

neutral ligand produces stronger electrical field around the Cu(II) ion, during the formation of $[\text{Cu}(\text{dipy})(\text{H}_2\text{O})_2]^{2+}$. The distorted octahedron $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ gets somewhat more strongly distorted towards square planar structure by the coordination of dipyridyl, thus creating the right geometry for coordination of secondary ligand and resulting in increase in the value of $K_{\text{M}(\text{dipy})\text{L}}^{\text{M}(\text{dipy})}$ (ref. 11).

The higher value of $K_{\text{M}(\text{dipy})\text{L}}^{\text{M}(\text{dipy})}$ compared with $K_{\text{M}(\text{o-phen})\text{L}}^{\text{M}(\text{o-phen})}$ in case of Ni(II) complexes may be due to the bigger size of *o*-phenanthroline molecule which offers increased steric hindrance. Besides, the metal ligand π -interaction is less in $[\text{Ni}(\text{o-phen})]^{2+}$ and hence its tendency to bind with the secondary ligand will be less than that of $[\text{Ni}(\text{dipy})]^{2+}$.

Thus the behaviour of present ligands is similar to that reported for other bidentate ligands⁸. If the ligand was tridentate, a lowering in the value of $K_{\text{Cu.A.L}}^{\text{Cu.A}}$ would have been observed, in the case of Cu(II) mixed ligand complex, dipyridyl already occupies two positions on the equatorial plane. The tridentate ligand with a double bond cannot occupy two positions in the equatorial and one in the axial direction^{12,13}. The tridentate ligand can occupy one position in the equatorial and two in the axial direction forming trigonal bipyramidal structure. Due to Jahn-Teller effect in Cu(II) complexes, the ligand will be put to strain in occupying two axial positions¹⁴. The strain would cause $K_{\text{Cu.A.L}}^{\text{Cu.A}}$ to decrease considerably as compared with $K_{\text{Cu.L}}^{\text{Cu}}$. However, $K_{\text{Cu.A.L}}^{\text{Cu.A}}$ is nearly equal to $K_{\text{Cu.L}}^{\text{Cu}}$. Hence it can be concluded that the OH group does not get coordinated and the Schiff base behaves as a bidentate ligand.

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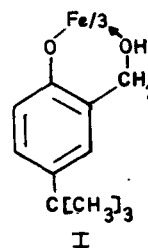
Spectrophotometric Studies of 2-Methylol-4-*tert*-butylphenol-Fe(III) Complex

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2-Methylol-4-*tert*-butylphenol (2M4TBP) forms 1:3 (metal:ligand) complex with Fe(III) at pH4, showing maximum absorbance at 600 nm. The complex obeys Beer's law in the range 1.0×10^{-4} - 1.0×10^{-2} M.

WITH a view to developing a suitable analytical technique for the estimation of reactants in phenol-formaldehyde reaction, the complex formation of phenol/phenolmethylol with Fe(III) was investigated by Dakshinamurthy and Santappa¹ and Dejong *et al.*². The present note deals with the spectrophotometric method of estimating 4-*tert*-butylphenol (4TBP)/2-methylol-4-*tert*-butylphenol (2M4TBP). A probable structure is proposed for the 2-methylol-4-*tert*-butylphenol-Fe(III) complex.



Stock solutions (0.2M) of 2-methylol-4-*tert*-butylphenol (2M4TBP)³ and 2,6-dimethylol-4-*tert*-butylphenol (2,6M4TBP) were prepared both in 50 and 80% dioxane-water. Suitable dilution of the stock solution with the same solvent system gave solution of lower concentration. Dioxane (AR, BDH) was purified using the procedure described by Baliah and Chandrasekharan⁴.

Ferric chloride solution was prepared by dissolving hydrated ferric chloride (AR, BDH) in sufficient water and hydrochloric acid (AR, BDH) to make up exactly *N*/2 solution. The exact normality of the solution was determined by titrating ferric content by the usual iodometric method.

Preparation of 2-methylol-4-*tert*-butylphenol-Fe(III) complex — To 30 ml of 2-methylol-4-*tert*-butylphenol were added 10 ml of ferric chloride of equal concentration. The resultant solution was green in colour. It was then made up to 50 ml for optical density measurements employing 50 and 80% dioxane-water as blank.

The method of Vosburgh and Cooper⁵ was employed to determine the nature of the complexes. Mixtures containing 1:1, 1:2 and 1:3 mole ratios of Fe(III) to 2M4TBP were prepared. Absorbance measurements were carried out between 400 and 700 nm. All the mixtures showed maximum absorbance at 600 nm, thus indicating the formation of a single complex. All the subsequent measurements were therefore carried out at 600 nm.

The complex was found to give constant maximum absorbance in the pH range 3.5-4.5. Therefore pH 4 was selected for all further studies and it was maintained using 41 ml of *M*/5 acetic acid and 9 ml of *M*/5 sodium acetate.

The composition of the complex was determined using mole ratio method⁶, keeping $[Fe^{3+}] = 2.0 \times 10^{-3} M$ and varying 4TBP/2M4TBP concentrations in the range $0.5-8.0 \times 10^{-3} M$. There was a rapid increase in the absorbance at 600 nm up to $[Fe^{3+}]/[2M4TBP]$ ratio 1:3 and thereafter it became constant thereby indicating a 1:3 stoichiometry of the complex. The above results were supported by the method of continuous variation^{7,8}.

A linear relationship was observed between concentration and optical density over the range 1.0×10^{-4} to $1.0 \times 10^{-2} M$ at 600 nm.

The suppression of colour formation with increase in dioxane content (50 to 80% dioxane-water) indicated that the complex might be a non-electrolyte. The formation of coloured complexes were noticed only in the case of 2M4TBP where formation of chelate rings are possible and 4-methylol-2,6-ditert-butylphenol did not form coloured complex with Fe(III). Evidence for the ionization of only one hydrogen of phenolic hydroxyl group obviously, was provided by the potentiometric titrations. All these observations can be explained by assigning structure (I) to 2-methylol-4-*tert*-butylphenol-Fe(III) complex.

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Complexometric Determination of Co(II), Ni(II) & Cu(II) Using 1-(2-Amino-3-hydroxy-4-pyridylazo)-, 1-(2,3-dihydroxy-4-pyridylazo)- & 1-(5-Chloro-4-pyridylazo-2,2-diol)-4-sulphonic Acids

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1-(2-Amino-3-hydroxy-4-pyridylazo)- (AHP-4S), 1-(2,3-dihydroxy-4-pyridylazo)-(DHP-4S) and 1(5-chloro-4-pyridylazo-2,3-diol)-(CPD-4S)-4-sulphonic acids have been employed as visual indicators for the complexometric determination of Co(II), Ni(II) and Cu(II) at 27°. There is a fairly wide pH range available for the determination of each metal ion. Effect of diverse ions has been studied and the accuracy and sensitivity of the method is comparable with the other complexometric methods known for Co(II), Ni(II) and Cu(II).

IN continuation of our earlier work^{1,2}, the usefulness of the title indicators for the complexometric titration of Co(II), Ni(II) and Cu(II) has been studied and the results are reported in this note.

Standard solutions of Co(II), Ni(II) and Cu(II) were prepared by dissolving requisite amount of analytical grade $CoSO_4 \cdot 7H_2O$, $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ respectively in acidulated doubly distilled water and standardized by the usual gravimetric and volumetric methods. Standard EDTA solution was prepared by dissolving the appropriate quantity of its disodium salt (BDH, AR) in doubly distilled water and was used as such in the present study.

Solutions (0.25%, w/v) of the dyes, viz. 1-(2-amino-3-hydroxy-4-pyridylazo)-4-sulphonic acid (AHP-4S), 1-(2,3-dihydroxy-4-pyridylazo)-4-sulphonic acid (DHP-4S), 1-(5-chloro-4-pyridylazo-2,3-diol)-4-sulphonic acid (CPD-4S) were prepared as described earlier¹.

Sodium acetate/acetic acid buffers were prepared by mixing 0.2M sodium acetate and 0.2N acetic acid in different proportions. $KH_2PO_4/NaOH$ buffers were prepared by mixing 0.2N KH_2PO_4 and 0.2N NaOH in different ratios. NH_4Cl/NH_4OH buffer of pH 10.0 was prepared by adding 57 ml

TABLE 1 — OPTIMUM CONDITIONS FOR TITRATIONS

Variables	Co(II) titrations			Ni(II) titrations			Cu(II) titrations		
	AHP-4S	DHP-4S	CPD-4S	AHP-4S	DHP-4S	CPD-4S	AHP-4S	DHP-4S	CPD-4S
Colour change at the end point	Red to orange	Magenta to orange	Magenta to orange	Red to orange	Magenta to orange	Magenta to orange	Magenta to orange	Magenta to orange	Magenta to orange
Useful pH-range	7.0-9.8	8.0-10.0	8.0-10.9	4.5-7.0	7.0-10.0	6.2-10.0	3.9-10.9	9.0-10.5	9.0-10.5
Buffer	$KH_2PO_4/NaOH$ (pH 8.0)	NH_4Cl/NH_4OH (pH 9.5)	$KH_2PO_4/NaOH$ (pH 10.5)	$KH_2PO_4/NaOH$ (pH 6.2)	NH_4Cl/NH_4OH (pH 9.5)	NH_4Cl/NH_4OH (pH 9.5)	CH_3COONa/CH_3COOH (pH 5.0)	NH_4Cl/NH_4OH (pH 10.0)	NH_4Cl/NH_4OH (pH 10.0)
Temp. range (°C)	10-60°	5-80°	10-80°	20-80°	25-80°	20-80°	5-80°	20-80°	20-80°
Std dev.	0.0103	0.0136	0.0094	0.010	0.010	0.0083	0.004	0.007	0.0083