

MIXED LIGAND-SULPHITO COMPLEXES OF CHROMIUM (III)

Kamal A.R. Salib*, Salah B. El-Maraghy and Saied M. El-Sayed

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

(Received January 13, 1989; revised March 13, 1989)

The reaction of Na_2SO_3 and $[\text{Cr}(\text{L})_2\text{X}_2]\text{Cl}$ complexes, $\text{L} = \text{ox}$, $\text{X} = \text{H}_2\text{O}$, $\text{L} = \text{bpy}$ or en , $\text{X} = \text{Cl}$, resulted in the replacement of the coordinated water molecules or chloride ions by hydroxide and/or sulphite ions. Although the medium of the reaction was acidic, hydroxosulphito products were obtained in the case of nitrogen containing ligands. The hydroxo group acts either as a unidentate ligand in monomeric species or as a bridging bidentate ligand in dimeric ones. The IR spectra of the complexes indicated the presence of a unidentate S-bonded coordinated sulphito groups. The magnetic moments and visible spectra of the complexes showed that they are hexaco-ordinated.

Key words: Sulphito, Chromium (III), Complexes, Synthesis.

INTRODUCTION

Cobalt (III) sulphito complexes were previously investigated in much detail [1-5], however, the corresponding chromium (III) compounds have received less attention. Sulphitoamine and sulphitoaquo chromium (III) complexes were obtained initially as the O-bonded sulphito intermediates which rapidly rearranged to the stable S-bonded isomers [6, 7].

We have prepared the following starting complexes: $\text{K}[\text{cis-Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 1/2\text{H}_2\text{O}$, $[\text{Cr}(\text{bpy})_2\text{Cl}_2]\text{Cl} \cdot 1.2\text{H}_2\text{O}$ and $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot 1.15\text{H}_2\text{O}$ and reacted them with Na_2SO_3 in acidic acetate buffer solution to avoid the formation of bridging hydroxo products quite common with Cr (III) complexes. However, in spite of this precaution, hydroxosulphito products are obtained in the case of bipyridine and ethylenediamine containing complexes.

EXPERIMENTAL

Chemicals. Potassium dichromate, chromium chloride hexahydrate, oxalic acid, bipyridine, ethylenediamine, sodium sulphite and other chemicals used were all reagent grade.

Preparation of the starting complexes. The following complexes were prepared. $\text{K}[\text{cis-Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 1/2\text{H}_2\text{O}$ [8], $[\text{Cr}(\text{bpy})_2\text{Cl}_2]\text{Cl} \cdot 1.2\text{H}_2\text{O}$ [9] and $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot 1.15\text{H}_2\text{O}$ [10], (bpy = bipyridine, en = ethylenediamine). Their analysis was satisfactory.

Preparation of sodium potassium bis (oxalato) disulphitochromate (III) monohydrate, $\text{Na}_4\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{SO}_3)_2] \cdot \text{H}_2\text{O}(\text{A})$. Potassium cis-bis (oxalato) diaquochromate (III) hemihydrate (1 g, 3.2 mmol) was dissolved in 30 ml acetate buffer solution, pH = 5.2. Successive amounts of sodium sulphite (0.4 g, 3.2 mmol), dissolved in the least amount of water, were added to the former solution to reach the molar

ratios 1:1, 1:2, 1:3 and finally 1:4. The pH was 4.7, 6.1, 6.4 and 6.6, respectively. During these additions the colour of the solution changed gradually from purple to green. Addition of acetone yielded a green oil which was washed several times with ethanol then ether until the product solidified. The green solid was further washed with a mixture of cold water and methanol. The yield was 0.7 g (43.0%) m.p. > 240°. Analysis for $\text{Na}_4[\text{cis-Cr}(\text{C}_2\text{O}_4)_2(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$: Calcd, Na, 17, K, 7.3, Cr, 9.7, C, 8.7, H, 0.4; S, 11.9%. Found Na, 17.9, K, 7.1, Cr, 9.9, C, 8.8, H, 0.7, S, 12.1%.

Preparation of hydroxosulphitobis (2, 2'-bipyridine) chromium (III) trihydrate-sodium chloride, $[\text{Cr}(\text{bpy})_2(\text{SO}_3)(\text{OH})] \cdot 3\text{H}_2\text{O} \cdot 0.2\text{NaCl} (\text{B})$. Dichlorobis (2, 2'-bipyridine) chromium (III) chloride dihydrate (1 g, 2.0 mmol) was dissolved in 30 ml acetate buffer solution, pH = 3.9. Successive amounts of sodium sulphite (0.25 g, 2.0 mmol), dissolved in the least amount of water, were added to the former solution to reach the ratios 1:1, 1:2, 1:3 and finally 1:4, whereas the changes of the pH of the solution were 4.7, 5.4, 6.3 and 6.6, respectively. The solution was then stirred for 4 hours. Excess acetone was added to precipitate sodium chloride, sodium acetate and excess sodium sulphite and was filtered. The filtrate left in the open to evaporate slowly resulting in a red solid. The yield was 0.9 g (82%), m.p. 170° (decomp.), at 110° the colour changes to deep brown. Analysis for $[\text{Cr}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{SO}_3)(\text{OH})] \cdot 3\text{H}_2\text{O} \cdot 0.2\text{NaCl}$, Calcd, Na, 7.3, C, 38.0, H, 3.6, N, 8.9, Cl, 11.2, S, 5.1%. Found: Na, 8.1, C, 38.0, H, 4.3, N, 8.2, Cl, 11.2, S, 5.1%.

Preparation of hydroxosulphitobis (ethylenediamine) chromium (III) hemihydrate-sodium sulphite, $[\text{Cr}(\text{en})_2(\text{SO}_3)(\text{OH})] \cdot 1/2\text{H}_2\text{O} \cdot 1/2\text{Na}_2\text{SO}_3 (\text{C})$. Cis-dichlorobis (ethylenediamine) chromium (III) chloride hydrate (1 g, 3.3 mmol) was dissolved in 20 ml acetate buffer, pH = 5. Sodium sulphite (0.825 g, 6.65 mmol) was dissolved in the least amount of water and was added dropwise to the above solu-

*Author to whom correspondence should be addressed.

tion with stirring for three hours. The pH of the resultant solution was 6. Excess acetone was added to precipitate the sodium chloride, sodium acetate and excess sodium sulphite. The solution was filtered and the filtrate left in the open to evaporate slowly resulting in a deep reddish violet solid. The yield was 0.93 g (84%), m.p. > 240°. Analysis for $[\text{Cr}(\text{C}_2\text{H}_8\text{N}_2)_2(\text{SO}_3)(\text{OH})] \cdot 1/2\text{H}_2\text{O} \cdot 1/2\text{Na}_2\text{SO}_3$, Calcd. Na, 6.8, C, 14.1, H, 5.3, N, 16.4, S, 14.1%. Found: Na, 6.1, C, 14.0, H, 5.1, N, 16.2, S, 13.2%.

Analyses. Chemical analyses were carried out at the Fine Chemical Analyses Center, Cairo University, Giza, Egypt.

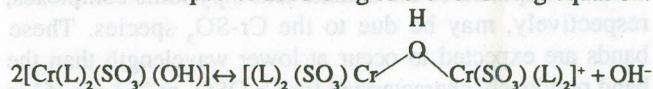
Spectra and magnetic measurements. The IR spectra were recorded in the range 400–4000 cm^{-1} on KBr discs using a Perkin-Elmer 598 spectrometer. Electronic spectra of the solids were recorded on a Beckman Acta MIV spectrophotometer provided with a diffuse reflectance attachment. Magnetic measurements were carried out at 20° by the Gouy method. Conductance measurements were carried out using a conductivity meter, Wissenschaftlich-technische Werkstätten, D8120 Weilheim, Mod. LBR 40A, West Germany.

RESULTS AND DISCUSSION

The prepared sulphito products are all soluble in water which may indicate that they are monomeric. The bipyridine and the ethylenediamine sulphito complexes also contain a coordinated hydroxy group. Harris *et al.* [7] obtained a similar product, $[\text{Cr}(\text{OH})_4(\text{OH})(\text{SO}_3)]$, by reacting $\text{Na}_2\text{S}_2\text{O}_3$ and $[(\text{Cr}(\text{OH})_6)(\text{ClO}_4)_3]$, molar ratio ~1-1/2:1, in the least amount of water. Their product, however, was insoluble in aqueous as well as acid solution and this was attributed to the formation of a dinuclear complex which commonly occurs with Cr (III) species. The bipyridine and the ethylenediamine sulphito complexes were also coprecipitated with NaCl and Na_2SO_3 , respectively. This was not a surprise since similar results were observed in the case of $\text{Na}[\text{Co}(\text{tren})(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$ where it was obtained coprecipi-

tated with either NaCl or NaClO_4 , $\text{tren} = 2,2', 2''$ -triaminotriethylamine [5], and trials to remove these coprecipitated salts by recrystallization were unsuccessful.

(i) **Conductivity measurements.** The aqueous solutions of the products conduct electricity. Their molar conductance are shown in Table 1. The conductance of the aqueous solution of the oxalate product is attributed to the presence of sodium and potassium cations and the anionic complex ions. However, its low value may be due to incomplete ionization of the product as previously observed in the case of $\text{K}_4[\text{Fe}(\text{CN})_6]$ [11]. The high conductivity of the aqueous solution of bipyridine and ethylenediamine products could be attributed partly to the presence of the coprecipitated NaCl or Na_2SO_3 molecules. Also, dimerization through OH bridges would lead to the presence of the highly conducting free OH^- ions. These dimers would be formed from the monomeric species according to the following equation:



This was evidenced by the presence of characteristic peaks due to the bending vibrations of OH bridges in the IR spectra of the solid products.

(ii) **IR spectra.** The IR spectra of the Cr (III) sulphito complexes, Table 1, showed peaks characteristic of S-bonded sulphito groups. The stretching vibrations are in the range 1120–1165 cm^{-1} and the bending vibrations are in the range 616–640 and 485 cm^{-1} . These vibrations are similar to those observed in the case of Co (III) sulphito complexes [12]. However, the latter complexes showed more splittings and the stretching vibrations extended over a wider range, 905–1185 cm^{-1} . The bending vibrations were quite similar. These results are in accord with the well known similarity of both Co (III) and Cr (III) complexes.

The hydroxyl groups present in the ethylenediamine and bipyridine containing sulphito complexes showed two bending vibrations. The first peak occurs at 1395 and 1370-

Table 1. Infrared frequencies (cm^{-1}) of the sulphito group(s), conductivity, magnetic moments and electronic spectra of mixed ligand-sulphito chromium (III) complexes.

Complex	IR frequencies of the sulphito groups (cm^{-1})		Conductivity $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ at 25°	μ_{eff} (B.M.)	Electronic spectra (cm^{-1})	Additional peaks (nm)	
	Stretching	Bending					
(A)	1190 s, sh, 1165 s, sh, 1120vs, b, 1055m, sh, 998w	640s; 618s	385	3.3	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ 17300+ 17300+ (74)**	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ 23600 24000 (116) ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ (P) 36400	209 (6100)
(B)	1180vs, 1160vs, 120vs, b	620s	465	3.1	19230* 19350+ 18700+	22350, 24850(sh) 24200 26200	379, 357, 322, 309, 300, 278 267, 257, 231, 213 315, 295
(C)	1150vs, sh, 1130-1100vs	635m, 616m, 485m, b	435	2.8	18700+	26200	315, 295

* Reflectance spectrum of the solid. + Visible spectrum of the aqueous solution. ** Values of ϵ .

1382 cm^{-1} , respectively. A similar peak at 1389 cm^{-1} was previously observed in the IR spectra of basic selenites and hydrated $\text{Cr}(\text{OH})_3$ [13] which contain bridging OH groups. The second peak appeared at 925 and 930 cm^{-1} respectively, and is assigned to Cr-OH bending mode, Scargill [14] assigned the bands at 970-1000 cm^{-1} in hydroxo complexes of ruthenium to the bending vibration of the M-O-H group. Thus, it seems that these complexes contain a unidentate hydroxyl group. Besides, dimeric forms, through OH bridges, do exist in the solid.

(iii) *UV-visible spectra.* The visible spectra of Cr(III) complexes showed three bands due to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$, ${}^4A_{2g} \rightarrow {}^4T_{1g}$ and ${}^4A_{2g} \rightarrow {}^4E_g$ (P) transitions, Table 1, characteristic of octahedral symmetry of the complexes. Additional bands in the spectrum of the bipyridine complex are due to the heterocyclic aromatic rings [15]. The bands at 209 and 213 nm in the spectra of the oxalato and bipyridine complexes, respectively, may be due to the Cr-SO₃ species. These bands are expected to occur at lower wavelength than the band previously characterized for Cr-OSO₂ at 264 nm [6] in comparison with the values reported for Co-OSO₂ and Co-SO₃ at 330 and 280 nm, respectively [4].

(iv) *Magnetic moments.* The magnetic moments determined for the complexes are shown in Table 1. Those due to the bipyridine and ethylenediamine complexes are somewhat low for magnetically normal octahedral complexes which may be due to antiferromagnetic exchange between adjacent chromium ions in the dimeric forms.

It could be concluded that the prepared Cr(III) complexes are hexaco-ordinated through bidentate oxalato, bipyridine or ethylenediamine ligands and S-bonded sulphito group (s) besides OH⁻ groups in the latter two complexes. The OH⁻ group acts as a unidentate ligand in the monomeric species and as a bridge in the dimeric ones.

Acknowledgement. We thank Dr. L.F. Larkworthy of the University of Surrey, England, for his help in the measurements of the electronic spectra and magnetic susceptibilities of the complexes.

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