latter peak probably due to tetragonal distortion or spin-orbit coupling. The band due to the transition $^4T_{1g} \rightarrow {}^4T_{2g}$ was beyond the range of the instrument. Hence, all these compounds have been found to have the high spin configuration and have absorption spectra characteristic of octahedral complexes in conformity with earlier observations by Graddon and Mockler[3,4].

The base adducts differ markedly from their beta-diketonato analogues in being unstable in solution as broad shoulder appears round 12000 cm^{-1} in the absorption spectra of the solution (in absence of added base) probably due to dissociation of the nitrogen ligand. This is quite expected as the two ligand oxygen atoms in the chelate are non-equivalent unlike the acetylacetonates, which have been confirmed by the crystal structure determination of bis (salicylaldehydato) Cu(II) showing unequal C–O bond lengths, the carbonyl C–O being decisively shorter than the phenolic C–O.

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August 10, 1976.

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TITRIMETRIC DETERMINATION OF METHIONINE, CYSTINE AND ITS α-SUBSTITUTED DERIVATIVES WITH CHLORAMINE-T

CYSTEINE, cystine and methionine are nautrally occurring amino acids and frequently found together. The determination of these sulphur containing amino acids in relatively pure substances as well as in presence of each other is therefore of practical interest.

Aqueous solutions of chloramine-T have been extensively employed for a variety of determinations[1] largely because of their stability, versatility, ready availability in pure state, high equivalent weight and low cost. Of late, this reagent has been employed to titrate thiols[2], cysteine[3] and glutathione[4] in the presence of acidified potassium iodide and starch or an excess of the reagent was used to determine certain amino acids[5], which was back titrated iodometrically.

As a part of a project on the determination of sulphur containing organic compounds *via* functional groups, reactions of chloramine-T with methionine, cystine and its α-substituted derivatives have been studied to evaluate their analytical potential. Samples are titrated in feebly acidic solutions in the presence of bromide ions when the appearance of the colour of free bromine serves to indicate the end point. Under the conditions of titration it is found that the sulphide group of methionine undergoes a two electron change forming the sulphoxide. In cystine, the disulphide linkage forms two sulphonic acid groups; 2 moles of cysteic acid being produced from each mole of cystine following a ten electron change. The substituted cystines also undergo the some oxidation. The sulphydryl group of cysteine consdmes hix equivalents of chloramine-T and, cysteic acid is the end product. Other sulphydryl compounds react less stoichiometrically with the oxidant and vitiate the mixture analysis when present in large amounts with sulphides or disulphides[6]. But cysteine because of its ready, precise and accurate oxidation can be tolerated even when present in amounts equivalent to 40% of the total titration. Samples of cystine or methionine containing cysteine are determined by titration with chloramine-T as described below, which yields the total; the cysteine alone can be determined by *o*-iodosobenzoate titration method[7].

Reagents

A 0·025 M solution of chloramine-T was prepared by dissolving a calculated weight of sample in water and standardising iodometrically[1].

Cysteine hydrochloride, cystine and methionine were high purity products and α-substituted derivatives of cystine were prepared by known methods[8,9].

Procedure

An accurately weighed amount of the sample containing 0·2–0·5 mmole of methionine or 0·04–0·1 mmole of cystine or its derivative was taken in a 150-ml Erlenmeyer flask and dissolved in 5–10 ml of 0·1 M hydrochloric acid. Alternatively, a suitable aliquot of sample in 0·1 M acid may be taken for analysis. About 0·5 g of potassium bromide was mixed with the sample taken which was finally diluted to about 30 ml. Thereafter, the contents were titrated with 0·025 M solution of chloramine-T to the appearance of the free bromine colour. The colour change is perceptible within 2 drops of the reagent, albeit. a blank titration is recommended on the same volume of hydrochloric acid-water mixture to correct for the excess reagent for the end point.

Results and Discussion

When determined by the present method, cystine, its α-substituted methyl, *n*-propyl, phenyl, isopropyl and *n*-butyl derivatives and methionine yielded results accurate to 0·2% and precise to 0·4% on comparison

with total sulphur analysis using volumetric Carius method and with Kjeldahl total nitrogen determination.

The blank which accounts for the excess reagent to note the end point is about 0·1 ml for 30 ml titration solution. A convenient method to confirm the end point involves the addition of about 0·2 g of potassium iodide to the titrated solution and to note the relatively dark colour of iodine. Moreover, the intensity of iodine colour may be taken as a rough measure of the extent of over-titration. The titration should then be repeated by adding first all but 1 ml less of the previously required titrant and then dropwise with noting the colour of solution after each addition.

Large amounts (10 moles of substance added to each mole of sulphur containing amino acid) of serine, glycine and alanine do not interfere but tryptophan interferes severely even when present in small amounts.

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INTERACTION OF Li^+ AND NH_4^+ WITH ELECTRON DONOR MOLECULES

INTERACTION of alkali and alkaline earth metal cations with electron donor molecules like ethers, ketones and amides has been recently investigated in order to understand the nature of ion solvation[1-3]. Thus, studies of electronic spectra and molecular orbital calculations have shown that the binding of alkali metal ions with such oxygen donor molecules vary in the order $Li^+ > Na^+ > K^+$. We considered it interesting to see whether Li^+ binds to sulphur donors as well. Another aspect of interest was to examine the binding of NH_4^+ to electron donor molecules. Such metal-ligand interaction studies are of relevance to biology[4].

TABLE I
CNDO/2 calculations on complexes of Li^+ with oxygen and sulphur donors

1:1 Complex	X = O			X = S		
	r, Å	$E_{kcal\ mol^{-1}}$	*u*, D	*r*, Å	$E_{kcal\ mol^{-1}}$	*u*, D
H_2X	2·36	46	7·9	2·40	53	3·9
H_2CX	2·30	85	9·5	2·45	59	7·4
H_2NHCX	2·30	116	9·5	2·40	79	12·3

CNDO/2 calculations were first made on the interaction of Li^+ with a few sulphur donor molecules. The results show that Li^+ binds quite strongly to sulphur donor molecules similar to oxygen donor molecules (Table I). On binding, the charge on the sulphur atom decreases, accompanied by a decrease in the positive charge on Li^+. In order to verify this conclusion from MO calculations, we examined the electronic spectra of a few compounds like ethylenetrithiocarbonate and thioformamide in presence of LiCl and found that the band due to the n–π^* transition of the C = S group is blue-shifted on binding with Li^+. This indicates that Li^+ binds to the lone pair orbital of the C = S group. We then recorded the electronic spectrum of N, N-dimethylthioformamide (DMTF) in methanol with different concentrations of LiCl. The results shown in Fig. 1 clearly indicate blue-shift of the

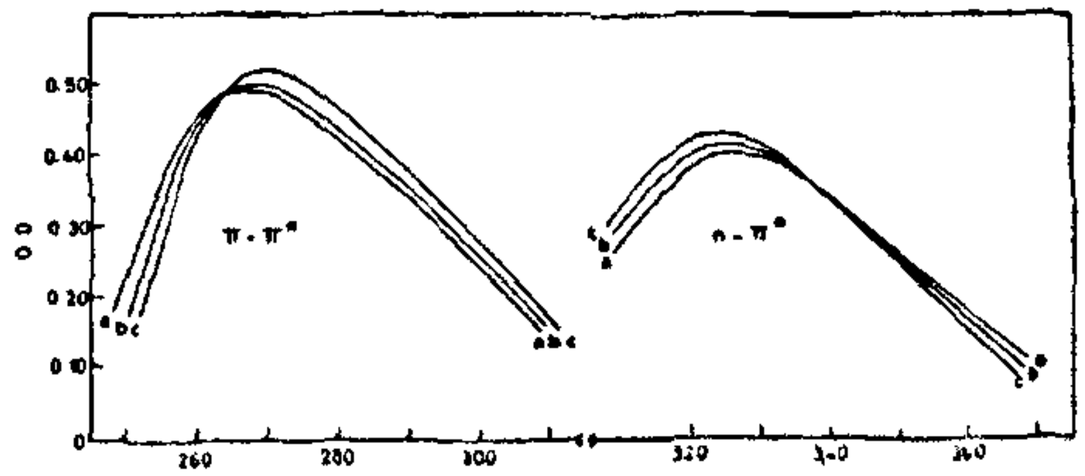

FIG. 1. Effect of Li^+ on the π–π^* and n–π^* bands of DMTF in CH_3OH solution. Molarity of LiCl is (*a*) 0·0, (*b*) 2·0 and (*c*) 4·0. Concentration of DMTF is 5×10^{-5} M and 1×10^{-2} M for π–π^* and n–π^* bands respectively.

n–π^* band and red-shift of the π–π^* band of the C = S group. More interesting is the occurrence of isosbestic points in the n–π^* and π–π^* bands around 338 and 264 nm respectively. The isosbestic points suggest the existence of equilibria involving the thioamide molecule. The nature of the solvation