SUMMARY

The formation of metal chelates has been utilised in the elucidation of the stereochemical problems, both of the chelating agents and of the metal chelates. The applications of chelating agents as reagents in inorganic analysis are well known. Besides, the theory of chelation has provided a foundation for new developments in a number of fields of pure and applied science. The aim of the present investigations was to apply the principle of chelation to the investigations on oximes.

On reviewing the chemistry of oximes, it appears that, broadly speaking, the investigations on oximes include the preparation, properties and structures of the oximes and their metal chelates and their applications in the various fields of science.

From the above studies it was considered that if α-oximino compounds of the substituted amides of acetoacetic acid (cf. Knorr, Ann., 1886, 236, 80; Naik, Trivedi and Mankad, J. Indian Chem. Soc., 1943, 20, 384) were prepared and converted into the corresponding α-β-dioximino compounds (cf. Knorr and Reuter, Ber. 1894, 27, 1169), these compounds would prove useful in the investigations on different aspects of oxime chemistry. It was believed that these oximes would exhibit internal chelation (H-bond) and that the principle of chelation would be applicable to these investigations.

With this view, it was proposed

(1) to prepare α-oximino and α-β-dioximino derivatives of some aryl amides of acetoacetic acid;

(2) to prepare the metal chelates of these oximes, using the salts of some transitional metals;

(3) to study the absorption spectra of these oximes and some of their soluble metal chelates;

(4) to determine the magnetic susceptibility of some of the metal chelates prepared;

(5) to discuss the stereoisomeric nature of the oximes and their metal chelates; and

(6) to investigate the applicability of some of these oximes as analytical reagents in the detection and the estimation of the metallic elements.

The aryl amides of acetoacetic acid(where aryl amide may be anilide, o-toluidide, o-chloranilide, o-anisidide, p-chloranilide, p-phenetidide, or 2:4-xylidide) were taken as the starting substances. The monoximes(i.e. α-oximes) were prepared from these amides by the action of nitrous acid; these are shown to possess an anti-acetyl structure from the considerations of extended Hantzsch' rule and the chelating reactions of these oximes. The α-β-dioximes were prepared from these monoximes by the action of hydroxylamine hydrochloride; these are shown to possess an anti-dioxime structure from the considerations of the formation of the dioximes, the chelating reactions of the dioximes and the configurations of α-and β-monoximes of acetoacetamides.

Ultraviolet absorption spectra of some monoximes and dioximes have been investigated in aqueous, alcoholic and chloroform solutions and the visible absorption spectra of some monoximes have been studied in the alcoholic and sodium hydroxide solutions. It is suggested from the results that the oximes are internally chelated. An attempt is made to study the effect of substituents in the benzene nucleus on the wave-length maxima of these oximes and to correlate the wave-length maxima with the conjugated systems present in the molecules.

It is suggested from (1)synthesis, (2)colour reactions, (3)pH effect and(4)magnetic measurements that the dioximes form metal chelates with metals like copper, nickel, cobalt, palladium, etc. It is further suggested that 5-membered rings are present in these metal chelates. pH of incipient precipitation and pH of complete precipitation of copper, nickel and palladium by these dioximes have been determined to study the relative stabilities of these metal chelates. The relative stabilities are in the order

$$Pd > Cu > Ni$$

The metal chelates of copper, nickel and palladium with these dioximes are prepared and they are formulated as $M(DH)_2$ where M is a bivalent metal atom and DH_2 is a dioxime molecule. Magnetic measurements of some of these metal chelates have been carried out using Gouy's magnetic balance. The results indicate a square planar structure for these chelates. The metal chelates formed by cobalt with the dioximes are formulated as $Co(DH)_2(H_2O)_2$ and are considered to have an octahedral configuration, involving d^2sp^3 strong covalent bonds.

Qualitative tests indicate that monoximes have specific reaction with ferrous iron, while dioximes have a characeteristic reaction with copper, nickel, cobalt, iron (ous), bismuth, uranium and palladium. These dioximes differ from other α-dioximes in the fact that they form insoluble copper chelates. Three of these dioximes (namely anilide, o-toluidide and o-chloranilide) have been investigated as reagents for the gravimetric estimation of copper, nickel and palladium. The pH ranges within which copper, nickel and palladium are completely precipitated by these dioximes are:

dioxime:	anilide	o-toluidide	o-chloranilid
metal			
copper	4.4-8.3	3.0-8.5	2.1-8.9
nickel	6.2-8.6	5.1-9.1	4.4-9.5
palladium	0.1-8.9	0.1-10-0	0.1-10.1

Estimations of palladium, copper and nickel have been carried out in presence of various anions and cations. It has been observed that anions like nitrate, cyanide and iodide interfere with the estimation of palladium from the acidic solutions. Estimation of copper in presence of nickel has not been attempted as the values of pH of incipient precipitation of nickel by the dioximes are lower than the values of pH of complete precipitation of copper by the corresponding dioximes. The studies on the solubility of these oximes in water reveal that although aqueous solutions of these dioximes cannot be used as reagents in analysis, these three dioximes are sufficiently water-soluble so as to prevent the precipitation of the excess reagent during estimation.