the NH_2 groups in this region previously have been assigned to the asymmetric deformation modes.

The *cis* and *trans*-dinitrobis-(ethylenediamine)-cobalt(III) complexes also were investigated. The bands corresponding to the nitro groups[2,15] were assigned. These were observed at approximately 1400, 1340 and 830 cm.$^{-1}$ in the five salts of this type which were studied. A splitting of the band in the 800 cm.$^{-1}$ region occurred in both the *cis* and *trans*-dinitro compounds. The absorption peaks occurred at 828 and 817 cm.$^{-1}$. In the case of the complexes which contained nitrate as the anion a strong peak was observed at 1376 cm.$^{-1}$, which was assigned to the nitrate ion.

Investigation of the NH_2 asymmetric deformation frequencies of the *cis* and *trans*-dinitro complexes again revealed a splitting of this band in the case of the *cis* isomer. The *trans*-dinitro complex, containing nitrate as the anion (Table I) showed a strong fairly symmetrical band at 1610 cm.$^{-1}$. However, as had been observed previously in the case of the *cis*-dichloro compound, the *cis*-dinitro complex (Table I) gave two peaks in this region, a strong band which occurred at 1575 cm.$^{-1}$ and a weaker one at 1617 cm.$^{-1}$. The chloride salt of the *cis*-dinitro complex gave three absorption bands in this region. These involved a strong band at 1566 cm.$^{-1}$ and bands at 1615 and 1598 cm.$^{-1}$, both of moderate intensity.

The nitrite salt of the *trans*-dinitro complex, however, exhibited three absorption bands in the 1600 cm.$^{-1}$ region. The two strongest bands were at 1617 and 1606 cm.$^{-1}$. The other band, which was extremely weak, occurred at 1633 cm.$^{-1}$. The band containing these peaks was symmetrical. It should be noticed that in this case the strongest absorption peak is observed at 1606 cm.$^{-1}$.

The strongest band of the *cis* complex was found at 1581 cm.$^{-1}$ and the others at 1571 and 1553 cm.$^{-1}$. In general, examination of the spectra reveals a more distinct and a greater splitting of the asymmetric deformation modes of the NH_2 groups in *cis* isomers than is observed in the corresponding *trans* isomers.

Mizushima and co-workers[5] have proposed that a bidentate ligand of the type $X\text{-}CH_2\text{-}CH_2\text{-}X$ exists in the *gauche* form when it is complexed. The calculated hydrogen deformation frequencies of the *gauche* form of $NCS\text{-}CH_2\text{-}CH_2\text{-}SCN$ have been reported.[5] These values have been used in making assignments of the absorption peaks observed for the ethylene groups. Due to the multiplicity of the peaks observed in the spectra of the diacido-bis-(ethylenediamine)-cobalt(III) complexes, which could be assigned to carbon–hydrogen vibrations, the observed peaks have been categorized and assigned by region. These assignments are listed in Table II. The absorption bands assigned fall into the general regions which are expected for the *gauche* form of the ethylene group. Furthermore, the low frequency rocking vibration expected of a *cis*-ethylene group at 740 cm.$^{-1}$ is not observed. No correlation was observed between the splittings of these absorption bands and the isomeric nature of the complex ion.

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(15) M. L. Morris and D. H. Busch, THIS JOURNAL, **78**, 5178 (1956).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, AND THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XXV. A *trans* Complex of Triethylenetetramine[1]

BY J. SELBIN[2] AND JOHN C. BAILAR, JR.

RECEIVED JULY 20, 1959

The isolation of both green and violet forms of the cation [Co trien Br_2]$^+$ is reported. That these are *trans* and *cis* isomers, as their respective colors would indicate, is confirmed by a comparison of the infrared spectrum for the known *cis*-[Co trien Cl_2]$^+$ with the spectra for the two dibromo cations. The large size of the bromide ion doubtless helps in forcing the formation of the planar configuration of the *trien* molecule, since adjacent (*cis*) bromide ions will introduce instability, particularly in the close-packed solid state.

Introduction

In 1948, Basolo[3] reported the preparation of [Co trien Cl_2]$^+$ and [Co trien $(NO_2)_2$]$^+$, where *trien* is an abbreviation for the quadridentate ligand, triethylenetetramine. Theoretically, these ions may exist in three different stereoisomeric forms, two *cis* and one *trans*, as shown in Fig. 1. Both *cis* forms, being asymmetric, should be capable of resolution into optical antipodes. Although he used several different preparative methods, Basolo obtained only one dichloro compound and on the basis of its blue-violet color he assigned to it a *cis* configuration. The colors of dihalo cobalt complexes are characteristic of the configurations and have long been used in structure determination, for all known *cis*-dichloro-tetrammine cobalt (and chromium) cations are violet, while their *trans* isomers are green. Likewise he obtained only one dinitro compound, although several different methods were used for its preparation. He could not resolve either of the complex cations.

Das Sarma and Bailar[4] observed that a purple solution of [Co trien Cl_2]Cl in methanol slowly changes to light gray-violet in color on standing,

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(1) Based in part upon a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois, 1957.

(2) Socony-Mobil Laboratories Fellow in Chemistry, University of Illinois, 1956–1957.

(3) F. Basolo, THIS JOURNAL, **70**, 2634 (1948).

(4) B. Das Sarma and John C. Bailar, Jr., *ibid.*, **77**, 5480 (1955).

just as a solution of the compound *cis*-[Co en$_2$ Cl$_2$]Cl does, although the latter finally becomes green, whereas the former does not. They estimated from spectral data that the compound in the gray-violet solution is about 40% *trans* and 60% *cis*. They also established beyond question that the blue-violet [Co trien Cl$_2$]Cl has the *cis* configuration by resolving the cation into optically active isomers. The foregoing resolution was repeated successfully during the course of this investigation.

None of these results point unequivocally to an instance in which all of the four nitrogen atoms of *trien* lie in a plane. This paper reports the isolation of both green and violet forms of the cation [Co trien Br$_2$]$^+$. The large size of the bromide ion probably helps in forcing the formation of the planar configuration, since adjacent (*cis*) bromide ions would introduce instability, particularly in the close-packed solid state.

Experimental

A. Preparation of Compounds. 1. *trans*-**[Co trien Br$_2$]Br·HCl and** *trans*-**[Co trien Br$_2$]Br.**—Method (a): To [Co trien Cl$_2$]Cl (31.2 g., 0.100 mole) dissolved in 75 ml. of water was added 41% hydrobromic acid (112 g., 0.60 mole). The solution was evaporated on a steam-bath until the surface was encrusted with green crystals (about one-fourth volume). The green crystals of [Co trien Br$_2$]Br·HCl were filtered, washed with alcohol and ether and dried overnight at 90°. Recrystallization was not possible, because upon dissolution of the green compound a violet-red solution forms which will not yield the green crystals unless hydrobromic acid is again added and the original evaporation procedure repeated.

Anal. Calcd. for [Co trien Br$_2$]Br·HCl: C, 14.97; H, 3.97; N, 11.64. Found: C, 14.73; H, 3.69; N, 11.99.

Titration of the above compound dissolved in water with standard sodium hydroxide proved the presence of one equivalent of acid per mole of compound. Heating the above compound at 110° for two days yielded a similar green-colored complex free of hydrogen chloride. The crystals had crumbled to a powder. The HCl coming off was detected by odor, by reaction with moist litmus and by reaction with ammonia. The fact that HCl is lost upon heating, rather than HBr, is proven by the analysis (below) of the product obtained and also confirms the formula given above.

Anal. Calcd. for [Co trien Br$_2$]Br: C, 16.20; H, 4.08; N, 12.59; Br, 53.90. Found: C, 16.52; H, 3.96; N, 12.74; Br, 53.6.

Method (b): Anhydrous cobalt(II) bromide (21.9 g., 0.100 mole) was dissolved in 40 ml. of water containing 6 ml. of concentrated (41%) hydrobromic acid. Anhydrous *trien* (14.6 g., 0.100 mole) was added slowly, and then 30% hydrogen peroxide (11.3 ml., 0.100 mole) was added dropwise with stirring. The temperature of the solution rose to about 60° and after all gas evolution ceased, several grams of ammonium bromide was added and the deep violet solution was cooled in an ice-bath. Dark violet crystals were deposited but, after filtration and washing with alcohol, the crystals appeared dark green, the violet material having been washed away. This product obtained by this more or less standard method for the preparation of complexes of this type gave an infrared spectrum identical with that of the green product obtained by method a.

Anal. Calcd. for [Co trien Br$_2$]Br: C, 16.20; H, 4.08; N, 12.59; Br, 53.90. Found: C, 16.52; H, 3.98; N, 12.54; Br, 53.7.

2. *cis*-**[Co trien Br$_2$]Br.**—[Co trien Cl$_2$]Cl (15.6 g., 0.0500 mole) was ground with silver carbonate (27.6 g., 0.100 mole) in a mortar, a small volume of methanol being added to give better contact. More methanol was added and the mixture was filtered to remove the AgCl and excess Ag$_2$CO$_3$. Upon evaporation of the deep red filtrate, a viscous, hygroscopic red oil was obtained, presumably [Co trien CO$_3$]$_2$CO$_3$. To this, an excess of concentrated hydrobromic acid was added cautiously until all of the carbon dioxide had been expelled. The solution was heated ten minutes on the steam-bath and then allowed to cool, whereupon red-violet crystals formed. These were filtered, washed with alcohol and ether and dried at 110° for 4 hr.

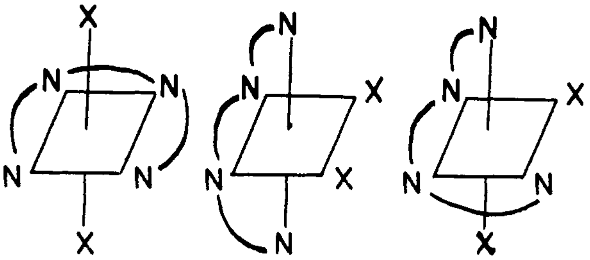

Fig. 1.—Possible stereoisomers of the complex cation [Co trien X$_2$]$^{+1}$; *trans*, *α-cis* and *β-cis* configurations, respectively.

Anal. Calcd. for [Co trien Br$_2$]Br: C, 16.20; H, 4.08; N, 12.59; Br, 53.90. Found: C, 16.37; H, 4.08; N, 12.12; Br, 53.5.

B. Spectral Measurements.—Infrared spectra were obtained using a model 21 Perkin–Elmer infrared spectrophotometer. The well-known KBr pellet method was employed for all spectral runs.

Results and Discussion

The preparation of green and violet solids, each with the composition required by the formula [Co trien Br$_2$]Br is, in this case, very good evidence that *cis* and *trans* isomers have been obtained. The red-violet *cis* compound dissolves readily in water, producing a red-violet solution. In dimethylformamide the complex is wine-red. The green *trans* compound dissolves slowly in water producing a dichroic solution which appears purple in tungsten light and greenish-blue in daylight. In dimethylformamide the complex is green. Aquation of both forms occurs in aqueous solution as evidenced by gradual color changes occurring over a period of several hours at room temperature. Color changes occur much more slowly in the dimethylformamide solutions, but even here there is indication that reaction with the solvent is occurring.

Although different visible and ultraviolet spectra may be obtained for the *cis* and *trans* compounds, both in water and in DMF, these spectra are not particularly valuable for differentiating between the *cis* and *trans* forms because of the solvation. The addition of three equivalents of AgNO$_3$ to a freshly prepared cold solution of the *trans* compound precipitated all of the bromide, indicating a rather rapid aquation but in the case of the *cis* complex only 5/6 of the bromine was immediately precipitated. It follows that the two compounds differ in their rates of aquation.

It was felt that it would be interesting to try to find a criterion, other than the well-established color criterion, for distinguishing the *cis* and *trans* dihalo cations. For example, it might be argued that the two differently colored compounds are just different crystalline modifications of the same substance. Toward this end, the infrared spectra of the three compounds, blue-violet-*cis*-[Co trien Cl$_2$]Cl, green-[Co trien Br$_2$]Br and red-violet-[Co trien Br$_2$]Br, were obtained using the KBr disc method. In the 2–15μ region there are ap-

TABLE I

WAVE LENGTH, IN MICRONS, OF STRONG BANDS WHICH DIFFER AMONG THE THREE COMPOUNDS STUDIED

cis- [Co trien Cl_2]Cl	Violet- [Co trien Br_2]Br	Green- [Co trien Br_2]Br
6.15	6.15	6.22
6.30	6.37	6.22
7.39	7.35	No band
7.64	7.64	7.66 (weak)
8.01	8.01	8.05
8.47	8.45	8.47 (weak)
9.34	9.32	9.49
10.06	10.06	9.96
No band	No band	10.11
No band	No band	10.32
12.00	12.01	12.18

proximately 25–30 "strong" or "moderately strong" bands for each compound. Most of these are identical (or very nearly so) for the three compounds but significant differences do occur for the violet and green compounds. This is illustrated by the spectral data reported in Table I, which give the wave lengths of the differentiating bands. A study of this table reveals that the spectrum of the violet dibromo compound is much more like the spectrum of the *cis*-dichloro compound than either of these is like the spectrum of the green dibromo compound.

It might be pointed out that our spectral results are in accord with the findings of Faust and Quagliano,[5] who reported that *cis* isomers should contain more absorption peaks than the *trans* since the latter have a center of symmetry while the former do not. Also, the conclusions of Merritt and Wiberley[6] concerning the distinction of *cis–trans* isomers using infrared spectra are borne out here. They reported that in the 6.2 to 6.4 μ region the *trans* isomer always has its maximum at wave lengths 0.04 to 0.08μ shorter than does the *cis* and that in the 12μ region the *cis* isomer shows a maximum 0.1–0.2μ shorter than does the *trans*. In our case the *trans* band is at 6.22μ while the two *cis* compounds have their bands at 6.30 and 6.37μ, respectively. Furthermore, the *trans* complex has a band at 12.18μ while the band of the *cis* complex comes at 12.00μ.

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Polymerization of Uranyl–Tiron Chelates[1,2]

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The interaction of uranyl ion with Tiron (pyrocatechol-3,5-disodium sulfonate) has been studied potentiometrically and spectrophotometrically in the *p*H range 2–11. Below *p*H 3.5 the solutions contain primarily 1:1 mononuclear chelate species although it appears that polymeric forms of the unhydrolyzed chelates may exist to some extent. Further reaction of the monomeric chelate with hydroxide ion results in hydrolysis and polymerization to a ternuclear species which is completely formed at *p*H 5.3. These reactions are independent of the amount of excess Tiron employed. Equilibrium constants have been calculated which describe the initial buffer region within approximately 0.03 *p*H unit over a wide range of metal chelate concentration. Further interaction of Tiron with the ternuclear complex in the *p*H range 5.3–8.5 produces a chelate compound containing $2^1/_3$ moles of Tiron per gram-ion of uranyl salt. The hydrolytic behavior of the UO_2^{++} ion has been investigated in the *p*H range 2.5–5.5. Evidence for the existence of a mononuclear hydrolyzed species, $UO_2(OH)^{+1}$, has been found and equilibrium constants have been calculated for the various hydrolytic and polymeric reactions involved. General equations for deducing the formulas of polynuclear metal chelate species have been derived.

Introduction

It is well known that the uranyl ion undergoes polymerization by the formation of bridges through oxo or hydroxo groups. On the basis of cryoscopic measurements, potentiometric titrations and spectrophotometric evidence, Sutton[3] proposed structures corresponding to $U_2O_5^{++}$ and $U_3O_8^{++}$ as well as a number of ions containing additional hydroxo ligands and has calculated equilibrium constants for the formation of the various species involved. Ahrland, *et al.*,[4] proposed higher polymers in which the metal ions are arranged in sheet-like structures. The interaction of uranyl ion with citrate, lactate, malate and tartrate ions has been investigated by potentiometric, spectrophotometric and polarographic techniques by Neuman, Havill and Feldman.[5–8] Evidence was found for the formation of binuclear and ternuclear chelates having combining ratios of ligand to metal which were equal to or less than unity, the stoichiometry depending upon *p*H conditions and on the particular ligand used. In no case was a ligand/metal ratio of greater than unity observed.

This research deals with the interaction in aqueous solution of the uranyl ion with Tiron (disodium pyrocatechol-3,5-disulfonate), a bidentate ligand which forms stable uranyl chelates over the whole *p*H range even at ratios of ligand to metal as low as 1:1 or less. The complexes were studied as a function of *p*H over a range of concentration

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(2) Abstracted from a dissertation submitted by Richard L. Gustafson to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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