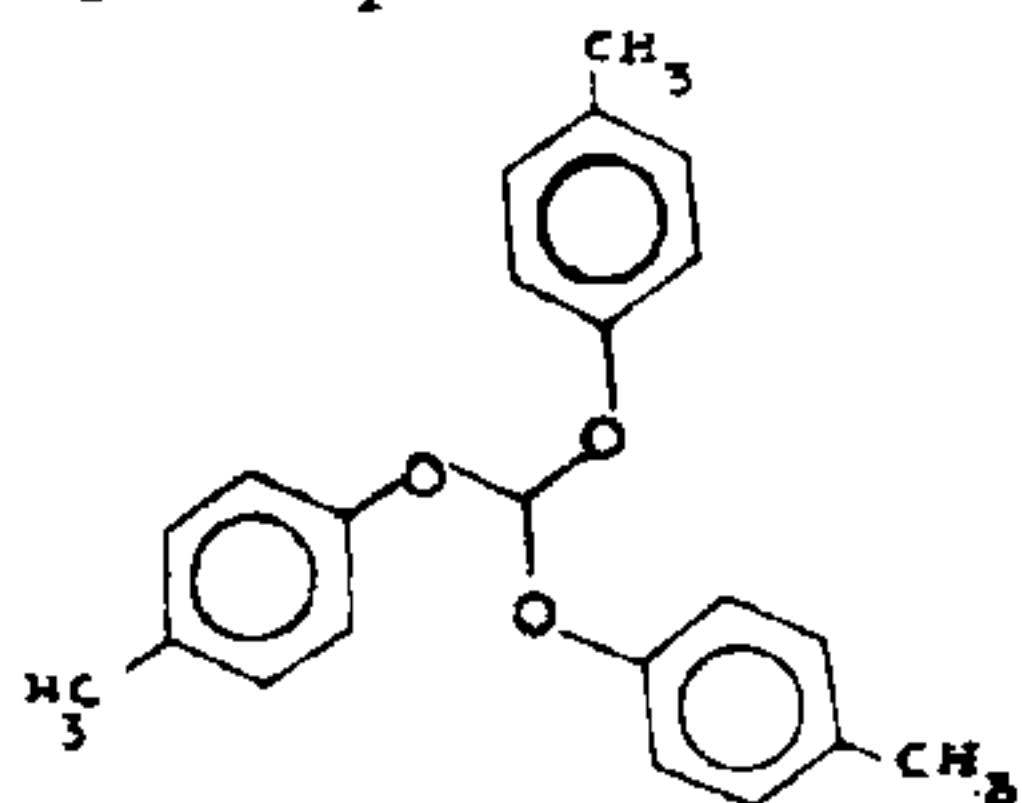
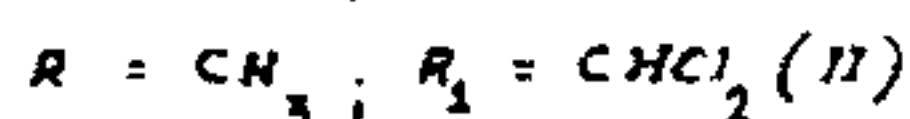
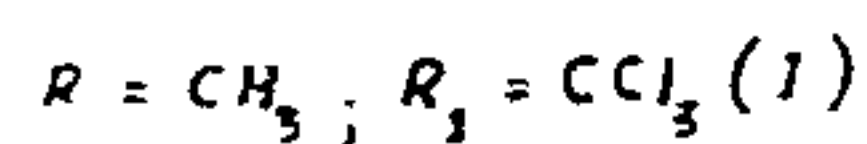
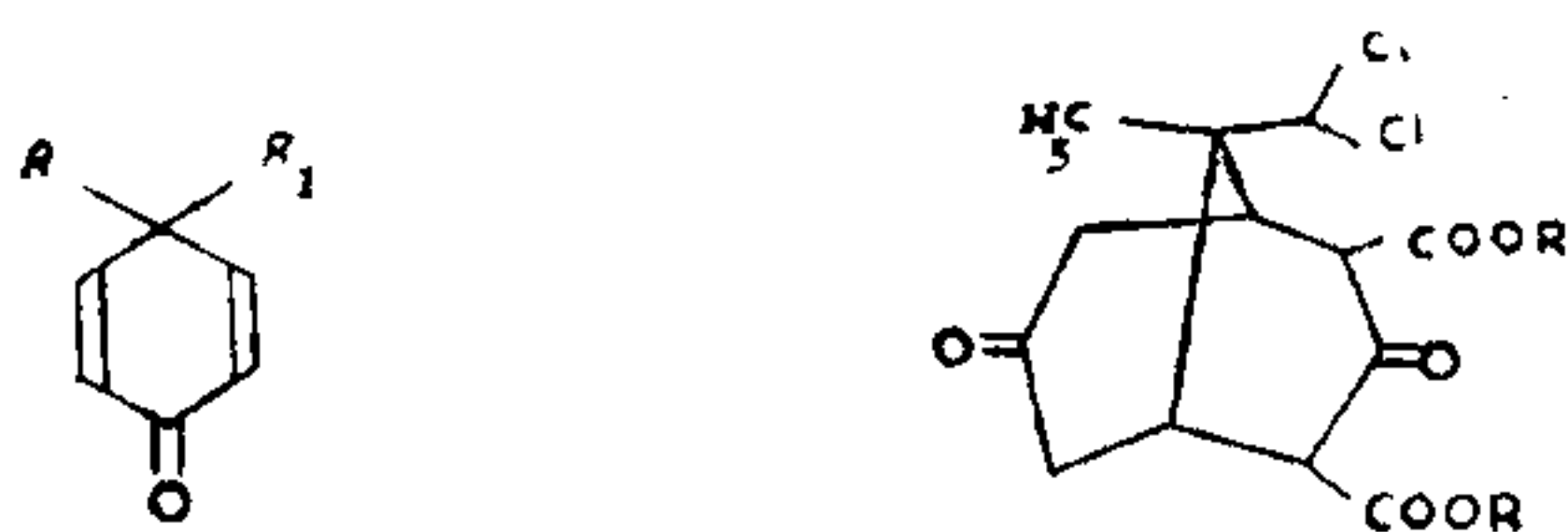


formula  $C_{22}H_{22}O_3$ . Its i.r. spectrum (KBr) showed bands at 1212, 1089  $cm^{-1}$  (aryl ether), 1611, 1587, 1508  $cm^{-1}$  (aromatic), 1381  $cm^{-1}$  (methyl) and 815  $cm^{-1}$  (*p*-disubstituted benzene). No band corresponding to ketone or ester carbonyl was observed. The n.m.r. spectrum ( $CDCl_3$ ) showed signals  $\delta$  2.35 (9H, s),  $\delta$  6.5 (1H, s) and around 7.2  $\delta$  (12H, m). In the mass spectrum, other peaks were observed at  $m/e$  227 ( $M - p\text{-Me-C}_6\text{H}_4 - \frac{1}{2}$ ),  $m/e$  107 ( $p\text{-CH}_3\text{-C}_6\text{H}_4 - \frac{1}{2}$ ) and at  $m/e$  91 ( $C_6H_5\text{-CH}_2^+$ ).

Upon the basis of the analytical and spectral data the above compound was assigned the structure as an ortho ester IV.



IV

The above structure is consistent with the observation that II reacts with sodium alkoxides alone in alcohol solution to give IV. Further, the acid hydrolysis of IV affords *p*-cresol as would be expected.

The formation of a stable orthoester from II constitutes an interesting reaction of these types of compounds, and 4-ethyl-4-dichloromethyl-2,5-cyclohexadienone is also found to give an orthoester, m.p. 54–55°.

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1. Merchant, J. R. and Desai, V. B., *J. Chem. Soc.*, 1964, p. 2258; 1968, C, 499.
2. Stetter, H. and Mayer, J., *Chem. Ber.*, 1959, 92, 2664.

### METAL-LIGAND BOND LENGTH FROM K-ABSORPTION FINE STRUCTURE OF COPPER IN SOME COMPLEXES INVOLVING SULPHUR LIGANDS

LEVY<sup>1</sup> and Mande and Chetal<sup>2</sup> have recently demonstrated the possibility of determining the average radius of the co-ordination sphere in a compound using the K-absorption fine structure data for the central metal ion in the solution state. The possibility was pointed out earlier by some other workers also<sup>3,4</sup>. Obashi<sup>5</sup> has investigated the fine structure spectra of cobalt in some complexes in the solid state. It has been found that in these the energy separations  $\Delta(C \sim D)$  obtained from the reported data give, through the Bragg relation

$$r = \sqrt{\frac{1^2 1}{\Delta E}}$$

(as used earlier<sup>3,4</sup>), values which are in reasonable agreement with the bond lengths obtained from X-ray diffraction. In the present paper, therefore, an attempt has been made to carry out similar measurements in the solid state on some copper complexes involving sulphur containing ligands.

The substances used are copper-thio-propionic acid [Cu(II)-TPA] and copper-thio-salicylic acid [Cu(II)-TSA] besides copper sulphate ( $CuSO_4 \cdot 5H_2O$ ) and copper metal. The complexes Cu-TPA and Cu-TSA have earlier been studied using other physico-chemical methods<sup>6,7</sup> as well as X-ray absorption spectroscopy<sup>8-10</sup>. The complexes have been shown to possess octahedral co-ordination symmetry.

The details of experimental set up have been described earlier<sup>8-10</sup>. Table I shows the

TABLE I

Substance	$\Delta$ (C~D) (eV)	(Å)	(X-ray diffraction) (Å)
Cu (metal)	25	2.45	2.55
$CuSO_4 \cdot 5H_2O$	38	1.99	2.00
Cu-TPA	29	2.28	..
Cu-TSA	31	2.20	..

results of measurements together with the values of bond length as reported on the basis of X-ray diffraction methods for  $CuSO_4 \cdot 5H_2O$  and copper metal.

It may be noted that the copper sulphur bond distances in some other complexes involving sulphur donor groups as measured by X-ray diffraction methods have been reported to be 2.1–2.3 Å<sup>11,13</sup>.

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1. Levy, R. M., *J. Chem. Phys.*, 1965, **43**, 1846.
2. Mande, C. and Chetal, A. R., *Curr. Sci.*, 1966, **35**, 509.
3. Hartree, D. R., Kronig, R., De L. and Peterson, H., *Physica*, 1934, **1**, 895.
4. Beaman, W. W., Fors, J. and Humphrey, J. N., *Phys. Rev.*, 1945, **67**, 212.
5. Obasbi, M., *Sci. Rep.*, No. 10, Osaka University, 1961.
6. Mishra, M. B. and Nigam, H. L., Communicated.
7. Mukerji, C., *D. Phil. Thesis*, Allahabad University, 1967.
8. Nigam, H. L. and Srivastava, U. C., *Chem. Comm.* (In Press).
9. —, *Inorg. Chimica Acta* (In Press).
10. Srivastava, U. C., Nigam, H. L. and Vishnoi, A. N., *Indian J. Pure Appl. Phys.* (In Press).
11. Bally, R., *Compt. Rend.*, 1963, **257**, 425.
12. Bron-mico, M., Dessy, G., Mugnoli, A. and Zambonelli, L., *Acta Cryst.*, 1965, **19**, 886.
13. Truter, M. R. and Rutherford, K. W., *J. Chem. Soc.*, 1962, p 1748.

### FREE ENERGY CHANGE OF COMBINATION OF SOME METAL-PROTEIN SYSTEMS

THE free energy change of combination of various metal ions, i.e., Zn<sup>++</sup>, Cu<sup>++</sup>; Cd<sup>++</sup> and Pb for the carboxyl and imidazole groups of p-toluene sulphonylated gelatin (PTSG), iodinated casein (IC) and ovalbumin have been determined by employing equilibrium dialysis method<sup>1-4</sup> at a constant temperature of 20 ± 0.1° C. Physiological and industrial importance and well characterised nature were the main guiding factors for the selection of

these proteins for the present investigations. PTSG and IC were prepared and characterised in this laboratory and the results have been communicated elsewhere.

Stock solutions (2.5% each) were prepared in doubly distilled water by adding potassium hydroxide and strength was determined by drying a known aliquot in an air-oven at 105° C. The metal contents of the stock solutions of zinc chloride, copper sulphate, cadmium chloride and lead nitrate were estimated by the usual methods. The ionic strength of the solutions was maintained at 0.15 by adding requisite amount of appropriate supporting electrolyte, i.e., potassium chloride or potassium nitrate.

The extent of binding, i.e., V<sub>M</sub> was calculated by Direct Comparison Method<sup>5</sup>. The free energy change of combination for the binding of the metal to the carboxyl and imidazole groups of these proteins were evaluated by employing Scatchard's equation<sup>6</sup>,  $\Delta G^\circ = -2.3026 RT \log V_M / (n - V_M - V_M) C_F$ ; where V<sub>H</sub> and V<sub>M</sub> are the active sites covered by hydrogen and metal ions respectively, C<sub>F</sub> is the concentration of free metal ions at equilibrium and n is the total number of intrinsically identical groups. The value of n and V<sub>H</sub> for ovalbumin has been taken from the literature<sup>7</sup>. The results are given in Table I. Examination of data in Table I reveals that all the metal ions except Cd<sup>++</sup> form complexes with the carboxyl as well as imidazole groups of these proteins. Cd<sup>++</sup> fails to form complex with the imidazole groups of PTSG. This discrepancy which could not be explained was also observed in case of transfusion gelatin<sup>4</sup>. The order of affinity computed from the free energy change of combination for the carboxyl and imidazole groups of the various proteins follows the order Cu<sup>++</sup> > Zn<sup>++</sup> > Cd<sup>++</sup> in IC and PTSG and Zn<sup>++</sup> > Cd<sup>++</sup> in ovalbumin.

TABLE I

Free energy change of combination  $\Delta G^\circ$  (in kcal/mole) of various metal-protein systems

Temperature = 20 ± 0.1° C

Metal ions	IC		PTSG		Ovalbumin	
	Metal-carboxyl complex (pH = 6.35)	Metal-imidazole complex (pH = 9.30)	Metal-carboxyl complex (pH = 5.50)	Metal-imidazole complex (pH = 7.50)	Metal-carboxyl complex (pH = 5.50)	Metal imidazole complex (pH = 7.50)
Cu <sup>++</sup>	.. -2.87	-4.34	-2.78	-4.28	..	..
Zn <sup>++</sup>	.. -2.54	-3.78	-2.38	-3.70	-2.56	-3.65
Cd <sup>++</sup>	.. -2.85	-3.03	-2.32	..	..	..
Pb <sup>++</sup>	.. ..	..	..	..	2.49	-3.17