TABLE 1 — STABILITY CONSTANTS OF THE METAL CHELATES OF THBQ

Metal ion	$\log K_1$	$\log K_2$	$\log \beta_2$
Th(IV)	7.30	3.20	10.50
Dioxouranium(VI)	7.00	3.00	10.00
Sc(III)	6.20	2.40	8.60
Ce(III)	6.10	2.30	8.40
Y(III)	6.00	2.30	8.30
La(III)	5.80	2.30	8.10

The average number of ligand molecules attached per metal ion $\bar{n}$, and free ligand exponent pL, were calculated by Eqs 2 and 3,

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V_0 + V_1)\,\bar{n}_H C_M} \qquad ..(2)$$

$$pL = \log_{10} \frac{\sum\limits_{n=0}^{n=j} B_n^H\,(1/\text{antilog } pH)}{(C_L - \bar{n}\,C_M)} \times \frac{V_0 + V_3}{V_0} \qquad ..(3)$$

Interpolation of plots of $\bar{n}$ values against pL at half $\bar{n}$ values gave the values of stability constants of the complexes reported in Table 1.

The proton-ligand formation curve shows four pK^H values for THBQ ($pK_1^H = 4.6$, $pK_2^H = 7.0$, $pK_3^H = 9.6$ and $pK_4^H = 10.1$). These values correspond to stepwise ionization of the four OH groups of THBQ. The values are in accord with those obtained previously[7] except for the last one (10.1) which was not determined before. It is obvious that the value $pK_2^H = 7.0$, is the overall pK for the first two protons and $pK_4^H = 10.1$, is the overall pK of the completely ionised THBQ molecule. Values of stepwise stability constants of the metal chelates evaluated on this basis, as revealed from the metal-THBQ formation curves are in the order : Th(IV) > dioxouranium(VI) > Sc(III) > Ce(III) > Y(III) > La(III). This order is in agreement with the following observations :

(i) Lanthanides are much less prone to complex formation than the actinides[8].

(ii) La(III) complexes are substantially dissociated in aqueous solutions[9].

(iii) Yttrium shows a great resemblence to the lanthanides[9].

(iv) Scandium has chemical properties quite distinct from those of lanthanides and yttrium. It is less basic and stronger complexing agent[9].

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Extraction of Iron(III) Azido Complexes with Monooctyl-α-anilinobenzylphosphonate

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Monooctyl-α-anilinobenzyl phosphonate (MOABP) has been used as an extractant for the blood red iron azide. Tris(monooctyl-α-anilinobenzylphosphonate)iron(III) azide and monooctyl-α-anilinobenzylphosphonateiron(III) azide complexes have been isolated from petroleum ether and bis(monooctyl-α-anilinobenzylphosphonate)iron(III) azide from chloroform.

THE use of monooctyl-α-anilinobenzylphosphonate (MOABP) in the extractive spectrophotometric determination of many metal ions has been reported earlier[1-5]. In this note nature of extractable ferric azide complexes with MOABP has been investigated spectrophotometrically.
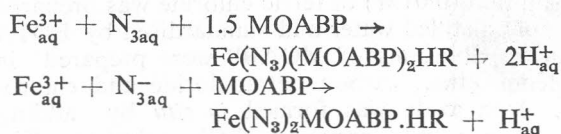
A solution (0.01M) of ferric chloride was prepared in doubly distilled water and standardised by EDTA titration. Solutions of MOABP were prepared in petroleum ether, carbon tetrachloride and chloroform. Iron azide was formed in situ by adding NaN$_3$ to a freshly prepared FeCl$_3$ solution. The blood red colour was extracted with MOABP dissolved in different solvents.

The distribution ratio (D) between the organic and the aqueous phases was followed spectrophotometrically after equilibration for 5 min.

Two complexes were isolated when 0.05M MOABP solution in petroleum ether was shaken for 1 hr with 0.02M and 1M FeCl$_3$, respectively, in the presence of 0.5M NaN$_3$ and 0.01M HCl. The solution was evaporated in vacuo to give tris- and mono-MOABP-iron(III) azido complexes. The bis-complex was only formed when a solution of 0.02M FeCl$_3$ was shaken with 0.01M MOABP in chloroform in the presence of 0.15M HCl and 0.5M NaN$_3$. The separated complexes analysed for Fe(N$_3$)$_3$.MOABP.2H$_2$O, Fe(N$_3$)$_3$.2MOABP.H$_2$O and Fe(N$_3$)$_3$.3MOABP corresponding to 1:1, 1:2 and 1:3 molar ratios respectively.

The azide exhibited a synergetic effect on the extraction with MOABP, similar to that exhibited by iron thiocyanate[6]. Fe-N$_3$-MOABP system in petroleum ether and chloroform exhibited λ_{max} at 460 and 450 nm mainly due to the electronic transition $^5T_2 \rightarrow {}^5E$. The extraction of $1 \times 10^{-4}M$ iron(III)

from HCl solution by $5 \times 10^{-3}M$ MOABP dissolved in different solvents showed that extraction is the least in $CHCl_3$ and highest in petroleum ether. The extent of extraction depended on the acidity of the solution. It decreased as [HCl] increased and reached a minimum at $1.5M$ HCl. The stepwise increase in [HCl] caused an increase in extraction by petroleum ether and CCl_4 while the increase in extraction was negligible by $CHCl_3$. The per cent extraction of $1 \times 10^{-4}M$ Fe(III) in the presence of $0.1M$ NaN_3 solution with $5 \times 10^{-3}M$ MOABP in petroleum ether or $CHCl_3$ at different acidities showed that maximum occurred at acid concentration in the range 0.1 to $0.2M$ HCl, the magnitude of extraction being more with petroleum ether. The plots of log D for $1 \times 10^{-4}M$ Fe(III) extraction in the absence and presence of NaN_3 at different acidities (0.1 to $3M$ HCl) were linear irrespective of the solvent used, with a slope of 2 and 1.5 in the absence and presence of NaN_3 respectively, indicating high complexing ability of azide towards Fe(III). The extraction mechanism probably involved adduct formation between the azido complexes and the extractant. The composition of the extractable complexes were determined in $0.1M$ HCl using the continuous variation method[7]. For a total molar concentration of $3 \times 10^{-3}M$ for Fe(III) and NaN_3 in the presence of $0.02M$ MOABP and for $1.5M$ NaN_3 and a total molar concentrations of $2 \times 10^{-3}M$ for Fe(III) and MOABP gave the compositions of the extractable species 1:1:3 and 1:2:2 ($Fe:N_3:MOABP$) respectively in petroleum ether and chloroform. The mechanism of extraction could be represented as follows :

$$Fe^{3+}_{aq} + N^{-}_{3aq} + 1.5 \ MOABP \rightarrow$$
$$Fe(N_3)(MOABP)_2HR + 2H^{+}_{aq}$$
$$Fe^{3+}_{aq} + N^{-}_{3aq} + MOABP \rightarrow$$
$$Fe(N_3)_2MOABP.HR + H^{+}_{aq}$$

The infrared bands of the separated mono and bis solid complexes gave a broad band in the vicinity of 3350 cm^{-1} indicating the presence of water of crystallisation in their structures. The δ band in the free NaN_3 was splitted in the prepared compounds with a decrease in intensity, due to complexation.

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Sodium N-Chlorobenzenesulphonamide (Chloramine-B) as an Analytical Reagent : Estimation of Thiosemicarbazide Alone & in Its Metal Complexes

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A simple, rapid and accurate method for the estimation of thiosemicarbazide (TSC) alone and in its metal complexes (with Zn, Cd, Hg, Ni, Pt and Pd) in aqueous medium by back titration with sodium N-chlorobenzenesulphonamide (chloramine-B) has been developed. The oxidation involves a twelve-electron stoichiometry per TSC molecule in aqueous medium of pH 2-7 and in the presence of $0.1N$ mineral acids. The proposed analytical method is useful for the rapid estimation of the ligand on a macroscale and also for computing the number of ligand molecules in a TSC-metal complex.

CHLORAMINE-T (CAT) has been extensively used as an oxidimetric titrant[1]. However, application of N-chlorobenzenesulphonamide (chloramine-B or CAB) as a titrant has been meagre[2]. The present note reports the use of CAB for estimating thiosemicarbazide (TSC) alone and in its complexes, in aqueous solution of pH 2-7 and in the presence of $0.1N$ mineral acids. The literature methods for the estimation of thiosemicarbazide in metal complexes are based on its oxidation by alkali metal hypohalites[3], chloramine-T[4], dichloramine-T[5], dibromamine-T[6] and lead tetraacetate[7].

Thiosemicarbazide (E. Merck) was purified by recrystallization from aqueous solution. $PdCl_2$ and H_2PtCl_6. $\times$ H_2O (Johnson-Matthey, London) were used for preparing the Pt(II) and Pd(II) complexes. The following TSC(L) complexes were prepared by methods reported by us elsewhere[7,8]. ML_2X_2, where M=Zn, Cd, Ni or Hg, X=Cl, NO_3 ClO_4 or $\frac{1}{2}$ SO_4; *cis* and *trans* PtL_2Cl_2; PtL_2X_2 where X=Br, I, CN, NCS or NO_3; *cis* and *trans* $PdL_2(NO_3)_2$; PdL_2X_2 where X=Cl, Br, I or NCS; Neutral complexes $M(L-H)_2$ where M=Ni, Pt or Pd. The complexes were recrystallized from aqueous solution and their composition was checked by elemental analyses and IR spectra[8].

Solution of TSC and its complexes ($\sim$2 mg/ml) were prepared in triply distilled water.

CAB was prepared[9] by passing pure Cl_2 through benzenesulphonamide dissolved in $4M$ NaOH solution for 1 hr at 70°C. The compound precipitated was filtered, washed, dried and recrystallized from water. Its purity was checked by estimating the amount of active chlorine present in the compound. An approximately $0.1N$ aqueous solution of CAB was prepared and standardised by the iodometric method. Compounds of accepted grades of purity were used in preparing other solutions. Standard buffer systems were employed.

It was found that the ligand was oxidized by CAB at all pH values. However, oxidation was slow at $pH < 2$ and $pH > 7$ and in $0.5N$ mineral acids. Reaction was faster in the pH range 2-7 and in $0.1N$