

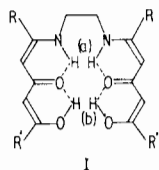
## Mono- and Dinuclear Copper(II) Complexes of Acyclic Schiff Bases

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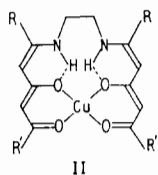
Ligands of the type (I) offer two possible compartments for complexation with metals.



One may be compared with the site in bis(acetylacetonate)ethylenediamine (a) and the other with that in a  $\beta$ -diketonate complex (b). We report the isolation of copper(II) complexes of (I) in which the metal occupies either site (a) or site (b) or in which both sites are occupied.

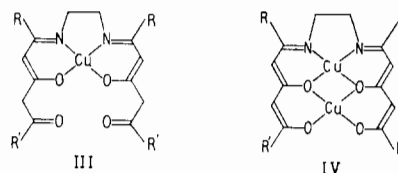
Ethylenediamine (en) reacts with the triketones benzoylacetone, anisoylacetylacetone, *p*-toluylacetylacetone and *p*-bromobenzoylacetylacetone, in ethanol, to yield yellow crystals of the corresponding Schiff bases (I)  $R = CH_3$ ;  $R' = C_6H_5$ ,  $p$ - $CH_3OC_6H_4$ ,  $p$ - $CH_3C_6H_4$  and  $p$ - $BrC_6H_4$ . The ligands have been characterised by chemical analysis, m.s., i.r. and  $^1H$  n.m.r.

Reaction of the Schiff bases (I),  $LH_4$ , in chloroform solution, with ethanolic copper(II) acetate, in equimolar ratio, yielded green precipitates analysing as  $CuLH_2$ . The i.r. and d.r.s. support the formulation of these complexes as (II) [e.g. for  $R = CH_3$ ,  $R' = C_6H_5$ , the i.r. shows bands at 1631, 1598, 1545 and 1527  $cm^{-1}$ , and the d.r.s. shows a peak at 574 nm which may be compared with a value of 560 nm for bis(benzoylacetone)copper(II)<sup>1</sup>].



It was not possible to obtain macrocyclic Schiff bases using the benzoylacetone, but the reaction of en with diacetylacetone or with dipropionylacetone gave only macrocyclic bases,  $L'H_4$ .<sup>2,3</sup> On reaction with copper(II) acetate in chloroform-ethanol the complexes  $CuL'H_2$  were formed in which the metal is incorporated into the macrocycle.<sup>3</sup> If, however, the macrocycle in chloroform is reacted with aqueous copper(II) acetate cleavage of the macrocycle occurs and purple compounds are recovered which analyse as  $CuLH_2$ , where in the ligand (I)  $R = R' = CH_3$ <sup>2</sup> or  $R = R' = C_2H_5$ . The formulation (III) is supported by i.r. and visible spectra [e.g. for  $R = R' = C_2H_5$ , the i.r. shows bands at 1710 ( $\nu_{C=O}$ , free) and 1600  $cm^{-1}$ , and the visible spectrum in chloroform solution shows a peak at 545 nm which may be compared with the value of 543 nm observed for bis(acetylacetonate)ethylenediamine copper(II) in the same solvent<sup>2</sup>].

The reaction of (I) in chloroform with ethanolic copper(II) acetate in a 1:2 molar ratio gave greenish brown precipitates analysing as  $Cu_2L$  (IV).



Typical of these complexes is that in which  $R = CH_3$ ,  $R' = C_6H_5$ . In this complex the i.r. shows bands at 1593, 1518 and 1500  $cm^{-1}$  and the d.r.s. a peak at 632 nm.

An extension of this reaction to the preparation of mixed metal systems has provided evidence for  $LCuNi$  ( $R = CH_3$ ,  $R' = C_6H_5$ ).

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## References

- 1 D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).
- 2 T. Yano, T. Ushijima, M. Sasaki, H. Kobayashi and K. Ueno, *Bull. Chem. Soc. Japan*, **45**, 2452 (1972).
- 3 D. E. Fenton and S. E. Gayda, *J. C. S. Chem. Comm.*, 960 (1974).