

Preparation and Characterization of Chromium(III) and some other Trivalent Metal–Sulfosalicylato Complexes

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Received November 22, 1984

Abstract

As part of an investigation on the separation of the lanthanides from each other and from other trivalent metals by ion-exchange displacement methods applied to their sulfosalicylato complexes, the preparation and characterization of several 1:1 and 1:2 complexes of the trivalent metals Al, Ga, Cr and Fe with the sulfosalicylate ion, of formula $M(III)-(Ssal)$ and $M(III)(Ssal)_2^{3-}$, are reported.

Paper electrophoresis data, combined with 1H NMR and IR spectroscopy, suggest that these complexes: (i) maintain their integrity in aqueous solution, (ii) do not form polynuclear species at high concentrations, and (iii) contain sulfosalicylato ligands that coordinate through oxygens of unidentate carboxylato and deprotonated hydroxo groups.

Formation and dissociation of all complexes is rapid, except for the chromium(III) complexes, which are kinetically inert.

Introduction

For several years we have examined the feasibility of single-step separations of the lanthanides from each other and from transition elements by applying ion-exchange displacement methods to solutions of their EDTA [1] and, more recently, sulfosalicylato complexes. The somewhat peculiar behavior of chromium(III) *vis-à-vis* the sulfosalicylato ligand noticed during these studies prompted us to investigate the chromium(III)–sulfosalicylate- H^+ system in more detail. We report here the preparation and characterization of a number of trivalent metal–sulfosalicylato complexes.

There is little published information on chromium(III)–sulfosalicylato complexes [2–4]. A 1:1 complex has been characterized to some extent [3, 4], and evidence has been found for the existence of an apparently unstable 1:2 complex [4]. Little is known about charge or bonding of these complexes.

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In order to elucidate these properties we have carried out numerous syntheses over an extensive ligand-to-metal ratio and pH range. The isolated products and their solutions were analyzed and studied by UV-visible, IR and 1H NMR spectroscopy, X-ray powder diffraction, ion-exchange methods and paper electrophoresis.

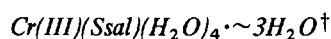
As some results could not be interpreted unambiguously we also isolated several other trivalent metal–sulfosalicylato complexes. A comparative study of the properties of these complexes yielded most of the sought information.

Experimental

Starting Materials

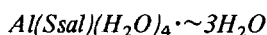
Sulfosalicylic acid dihydrate, anhydrous $AlCl_3$, $Fe(NO_3)_3 \cdot 9H_2O$ and Cs_2CO_3 were of commercial p.a. grade. Hydrated $Cr(OH)_3$ was prepared as the green A-hydroxide or blackish 'B-hydroxide' [5]; a ca. 1 M solution of $Ga(NO_3)_3$ was obtained by dissolving metallic gallium in 6 M HNO_3 at room temperature.

Preparations

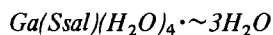


To a solution of 0.0100 mol (2.54 g) of sulfosalicylic acid dihydrate in 40 ml water was added 0.0100 mol (1.46 g) of solid $Cr(OH)_3 \cdot 2.4H_2O$. The solution, which slowly turned blue, was stirred for at least 2 h until virtually complete dissolution of $Cr(OH)_3$. Depending on the quality of $Cr(OH)_3$ used, heating to 80 °C may be necessary. After filtering off the undissolved residue, the solution of pH 3–4 was evaporated to almost complete dryness. A glassy turquoise-blue solid was isolated. Alternatively, twice the solution volume of isopropanol was added when a finely divided light blue solid precipitated immediately. The filtered solid was air-dried.

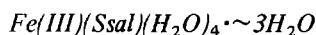
† In the remainder of this paper, sulfosalicylic acid will be abbreviated to H_3Ssal , the sulfosalicylate trianion to $Ssal$, etc. Aquo ligands and water of hydration are mentioned insofar as directly relevant.



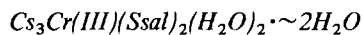
A solution of 0.0100 mol (1.33 g) of anhydrous AlCl_3 in 20 ml water was added to 0.0100 mol (2.54 g) of $\text{Na}_2\text{HSsal} \cdot \sim 2\text{H}_2\text{O}$ (prepared by partial neutralization of H_3Ssal with a NaOH solution) dissolved in 20 ml water. After stirring for 10 min at room temperature 2 M NaOH solution was added until the pH reaches 4.0. The complex precipitated as a finely divided white solid on adding 80 ml isopropanol to the filtered solution. The filtered solid was air-dried.



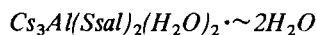
To a stirred solution of 0.0100 mol (2.54 g) of $\text{Na}_2\text{HSsal} \cdot \sim 2\text{H}_2\text{O}$ in 20 ml water was slowly added 0.0100 mol (2.56 g) of $\text{Ga}(\text{NO}_3)_3$ dissolved in *ca.* 10 ml water. The solution was stirred for 15 min, alkalized with 2 M NaOH to pH 3.7, and stirred for another 15 min. The complex precipitated on addition of 60 ml isopropanol to the filtered solution, and was collected as a white solid, dried *in vacuo*.



Similar to that of GaSsal , using a *ca.* 1 M solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The isolated complex, precipitated at pH 3.8, is intensely purple-violet.

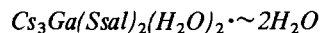


To a stirred solution of 0.0200 mol (5.08 g) of sulfosalicylic acid dihydrate in 40 ml water was added 0.0100 mol (1.46 g) of solid $\text{Cr}(\text{OH})_3 \cdot \sim 2.4\text{H}_2\text{O}$. After virtually complete dissolution of $\text{Cr}(\text{OH})_3$, which may take up to 2 h and/or heating to 80 °C, the residue was filtered off. To the filtrate was slowly added at least 0.0150 mol (4.89 g) of solid Cs_2CO_3 , until a pH of 5.5 to 7.2 is reached. The compound was collected as a light-blue solid that precipitated on addition of 80 ml isopropanol.

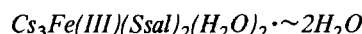


A solution of 0.0100 mol (1.33 g) of anhydrous AlCl_3 in 20 ml water was added to 0.0200 mol (5.96 g) of $\text{Na}_2\text{HSsal} \cdot \sim 2\text{H}_2\text{O}$ dissolved in 25 ml water. The solution was stirred for 10 min, alkalized with

solid Cs_2CO_3 to pH 7.5 to 8.0 and stirred for another 10 min. Addition of 100 ml isopropanol precipitated a white crystalline solid, recrystallized twice from hot (80 °C) water, and air-dried.



A solution of 0.0100 mol (2.56 g) of $\text{Ga}(\text{NO}_3)_3$ in *ca.* 10 ml water was added dropwise to a stirred solution of 0.0200 mol of $\text{Na}_2\text{HSsal} \cdot \sim 2\text{H}_2\text{O}$ in 20 ml water. The solution was stirred for 5 min, alkalized with solid Cs_2CO_3 to pH 5.5 to 5.9 and stirred for another 5 min. The compound separated on addition of 80 ml isopropanol; it was filtered off as a white solid and dried *in vacuo*.



Similar to that of the preceding complex. The final pH of the solution was 6.1 to 6.5. Addition of isopropanol precipitated a red-orange solid.

Analytical Data

Chromium(III) was determined in ammoniacal solution by back-titrating at 40 °C an excess of EDTA with a nickel salt solution; iron(III) by standard stannous chloride reduction/bichromate titration after separation as the hydroxide. Gallium and aluminium were estimated gravimetrically as the 8-hydroxyquinoline complex at pH 8.5 to 9.0. Cesium was weighed as the tetraphenylborate salt. Water of hydration was determined thermogravimetrically with a Perkin-Elmer TG/DSC instrument; the reported values correspond to the weight loss at 110 °C.

The organic content was determined indirectly: after catalytic oxidation of the sulfosalicylate ligand, the liberated sulfate was titrated potentiometrically with lead perchlorate using a Metrohm lead-sensitive electrode. The absence of sodium was verified by flame emission spectroscopy. The results are given in Table I.

Physical Measurements

UV-visible absorption spectra were recorded on a Perkin-Elmer 340; IR spectra (KBr pellets and Nujol

TABLE I. Analytical Data.

Compound	Cs found (calc.)	M(III) found (calc.)	S found (calc.)	H ₂ O (hydration) found (calc.)
$\text{Cr}(\text{III})\text{Ssal}(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}$	—	12.86(13.21)	8.30(8.15)	14.9(13.8)
$\text{Fe}(\text{III})\text{Ssal}(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}$	—	14.01(14.06)	8.11(8.08)	14.4(13.6)
$\text{AlSsal}(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}$	—	7.25(7.27)	8.84(8.71)	14.8(14.7)
$\text{GaSsal}(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}$	—	16.82(16.95)	7.94(7.80)	13.8(13.2)
$\text{Cs}_3\text{Cr}(\text{III})(\text{Ssal})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$	41.08(41.97)	5.54(5.47)	6.82(6.75)	4.40(3.80)
$\text{Cs}_3\text{Fe}(\text{III})(\text{Ssal})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$	41.60(41.80)	5.88(5.85)	6.70(6.72)	4.04(3.78)
$\text{Cs}_3\text{Al}(\text{Ssal})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$	42.10(43.10)	3.08(2.92)	6.90(6.93)	4.06(3.90)
$\text{Cs}_3\text{Ga}(\text{Ssal})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$	41.02(41.20)	7.29(7.21)	6.80(6.63)	4.10(3.73)

mulls) on a Perkin-Elmer 577 instrument; ^1H NMR (60 MHz) spectra were obtained with a Bruker WP-60 FT spectrometer. X-ray powder diffractograms were recorded with a Philips Debye-Scherrer-type powder diffractometer, using $\text{CuK}\alpha$ radiation. A CAMAG high-voltage water-cooled paper electrophoresis setup was used. The experimental conditions varied with the composition of the electrolyte; typically they were: 0.2 M electrolyte concentration; 0.001–0.1 M sample concentration; Whatman No 1 or S & S 2043a paper strips of 40×1.0 cm; 1.200 v/80 mA/1 h electrophoresis; spot visibility enhanced by UV fluorescence (Cr) or by spraying with quinalizarine red solution (Al, Ga). The iron(III) complexes were intensely colored. The ion-exchange experiments were carried out on 400 mesh Dowex 50W resin-filled columns (effective height: 15–20 cm).

Results

Preparation and Stoichiometry

The preparations reported here of the chromium(III)–sulfosalicylato complexes are based on the direct reaction between $\text{Cr}(\text{OH})_3$ and H_3Ssal or Na_2HSsal , in order to avoid the presence of other anions that might react with Cr(III) to form mixed-ligand complexes. This precaution is not essential; solids isolated from solutions containing up to 4 mol of sulfate per mol of chromium(III) do not incorporate any sulfate. The existence of mixed-ligand complexes in solution, on the other hand, is very possible, witness for example the shifts in the visible-light absorption spectra: the absorption maximum of a 1 M solution of Cr(III)Ssal in water at pH 4 is at 580 nm, with a shoulder at 442 nm; in a 0.2 M Na_2SO_4 solution at the same pH it is at 590 nm, with a shoulder at 432 nm.

Similarly, no mixed-ligand complexes have been isolated with Al, Ga and Fe(III) (but see also below).

Stoichiometry is to a large extent determined by pH, usually much less so by the ligand/metal ratio. Nevertheless, the overlap of the stability ranges of complexes of Fe(III) and Al with Ssal is important [6, 7], and necessitates careful control of pH. Thus for example at pH 4 only the 1:1 complex of chromium(III) can be isolated at ligand/metal ratios of up to 25:1. At appropriate pH the 1:2 complexes can be precipitated from fairly concentrated solutions containing the stoichiometric quantities of reagent. We have not attempted to construct any distribution diagrams.

The use of 'B-type' $\text{Cr}(\text{OH})_3$ should be avoided, as it tends to become unreactive on standing. Generally, the reaction rate for the formation of the Cr(III) complexes is much lower than for the other trivalent metal–sulfosalicylato complexes.

Paper Electrophoresis

Paper electrophoresis experiments were carried out in the pH range 1–10, with complexing and non-complexing electrolytes, including sodium perchlorate, sodium acetate, sodium sulfate, sodium nitrate and sodium sulfosalicylate. The electroendosmosis effect was corrected for, using glucose as neutral standard. Sample solutions were either freshly made up from the constituent reagents (Fe, Al, Ga complexes), or from previously isolated solids (all complexes). The apparent mobilities are assigned in Table II.

Electrophoretograms of solutions that contain either freshly mixed constituents or redissolved solids are identical, except for Cr(III), *i.e.* final equilibrium is reached rapidly compared to the duration of the electrophoresis experiment.

Electrophoretograms of the iron(III) sulfosalicylates show sharp, intensely colored bands, the positions of which confirm the neutrality of the 1:1 complex and the increasing charges of the anionic 1:2 and 1:3 complexes. Small shifts in the relative concentration of these complexes at specific pH values are found when a non-complexing electrolyte is replaced by sodium sulfosalicylate, as one would expect. At pH values below 2 decomposition takes place; in acetate medium more stable iron(III) acetates are formed at pH ~ 2.4 .

Very similar results are found for the 1:1 and 1:2 chromium(III), aluminium and gallium complexes. Identical values are obtained for dilute and concentrated solutions.

The electrophoresis data show that all 1:1 complexes are neutral (apparent mobility $0.00 \text{ cm}^2 \text{ volt}^{-1} \text{ h}^{-1}$ at 20°C) the 1:2 complexes are all anionic and possess similar apparent mobilities ($0.26\text{--}0.32 \text{ cm}^2 \text{ volt}^{-1} \text{ h}^{-1}$, depending on the electrolyte). The only stable 1:3 complex, anionic $\text{Fe}(\text{III})(\text{Ssal})_3$, is characterized by an apparent mobility of $0.51 \text{ cm}^2 \text{ volt}^{-1} \text{ h}^{-1}$. In some cases in Na_2SO_4 electrolyte mixed Ssal–sulfato complexes seem to be formed (Cr(III), Fe(III), Al) which show an apparent mobility of $0.35\text{--}0.40 \text{ cm}^2 \text{ volt}^{-1} \text{ h}^{-1}$.

^1H NMR and IR Spectroscopy

While the chromium(III) and iron(III) complexes yield ^1H NMR spectra that consist of a single broad to very broad resonance, those of the aluminium and gallium homologs are much more informative. The relevant data are given in Table III, together with those of sulfosalicylic acid at selected pH values [10].

The NMR spectra consist of three distinct signals, two doublets and a quartet, all generated by the benzene ring protons; the multiplets are assigned to the C_6 , C_4 and C_3 proton respectively, going upfield [10]. There is an appreciable shift of the C_3 proton signal and smaller shifts of the C_6 and C_4 proton signals, all upfield, compared to the resonances of

TABLE II. Electrochemical Apparent Mobility Data. Apparent Mobility of Species Present ($\text{cm}^2 \text{ volt}^{-1} \text{ h}^{-1}$) at 20 °C. All Species with Mobility $> 0.00 \text{ cm}^2 \text{ volt}^{-1} \text{ h}^{-1}$ Migrate Towards the Anode.

Electrolyte	pH	CrSsal/Cs ₃ Cr(Ssal) ₂	FeSsal/Cs ₃ Fe(Ssal) ₂	AlSsal/Cs ₃ Al(Ssal) ₂	GaSsal/Cs ₃ Ga(Ssal) ₂
0.2 M H ₃ Ssal	0.8	no complex formed	0.04	0.04(weak)	0.03
0.2 M NaH ₂ Ssal	4.0	0.00; 0.26(weak)	0.00; 0.27	0.01	0.00; 0.27
0.2 M Na ₂ H ₂ Ssal	5.8	0.00(weak); 0.30	0.00(weak); 0.31	0.00; 0.32	0.32
0.2 M Na ₃ Ssal	9.6	0.26(weak) ^a	0.28; 0.51	^c	^c
0.2 M CH ₃ COOH	2.4	0.04(weak) ^a	^b	0.04	0.02; 0.25(weak)
0.2 M Na ₂ SO ₄	6.0	0.00; 0.29; 0.40(weak)	0.00; 0.25; 0.35(weak)	0.01; 0.30; 0.42(weak)	0.03(weak); 0.30
0.2 M NaClO ₄	6.5	0.00(weak) ^a	0.00; 0.26	0.00; 0.24	0.02; 0.27
0.1 M Na ₂ H ₂ Ssal/ 0.1 M NaNO ₃	5.5	0.00(weak); 0.30	0.27	0.29	0.30
0.1 M Na ₂ H ₂ Ssal/ 0.1 M Na ₂ SO ₄	5.5	0.00(weak); 0.30	0.30	0.29	0.30
0.1 M Na ₂ H ₂ Ssal/ 0.1 M NaCl	5.5	0.00(weak); 0.27	0.00(weak); 0.27	0.28	0.29

^aPartial decomposition.

^bDecomposition with formation of acetate complex.

^cTotal decomposition.

TABLE III. ¹H NMR^a and Selected IR^a Data.

Compound	pH	C ₃ (H)	J(3-4)	C ₄ (H)	J(4-3)	J(4-6)	C ₆ (H)	J(6-4)	$\nu_{\text{sym}}(\text{CO}_2)$	$\nu_{\text{asym}}(\text{CO}_2)$	Δ
H ₃ Ssal	1.0	7.02	8.5	8.12	8.5	2.5	8.38	2.5	—	—	—
NaH ₂ Ssal	4.0	6.92	8.5	7.78	8.5	2.5	8.19	2.5	1380	1560-1590	180-210
Na ₂ H ₂ Ssal	7.0	7.01	8.8	7.82	8.8	2.5	8.24	2.5	1380	1570	190
N ₃ Ssal	13.0	6.23	9.0	7.10	8.7	2.6	7.30	2.3	1380	1565	185
Cr(III)Ssal	4.0	very broad resonance centered at ca. 8.1 ppm							1330	1560	230
Fe(III)Ssal	2.5	broad resonance centered at ca. 7.7 ppm							1380	1580-1610	200-230
AlSsal ^b	4.1	6.68	8.6	7.67	8.6	2.5	8.21	2.5	1330	1580-1600	250-270
GaSsal	3.8	6.52	8.5	7.58	8.5	2.5	8.15	2.5	1380	1600	220
Cs ₃ Cr(III)(Ssal) ₂	7.2	very broad resonance centered at ca. 8.2 ppm							1330	1570	240
Cs ₃ Fe(III)(Ssal) ₂	6.0	broad resonance centered at ca. 7.7 ppm							1385	1585-1615	200-230
Cs ₃ Al(Ssal) ₂	7.2	6.62	8.6	7.62	8.6	2.5	8.15	2.5	1330	1580-1600	250-270
Cs ₃ Ga(Ssal) ₂	5.6	6.50	8.5	7.55	8.6	2.5	8.10	2.5	1380	1580-1610	200-230

^aChemical shifts in ppm with respect to Tiers' salt; coupling constants in Herz; IR frequencies in cm^{-1} . ^bAlso weak resonances at 6.72 ppm (J(3-4): 8.6 Hz); 7.69 ppm (J(4-3): 8.6 Hz; J(4-6): 2.5 Hz); 8.23 ppm (J(6-4): 2.5 Hz).

sulfosalicylic acid at the same pH. Similar, although larger, shifts are found for the signals of the sulfosalicylate anion at pH 13, where the phenolic proton is dissociated.

In the IR spectra only the frequencies assigned to the $\nu_{\text{sym}}(\text{CO}_2)$ and $\nu_{\text{asym}}(\text{CO}_2)$ vibrations vary significantly. They are also included in Table III, as well as their difference Δ . No metal–oxygen bands can be clearly distinguished.

Ion-Exchange Experiments

(1) If one fixes chromium(III) on a cation-exchange column (originally in Na^+ form), almost no elution takes place with a 0.01–0.1 M Na_2HSsal or $(\text{NH}_4)_2\text{HSsal}$ solution at pH 4–7, although this pH range is optimum for complex formation. At 80 °C however, the reaction between retained Cr(III) and the sulfosalicylate eluent is rapid.

(2) A 0.01–0.1 M solution of Cr(III)Ssal or $\text{Cs}_3\text{Cr(III)(Ssal)}_2$ passes a cation-exchange column in Na^+ form essentially unchanged on elution with either water or Na_2HSsal solution. The same is true when the column is in H^+ form and even when contact with the column in acid form is maintained overnight. But at 80 °C decomposition of the complexes on a column in H^+ form is rapid; under these conditions Cr(III) is almost quantitatively retained.

This behavior is in contrast with that of the sulfosalicylato complexes of the lanthanides and of other trivalent metal ions tested; these are rapidly formed or decomposed.

X-Ray Diffraction Data

X-ray powder diffractograms show that the 1:1 complexes are amorphous. Those of the cesium salts of the 1:2 complexes are complex, but are very similar to each other, and suggest that the latter are isostructural.

Discussion

Although M(III)–Ssal complexes have apparently been studied in solution exclusively, their preparation and isolation is fairly straightforward, complicated only by their very high solubility in water. Thus, only cesium salts of the 1:2 complexes have been isolated pure. Under conditions similar to those used for the preparation of these compounds, the exact composition and charge of the iron(III)–sulfosalicylato complexes in solution have been shown to be [6, 8] FeSsal , Fe(Ssal)_2^{3-} and Fe(Ssal)_3^{6-} (neglecting the aquo ligands). Similarly, good evidence exists for the formulation of the aluminium and gallium complexes in solution as M(III)Ssal and $\text{M(III)(Ssal)}_2^{3-}$ (M(III) = Al, Ga) [9, 11].

We have found little specific information on other M(III) complexes, nor on the nature of the remaining

ligands and the coordination of the central atom. The electrophoresis results strongly suggest that:

(i) no polynuclear species are formed in concentrated solution;

(ii) all complexes contain totally deprotonated sulfosalicylato ligands;

(iii) the composition of each sulfosalicylato complex is identical in solution and in the solid state.

The complexes can then be formulated consistently as M(III)(Ssal) and $\text{M(III)(Ssal)}_2^{3-}$ (M(III) = Cr, Fe, Al, Ga).

The similarity between the various $\text{M(III)(Ssal)}_2^{3-}$ complexes is accentuated by the structural isomorphism found for their cesium salts. Additional support can be derived from the ^1H NMR and IR spectra. The shifts found for the benzene ring protons can be interpreted as being caused by the dissociation of the hydroxyl group proton, with concomitant binding of the metal to the phenolate oxygen. The existence of 1:3 complexes suggests that the sulfosalicylate ion can function as a bidentate ligand. The second most likely binding site, the carboxylate group, should then be unidentate. This idea is supported by the complexes' IR spectra, in particular by the frequencies of the bands assigned to $\nu_{\text{sym}}(\text{CO}_2)$ and $\nu_{\text{asym}}(\text{CO}_2)$ and their difference Δ [11].

The large Δ values are consistent with the presence of unidentate carboxylato ligands [11], that are possibly also hydrogen bonded to one of the metal's aquo ligands.

The displacement of a phenolic hydrogen is surprising, considering the $\text{p}K_3$ value of 11.6 [6] of sulfosalicylic acid. However, the intense color of the iron(III)–phenolate oxygen chromophoric bond [6, 8]. The chelate effect is large in such complexes that form six-membered rings, except possibly for aluminium with its small ionic radius [9]. In fact, the formation constants of the aluminium complexes ($\text{ML}/\text{M.L} = 12.3^*$; $\text{ML}_2/\text{M.L}^2 = 20.0$) are appreciably smaller than those of, e.g., iron(III) ($\text{ML}/\text{M.L} = 14.6$; $\text{ML}_2/\text{M.L}^2 = 25.1$) [7b, 9, 13]. Thus only for iron(III) can a 1:3 complex be isolated, albeit impure.

The NMR spectra of the aluminium complexes suggest that the latter may exist, at least partially, in hydrolyzed form, for example as $\text{Al(HSsal)(H}_2\text{O)}_3\text{-(OH)}$ (*cf.* set of resonance peaks shifted downfield, although not back to the sulfosalicylate position). As the chromium(III) complexes are less stable ($\text{ML}/\text{M.L} = 9.6$) [3, 4], they may also exist in hydrolyzed form. 'Normal' and hydrolyzed forms coexist in solutions of the 1:2 neodymium complex at appropriate pH and ligand concentration [12]; the stability of the lanthanide complexes is indeed lower than that of other trivalent metal complexes (e.g. for Nd^{3+} : $\text{ML}/\text{M.L} = 6.2$; $\text{ML}_2/\text{M.L}^2 = 11.2$) [13]. Recent kinetic

* \log_{10} values are given.

studies of nickel(II) complexes with various salicylate derivatives have led to analogous formulations [14], as do potentiometric studies of the aluminium–salicylate–H⁺ system [7b]. We propose then the formulae used in Table I, based on full deprotonation of the sulfosalicylato ligand for all isolated complexes. We do not rule out the existence of mixed aquo–hydroxo complexes of aluminium and chromium at higher pH.

The results of the ion-exchange experiments contrast with the low stability of the chromium(III)–sulfosalicylato complexes. They may be explained by the kinetic inertness of both the aquo–chromium(III) ion and the chromium(III)–sulfosalicylato complexes. Experiment 2) also confirms the non-cationic character of both complexes. The kinetic sluggishness is characteristic of the chromium(III) complexes.

Conclusion

M(III)Ssal (M(III) = Al, Ga, Cr, Fe; Ssal = sulfosalicylate trianion) and M(III)(Ssal)₂³⁻ are well-characterized complexes. Their formation and dissociation rates are high, except for chromium(III). Chromium(III) sulfosalicylates are kinetically inert. The complexes are difficult to isolate because of their high solubility in water. Their constitution does not seem to change on dissolution in water, apart from occasional acid dissociation of an aquo ligand (Al, perhaps Cr). ¹H NMR and IR data suggest that the metal is bonded to the ligand or ligands through unidentate carboxylate groups and through phenolate oxygens.

Acknowledgements

We thank the Swiss National Science Foundation for financial support, Dr. C. Vercaemer, Dowell-

Schlumberger Central Laboratory, St. Etienne, France, for making available the X-ray diffraction and DSC/TGA equipment, and Dr. Z. Proso, Laboratoire de Radiochimie (Prof. Lerch) of the EPF Lausanne for his help with the electrophoresis experiments.

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