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Synthesis and Reactivity of Cobalt(III) Complexes Containing 2,2′-Bipyridyl and 1,10-phenanthroline. I. Sulphite Group as Unidentate and Bidentate Ligand

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Baldwin [1] reported on the preparation of compounds $[Coen_2SO_3Cl]^0 \cdot H_2O$ and $[Coen_2(SO_3)_2]Na$ via reactions between *cis* and *trans*-$[Coen_2Cl_2]Cl$ and Na_2SO_3 in different relative ratios and under different experimental conditions. In these compounds the sulphite group is present as unidentate ligand attached through sulphur. From the same reagents, by slow evaportation in darkness for a six week period Baldwin obtained as product $[Coen_2SO_3]Cl$ where the sulphite group acts as a bidentate ligand through the two oxygen atoms.

We have examined the reactions of closely related compounds *cis*-$[Co(AA)_2Cl_2]Cl$, AA being 2,2′-bipyridyl and 1,10-phenanthroline respectively, with sodium sulphite. In every case *cis*-$[Co(AA)_2SO_3]Cl$ was produced, having bidentate sulphite group coordinated through the oxygen atoms. The only possible isomer for octahedral complexes of Co(III) with two bipyridyl or two phenanthroline molecules is the *cis* isomer and the products obtained in the reactions were largely predictable.

In order to obtain a sulphite-containing complex where sulphite is unidentate-coordinate through sulphur, we decided to make one of the two reaction sites in the dichlorochloride complex inactive through substitution of one of the coordinated chlorine atoms with an inert ligand such as the cyano group.

We therefore synthesized the cation $[Co(AA)_2CNCl]^+$ from dichloro–chloride and KCN in a 1:1 ratio and subsequently obtained $[Co(AA)_2SO_3CN]^0$ by reacting with Na_2SO_3.

Compounds $[Co(AA)_2SO_3CN]^0$ neither undergoes aquation in water nor basic hydrolysis when prolongedly heated in alkaline solution. On the other hand it undergoes substitution reactions with sulphite group, giving rise to products to be described in a forthcoming paper.

In the scheme 1 the investigated reactions are presented. The starting compound (1), was synthesized according to the prescriptions of ref. [2]. It might be noted that, from (2), compound (1) is obtained, while (3) is produced from (4) with SO_2 release similarly to what occurs in ethylenediamine containing complexes.

A comparison of the two series of compounds containing phenanthroline and bipyridyl bears out the fact that the latter are easier to prepare, more reactive and more versatile than the former.

Experimental

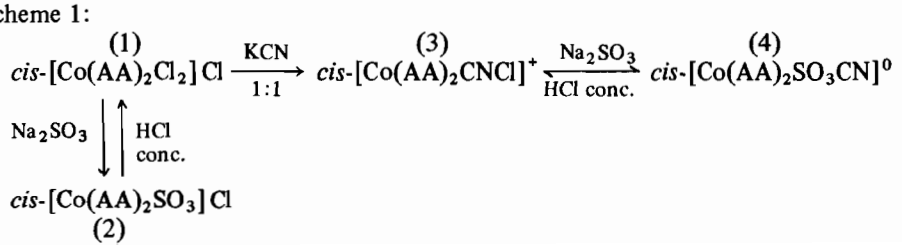
Cis-*sulphitebisphenanthrolinecobalt(III) Chloride*

1.164 g (2.02×10^{-3} mol) of *cis*-dichlorobisphenanthrolinecobalt(III) chloride were dissolved in a minimum of water necessary, then mixed with a warm solution of 1.246 g (9.9×10^{-2} mol) of sodium sulphide similarly prepared. The color turned from wine-red to dark orange. Concentration upon a water bath followed until a solid separated on the surface. Upon cooling and filtering, the orange precipitate was washed with ethyl alcohol and ether (25% yield). The IR spectrum of the product recrystallized from aqueous solution presents bands at 1140, 1120, 1105, 1010, 980, 640, 620 cm^{-1} attributed to bidentate coordinating sulphite group. Found: % C 49.89; H 3.66; N 9.67; S 6.01. Calculated for $Co(C_{12}H_8N_2)_2SO_3Cl \cdot 2H_2O$: % C 50.52; H, 3.51; N 9.82; S 5.61.

Cis-*cyanosulphitebisphenanthrolinecobalt(III)*

To a solution containing 3 g (4.85×10^{-3} mol) of *cis*-chlorocyanobisphenanthrolinecobalt(III) perchlorate in 1:1 water–alcohol mixture, a solution containing 0.613 g (4.85×10^{-3} mol) of sodium sulphite in a minimum of water was added. The color turned immediately from deep red to orange-yellow. Concentrating on a water bath and cooling on ice one finally obtained a lemon-yellow precipitate which was filtered off and washed with ethyl alcohol and ether (60% yield). The IR spectrum of the product recrystallized from water solution showed the cyano group band at 2140 cm^{-1} and four bands at 1145, 1090, 990, 620 cm^{-1} which are assigned to the unidentate

Scheme 1:



coordinating sulphite group. Found: % C 54.8; H 3.15; N 12.06; S 5.61. Calculated for $Co(C_{12}H_8N_2)_2SO_3CN \cdot H_2O$: % C 55.10; H 3.31; N 12.90; S 5.89.

Cis-*sulphitebisbipyridylcobalt(III) Chloride*

To 0.5 g (9.75×10^{-4} mol) of *cis*-dichlorobisbipyridylcobalt(III) chloride dissolved in a minimum of water 0.925 g (7.35×10^{-3} mol) of Na_2SO_3 likewise dissolved in a minimum of water are added. The purple color of the solution turned to deep orange. Concentration and cooling on ice followed. A pale yellow precipitate separated out and was filtered off and washed with ethyl alcohol and ether (30% yield). The IR spectrum of the product recrystallized from water solution showed bands at 1146, 1123, 1065, 1023, 985, 640, 620 cm^{-1} characteristic of bidentate coordinating sulphite group. Found: % C 45.67; H 3.61; N 10.23; S 6.25. Calculated for $Co(C_{10}H_8N_2)_2SO_3Cl \cdot 2H_2O$: % C 45.97; H 3.83; N 10.72; S 6.13.

Cis-*cyanosulphitebisbipyridylcobalt(III)*

To 0.75 g (1.4×10^{-3} mol) of *cis*-chlorocyanobisbipyridylcobalt(III) perchlorate dissolved in hydroalcoholic mixture 0.177 g (1.4×10^{-3} mol) of Na_2SO_3 dissolved in a minimum of water are added. The color of the hydroalcoholic solution turned from orange-red to pale yellow. On concentration by heating then cooling on ice a pale yellow precipitate was obtained which was filtered off and washed with ethyl alcohol and ether (40% yield). The IR spectrum of the product recrystallized from aqueous solution showed a band at 2140 cm^{-1} typical of the cyano group and four bands at 1160, 1090, 985, 620 cm^{-1} characteristic of an unidentate coordinating sulphite group. Found: % C 50.03; H 3.82; N 14.01; S 6.64. Calculated for $Co(C_{10}H_8N_2)_2SO_3CN \cdot H_2O$: % C 50.91; H 3.63; N 14.30; S 6.46.

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