being responsible for the spectral changes. Values of K_a calculated from spectral changes at 590 and 280 nm are the same within experimental error. Addition of strong acid to solutions of Co(tga) results in only slight spectral changes, but the extinction coefficient of the LTMCT band at 282 nm does decrease sufficiently (from 11,700 to 10,800 M⁻¹ cm⁻¹) to allow determination of a K_a value. Calculated values of K_a are listed in Table 1 along with comparable K_a values selected from the literature.

The data of Table 1 show that the coordinated thiolato ligand of Co(cys) has about the same Brønsted basicity as a coordinated carboxylato ligand. Coordination to a highly charged metal center therefore exerts a leveling effect on the Brønsted acidities of thiols and carboxylic acids; noncoordinated carboxylic acids are at least four orders of magnitude more acidic than noncoordinated thiols, but after coordination the K_a values differ by less than one order of magnitude. This presumably results from protonation of the remote (i.e. not coordinated) oxygen atom of the carboxylato ligand, and in this context it is interesting to note that $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ is protonated on the remote oxygen atom rather than on the coordinated sulfur atom[14]. It is clear that protonation of coordinated carboxylato ligands, similar to the protonation of coordinated carboxylato ligands, can be important in determining the reactivity of these species[15].

The similar basicities coordinated RS⁻ and coordinated RCOO⁻ make it difficult to determine if Co(tga) is protonated at the thiolato site or at the carboxylato site, but the available spectral and K_a evidence cause us to tentatively favor the latter choice. The slight temperature dependence of the K_a governing eqn (5) allows estimation of ΔH_{K_a} and ΔS_{K_a} as 1.4 kcal/mol and 8.5 eu respectively. The small value of ΔH_{K_a} is consistent with the small enthalpy change expected for the protonation process [13]. The ionic strength dependence of the K_a governing Co(tga) protonation is likewise consistent with that expected for protonation of a positively charged center [13]. Co(cys) is not sufficiently basic to allow determination of K_a at $\mu = 4.0$ M, and therefore K_a was only determined at $\mu = 8.0$ M; the ionic strength dependence of Co(cys) protonation is expected to be greater than that for Co(tga) protonation because of the larger formal charge of the Co(cys) complex[13].

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Studies on Th(IV) and Zr(IV) complexes of oxygen donor ligands—VIII. Th(IV) complexes of 2,2'-bipyridine-1,1'-dioxide[†]

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Complexes of 2,2'-bipyridine-1,1'-dioxide (BipyO₂) with a wide variety of metal salts have been isolated and characterized [1]. Comparatively less is known about the complexes of Th(IV) with aromatic amine N-oxides [2–8]. The BipyO₂ complexes of Th⁴⁺ were, therefore, synthesised and characterized by conventional techniques including their thermal behaviour.

All the Th(IV) complexes correspond to the compositions ThX₄ · BipyO₂ (X=NO₃, NCS); ThX₄ · 3 BipyO₂ (X=Cl, Br) and ThI₄ · 4 BipyO₂. The analytical and other physical data on all the complexes are reported in Table 1. The complexes are quite stable except iodo complex which decomposed ~ low giving off iodine vapour. All the complexes decomposed ~ 250°. The complexes are soluble in polar solvents but insoluble in non-polar solvents. The conductivity data of the complexes show that except iodo complex, all other complexes are non-electrolytes. The iodo complex is uni-bivalent in nature. The molecular weight determination of the complexes also conform the same electrolytic behaviour.

The absorption frequencies of diagnostic value, namely NO stretching, NO bending and CH out-of-plane bending modes which are reported to be affected on complexation are briefly discussed. In the spectra of BipyO₂ absorptions of very strong intensities at 1265 and 1260 cm⁻¹ have been assigned to NO stretching mode. It undergoes a significant negative shift (20-50 cm⁻¹) on complexation, which is attributed to coordination of the oxygen atoms of the base causing decrease in π -character of the N-O bond[10]. Absorptions of strong intensities at 855 and 840 cm⁻¹ have been assigned to NO bending mode and from the tabulated data, it appears that only a slight shift of these vibrations are observed on complexation[10]. Absorptions associated with CH out-of-plane deformation modes, as expected, undergo slight positive shift due to tightening of the aromatic ring on

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Table 1. Analytical data and IR absorption frequencies (cm⁻¹) of Th(IV) complexes of BipyO₂.

Complex	Colour	Metal % Fou n d (Calcd)	Nitrogen % Found (Calcd)	Anion % Found (Calcd)	ohm ⁻¹ cm ²	Mol.√t. Found (Calcd)	V(NO)	δ(NO)	7 (СН)	്(M-O)
						-		·····	·	
Th(NO3)4.Bipy02	White	34.42 (34.73)	12.82 (12.57)	- -	a	(6 68)	1220vs 1200s	840m 825m	758s	390m
ThCl ₄ .3BipyO ₂	White	25.02 (24.73)	8.81 (8.95)	15.31 (15.13)	9.6°	(938)	1260m 1220s	850m 838m	770m 732w	380m
ThBr ₄ .3BipyO ₂	√hite	.20 .96 (20 .7 8)	7.40 (7.52)	28.52 (28.67)	a 8.3 ^c	(1116)	1255m 1230s	845m 832m	775s 745m	36 ¹ +m
This, HBipyO2	Yellow	15.73 (15.54)	7.73 (7.50)	34.13 (34.04)	49.7 ^b 76.5 ^c	490 (1492)	1260m 1228s	850m 838m	77 0s	360m
Th(NCS)4.Bipy02	White pink	35 .91 (35 . 58)	12 .9 8 (12.88)	35.69 (35.58	4.8 ^b 7.5c	603 (652)	1260m 1220m	850m 835m	768s 738w 715w	330w

Insoluble in mitrobenzene. а

b -

Conductivity in nitrogenzene. Conductivity in dimethylsulphoxide.

complexation[10]. The bands observed in 390-330 cm⁻¹ region are assigned as ν (M–O)[4, 11].

The absence of the v_3 band of ionic nitrate (D_{3h}) around 1360 cm⁻¹, and the occurrence of two strong bands at 1530 and 1290 cm⁻¹ in the spectrum of $Th(NO_3)_4 \cdot BipyO_2$ suggest the coordination of nitrate in this complex [12]. The bidentate nature of nitrato groups has been established by comparing the spectral bands of Th(NO₃)₄ · BipyO₂ with those of Th(NO₃)₄ · 5H₂O [13], where the bidentate character of the nitrato groups has been established by the X-ray analysis [14]. In Th(NO₃)₄ · BipyO₂ the NO₃⁻ vibrations occur at $1530(\nu_1)$, $1290(\nu_4)$, $1040(\nu_2)$, $817(\nu_6)$, 758(ν_3), 700(ν_5), while in Th(NO₃)₄ · 5H₂O the corresponding bands occur at 1520, 1290, 1030, 808, 745, 715 cm⁻¹ respectively. In Th(NCS)₄ · BipyO₂, the bands at 2040, 835 and 460 cm⁻¹ can be assigned to $\nu CN(\nu_1)$, $\nu CS(\nu_3)$ and $\delta NCS(\nu_2)$ respectively. These frequencies are normally associated with the terminal N-bonded isothiocyanate[15]. The IR spectra of the halo complexes closely resemble one another.

In conclusion the coordination number of Th(IV) in nitrate and halo complexes is found to be 10, whereas in thiocyanate complex the coordination number is 6.

The differential thermal curve of ThCl₄ · 3BipyO₂ shows a small endothermic peak at $\sim 65^{\circ}$ due to moisture. A very sharp endothermic peak at $\sim 270^\circ$ obtained is due to the decomposition of the complex. A broad exotherm at $\sim 380^\circ$ is due to the oxidation of carbon formed during the decomposition of the complex, and finally a small exothermic peak at $\sim 730^\circ$ corresponds to metal oxidation. In ThBr₄ · 3BipyO₂, an endothermic peak at $\sim 50^{\circ}$ is due to moisture, exothermic peak at $\sim 240^{\circ}$ is due to the decomposition of the complex. The exothermic peak at $\sim 430^\circ$ is due to the oxidation of carbon. A final small endothermic peak at $\sim 750^\circ$ corresponds to the metal oxidation.

The weight loss values observed in the thermal decomposition of Th(IV) complexes of BipyO2 correspond very closely with the following schemes.

$$(i) \quad ThCl_4 \cdot 3BipyO_2 \xrightarrow[-3BipyO_2]{278^\circ} ThCl_4 \xrightarrow[O]{393^\circ} ThOCl_2 \xrightarrow[O]{555^\circ} ThO_2$$

(ii)
$$\text{ThBr}_4 \cdot 3\text{BipyO}_2 \xrightarrow{250^\circ}_{-3\text{BipyO}_2} \text{ThBr}_4 \xrightarrow{300^\circ}_{(O)} \text{ThOBr}_2 \xrightarrow{730^\circ}_{(O)} \text{ThO}_2$$

(iii)
$$\text{Th}(\text{NCS})_4 \cdot \text{BipyO}_2 \xrightarrow[-\text{BipyO}_2]{235^\circ} \text{Th}(\text{NCS})_4 \xrightarrow[-\text{O}]{560^\circ} \text{ThO}(\text{NCS})_2$$

 $\xrightarrow{700^{\circ}}$ ThO₂

On the basis of thermal studies, the thermal stability of Th(IV) complexes of BipyO₂ is in the order,

Chloride > Bromide > Thiocyanate

EXPERIMENTAL

Ligand was prepared as described previously[4], and Th(IV) halides were prepared by the method of Patel [9].

Methanolic solutions of the ligand and the ThX_4 (X = Cl, Br, 1, NCS) were mixed in appropriate molar proportions with constant stirring. Bromo and thiocyanato complexes were immediately precipitate out, while the chloro and iodo complexes were obtained by the addition of excess of diethyl-ether. Th(IV) nitrato complex was prepared using ethyl-acetate as solvent to obtain better-yield. All the complexes were collected and washed with suitable solvents and dried in vacuo.

The metal and halides in the complexes were estimated as reported earlier[9]. The electrical conductance was measured at room temperature with a Toshniwal conductivity bridge and molecular weight was determined cryoscopically in freezing nitrobenzene. The IR was carried out on Perkin Elmer IR spectrophotometer Model 521; d.t.a. in air atmosphere using alumina as diluent on DTA-02 universal (DDR) and t.g.a. performed in static air using RG-Electrobalance with a platinum boat

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Ni(II) undecatungstogallate(III). Preparation, properties, structure and salts

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In earlier papers we reported the results of our studies with salts of the Co(II), Cu(II), and Mn(II) derivatives of the undecatungstogallate(III) anion[1, 2]. In this paper we wish to report the results of our research with salts of Ni(II)undecatungstogallate(III).

Each of these heteropoly anions has the "Keggin-type" structure and is an isomorph of the series which was first clearly elucidated and formulated as undecatungsto complexes by Baker *et al.*[3]. Subsequently, others have reported members of this series, including heteropoly molybdates, using the undec formulation [4-8]. Baker and Figgis have proposed a more general formulation for the undecatungsto (or molybdo) heteropoly complexes [9].

By a comparison of spectra we have shown that the Ni(II) ions in this new complex are octahedrally coordinated. This was not unexpected since the Ga(III) ions are in the central tetrahedral cavity of the parent and Keggin-type undecatungstogallate(III) anion[10]. Other studies to be reported here include: preparation of the pure Na and NH₄-Na salts of the new heteropoly tungstate complex, analysis for all constituents except constitutional oxygen in the anion, potentiometric titrations, cryoscopy in saturated sodium sulfate solution and X-ray crystallography.

EXPERIMENTAL

Preparation of sodium Ni(II)-undecatungstogallate(III). A sample of Na₂WO₄·2H₂O (J. T. Baker's Analyzed Reagent) weighing 52.00 g was dissolved in approx. 75 ml of water. To this solution, at room temperature, 10.00 ml of a gallium nitrate solution (prepared by dissolving 25.02110 g of the metal, 99.999% pure, obtained from AIAG, in a minimum of concentrated nitric acid and diluting to 250 ml) was added and the pH was brought to a value of 6.5 with 6 M nitric acid. These amounts of reagents correspond to an atomic W/Ga ratio of 11.0:1.0. The resulting solution was heated on a steam bath until all precipitated gallium hydroxide had dissolved, indicating that the undecatungstogallate(III) complex had completely formed. As this solution cooled from 85° to 67°C, approx. 20 ml of a solution containing 4.172 g of Ni(NO₃)₂·6H₂O (99.6%) was added dropwise with constant stirring. This gave an atomic Ga/Ni ratio of 1.0:1.0. The light green product was recovered from the solution, at room temperature, by addition of acetone according to the method of Rollins[11]. It was taken up with water and recovered a second time by addition of acetone. The product, free of nitrates (brown ring test), was dried in a vacuum oven at 75°C overnight, ground to a fine powder in a mortar, allowed to equilibrate (hydrate) with the

ambient atmosphere, and then enclosed in a vial. It weighed 41.5 g for a yield of 63% based on the W taken.

Analysis of Na_{6.9}[H_{2.1}NiO₆GaO₄W₁₁O₃₀]·14H₂O. The sodium analysis was performed by flame photometry using a NIL flame photometer obtained from the National Instrument Laboratories, Inc. Nickel was determined by atomic absorption spectrophotometry (Perkin-Elmer instrument Model 303). Assay of the $Ni(NO_3)_2$ ·6H₂O (99.6%) used to prepare the standard solutions was verified by EDTA titrations according to Flaschka[12]. The standard Zn(II) used for the back-titration, was prepared from ZnO. The ZnO (J. T. Baker's Analyzed Reagent) was assayed gravimetrically by the author[13], and solutions of it were also used to prepare standard EDTA solutions according to Harris and Sweet[14]. Nickel in the heteropoly complex was also determined by the EDTA method cited above after first removing it as Ni(OH)₂ from a solution of the complex which had been boiled, with an excess of NaOH, sufficiently to completely breakup the complex. Gallium was determined by the EDTA method of Rollins and Haynes[15]. Tungsten was determined by the gravimetric cinchonine method [16]. The dehydrations were carried out in a muffle furnace at 700°C. (Found: Na, 4.93; Ni, 1.82; W, 64.0; H₂O (total) 8.33. Calc. 1.85; Ga, for Na_{6.9}[H_{2.1}NiO₆GaO₄W₁₁O₃₀]·14H₂O: Na, 4.95; Ni, 1.83; Ga, 2.18; W, 63.2, H₂O (total) 8.46).

Preparation and analysis of (NH4)6.2Na0.3- $[H_{2.6}Ni_{1.1}O_6Ga_{0.9}O_4W_{11})_{30}]$ ·18H₂0. This double salt was prepared by addition of ammonium nitrate to a solution containing the Ni(II) undecatungstogallate(III) anion which was prepared by the procedure described above. The amounts of reagents used to prepare the heteropoly complex were the same as above, the nickel nitrate solution was added while the preparative solution cooled from 60° to 45°C, and 40 g of NH4NO3 was used. The product which consisted of large light green cubes, was recovered by filtration, washed with deionized water, and then recrystallized from a minimum of water. It weighed 16.8 g for a yield of 25.6% based on the W taken.

The ammonia analysis was performed with a micro-Kjeldahl apparatus according to Pregl and Grant [17]. The sodium, nickel, gallium and tungsten analyses were carried out as described above. The dehydration-deaminations were carried out at 700°C in a muffle furnace. (Found: NH_4^+ , 3.48; Na, 0.22; Ni, 2.24; Ga, 1.86; W, 62.7; (H₂O + NH₃), 15.5₆. Calc. for (NH_4)_{6.2}Na_{0.3-}[H_{2.6}Ni_{1.1}O₆ Ga_{0.9}O₄W₁₁O₃₀]:BH₂O: NH_4^+ , 3.45; Na, 0.21; Ni, 2.00; Ga, 1.94; W, 62.5; (H₂O + NH₃), 15.7₂).

Acid-base titrations. The amount of NaOH required to

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