NOTE

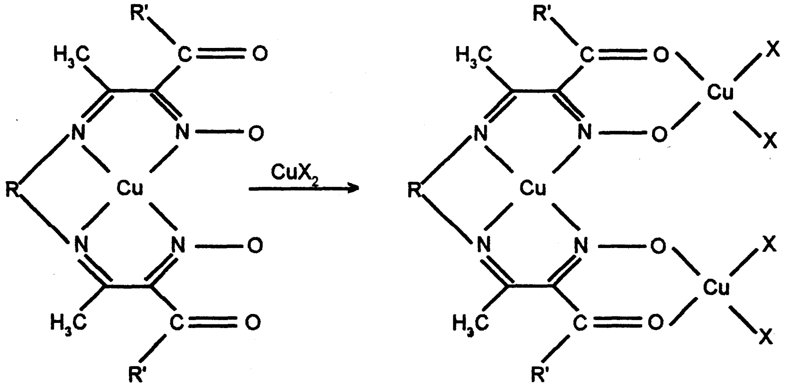
Trinuclear Copper(II) Complexes

H.C. RAI* and ARCHANA
Department of Chemistry, L.S. College, Muzaffarpur-842 001, India

An interesting group of trinuclear copper(II) complexes have been obtained by the action of copper halides on the mononuclear complexes and charcterized on the basis of elemental analysis, spectral and electrochemical studies.

Though works on adducts appear to be wide ranging with fluoroboro-bridged macrocyclic complexes[1–10], the study of the effects of substitutents on the macroring on the physico-chemical properties of the cyclops has been limited. The substituents on the tetraaza macrocycles, with rings varying from 12 to 16 membered and even substituents on naturally occurring macrocycles such as chlorophylls and porphyrins have remarkable effects on their physico-chemical properties.The behaviour of the Me_4 cyclopeans and Ph_4 cyclopeans systems reported earlier[1, 2] has prompted us to study the effect of new substituents on the ring on the physico-chemical properties of cyclopean macrocycles. During the course of the study, we have succeeded in isolating a new series of cyclopean ligands and the results of the investigation are reported here.

Precursor mononuclear copper(II) complexes (Fig. 1) have been prepared as reported in the literature[1, 2] and allowed to interact with copper(II) halides in dry alcoholic medium to give trinuclear copper(II) complexes as shown in Fig. 2.



R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_2-NH-(CH_2)_2-$, $-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-$
R' = CH_3, OC_2H_5 Fig.-1

R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_2-NH-(CH_2)_2-$, $-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-$
R' = CH_3, OC_2H_5; X = Cl^-, Br^- Fig.-2

Elemental analyses as per standared procedures conform to the proposed formulation within 1%.

Infrared spectra of the complexes also point to the postulated structure. In the parent mononuclear complexes, structurally important ν(C=N) and ν(N—O) bands are observed near 1695, 1590 and 1160 cm^{-1} of $R' = CH_3$ and at 1720, 1600 and 1190 cm^{-1} for $R' = OC_2H_5$. These bands, particularly ν(C=O) and ν(N—O) are significantly perturbed in the trinuclear species shifting bathochromically by about 60 and 30 cm^{-1} for $R' = CH_3$ and $R' = OC_2H_5$, respectively.

Electronic spectra of the trinuclear complexes exhibit a wide symmetric band centered at about 15,000 cm^{-1} which is indicative of the existence of two kinds of chromophores CuN_4 and CuO_2X_2 in each molecule.

The mononuclear complexes undergo metal based one electron reduction in two successive steps. The $E_{1/2}$ values for each polarographic wave are observed within a narrow region for the series and occur near –0.5 and –1.05 V respectively.

The complexes ($R' = CH_3$) show three waves, the $E_{1/2}$ values of which occur near –0.45, –0.72 and –1.52 V respectively. From the analysis of the first two polarographic waves and from wave height considerations the successive redox steps are found to be accompanied by one and two electron transfer respectively. The electron transfer in the first step is believed to involve one of the chromophoric centres CuO_2X_2. The following two electron transfer steps seem to involve the chromophores CuN_4 and CuO_2X_2. The final step of reduction seems to be associated with ligand reduction process.

The complexes with $R'=OC_2H_5$ exhibit three waves of nearly equal wave height. The $E_{1/2}$ values are estimated to be about –0.42, –0.65 and –0.55 V and each step is accompanied by one electron transfer most probably successively to the chromophore CuO_2X_2 and CuN_4, respectively.

The sharp difference in the redox behaviour of $R'=CH_3$ and $R'=C_2H_5$ during the transfer for the second and third electron is due to the difference in ligand field structure of the nitroso ligands arising from the difference in the nucleophilicity of the acetyl and ethyl substituents on the ligand frames whose carbonyl functions are involved in coordination with the metal ion with the nitroso groups.

REFERENCES

1. Bhagirathi Sahoo, J Chakravorty and B.Sahoo, *Indian J. Chem.*, **23A,** 209 (1984).
2. Bhagirathi Sahoo and B. Sahoo, *Indian J. Chem.*, **22A,** 560 (1983).
3. Bhagirathi Sahoo, N.C. Patra, A.K. Rout and B. Sahoo, *Indian J. Chem.*, **27A,** 680 (1988).
4. R. Shankar, A.K. Rout and B. Sahoo, *Indian J. Chem.*, **26A,** 156 (1987).
5. O.P. Anderson and A.B. Packard, *Inorg. Chem.*, **19,** 2123, 2941 (1980).
6. ————, *Inorg. Chem.*, **18,** 1940, 3064 (1979).
7. A.W. Addison, M. Carpenter, L.K. Lau and M. Nicholas, *Inorg. Chem.*, **17,** 1545 (1978).
8. J. Chakravarty, K.B. Naik, K.L. Singh and B. Sahoo, *Indian J. Chem.*, **22A,** 35 (1983).
9. H.C. Rai, Sushma Sinha and B.K. Rai, *Asian J. Chem.*, **12,** 922 (2000).
10. O.P. Anderson and J.C. Marshall, *Inorg. Chem.*, **17,** 1258 (1978).

(*Received:* 27 March 2000; *Accepted:* 26 July 2000) AJC-2101