be addressed.

0020-1693/87/$3.50

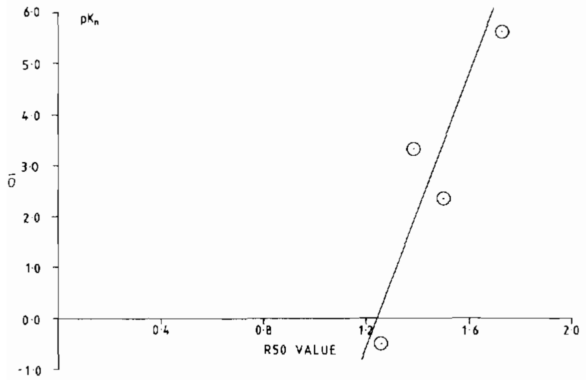

Fig. 1. Plot of pK_η vs. R50 for O-donor ligand complexes.

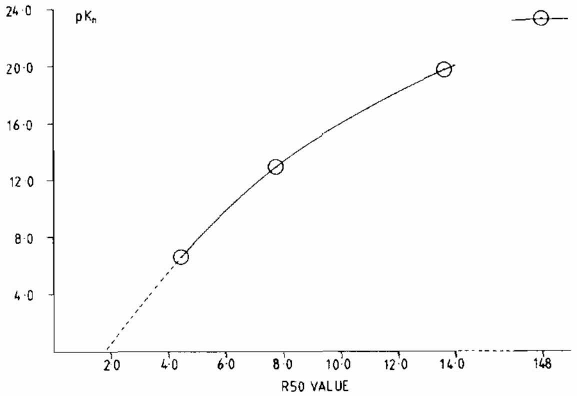

Fig. 2. Plot of pK_η vs. R50 for N-donor ligand complexes.

the O-donor complexes have lower R50 values than the N-donor complexes, inferring that the copper–donor atom bond strength decreases in the order, Cu–S > Cu–N > Cu–O. Cleavage of this bond is likely to be the most important factor involved in the reaction of a copper complex with a sparingly soluble metal sulphide. This bond strength order is supported by other evidence, such as electronegativity differences between copper and donor atom for example.

If metal sulphides do play a role in conditioned copper deficiency then those copper complexes present in the diet as predominantly O-bonded chelates will be most susceptible to reaction with metal sulphides and thus rendered unavailable to the animal. Furthermore, it is now possible to predict quantitatively the extent of reaction of a range of copper chelates and to consider those biologically important complexes in this context.

The copper sulphide species formed as a result of these reactions has still to be characterised; the zinc complex formed was identified in most cases as the product of a metathetical reaction,

$$[\mathrm{CuLn}]^{x\pm}{}_{(\mathrm{aq})} + \mathrm{ZnS} \rightleftharpoons \text{`CuS'} + [\mathrm{ZnLn}]^{x\pm}{}_{(\mathrm{aq})}$$

Acknowledgements

We thank the Scottish Education Department for the award of a studentship to one of us (J.H.) and gratefully acknowledge assistance given by K. Tonge with SSA determinations.

References

1 D. L. Perry, L. Tsao and J. A. Taylor, *Proc. Electrochem. Soc., 10,* 169 (1984).
2 S. R. Cooke, *Adv. Colloid Sci., 3,* 321 (1950).
3 C. F. Mills, personal communication.
4 C. F. Mills, in 'Biological Roles of Copper Ciba 79', Excerpta Medica, Holland, 1980, p. 49.
5 J. Healy, J. R. Lusty, W. B. Simpson and C. F. Mills, *Inorg. Chim. Acta, 135,* L13 (1987).
6 J. Healy, to be published.
7 (a) D. J. G. Ives and H. L. Riley, *J. Chem. Soc.,* 1998 (1938); (b) G. G. Schlessinger, 'Inorganic Laboratory Preparations', Chemical Publishing Company Inc., New York, 1962, p. 168; (c) W. J. Eilbeck, F. Holmes and A. E. Underhill, *J. Chem. Soc. A,* 757 (1967); (d) G. G. Schlessinger, 'Inorganic Laboratory Preparations', Chemical Publishing Company Inc., New York, 1962, p. 164; (e) G. Basu, G. M. Cook and R. L. Belford, *Inorg. Chem., 3,* 1361 (1964); (f) E. Billig, R. Williams, I. Bernal, J. H. Walters and H. B. Gray, *Inorg. Chem., 3,* 663 (1964); (g) R. Williams, E. Billig, J. H. Walters and H. B. Gray, *J. Am. Chem. Soc., 88,* 43 (1966).
8 K. B. Yatsimirskii and V. P. Vail'ev, 'Instability Constants of Complex Compounds', D. Van Nostrand, New York, 1966.
9 J. Bjerrum, G. Schwarzenbach and L. G. Sillen, 'Stability Constants of Metal–Ion Complexes. Part I: Organic Ligands', The Chemical Society Special Publication No. 6, London, 1957.
10 J. Healy, to be published.