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Synthesis, Geometrical Isomerism, and Absolute Configuration of Dinitrobis(trimethylenediamine)cobalt(III) Ion

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Received June 16, 1975 AIC50432C

Cis and trans geometrical isomers of dinitrobis(trimethylenediamine)cobalt(III) ion, $[Co(tn)_2(NO_2)_2]^+$, (trimethylenediamine = 1,3-diaminopropane) have been synthesized. The cis isomer was obtained by the action of sodium nitrite and acetic acid on carbonatobis(trimethylenediamine)cobalt(III) chloride, and the corresponding trans isomer was obtained by reaction between trimethylenediamine and sodium hexanitrocobaltate(III). Their geometrical configuration was determined by the resolution of the cis isomer into enantiomers, as well as by paper chromatography, electronic absorption, and ir spectra. It was established that the cis(NO_2) isomer described previously[1] is not the *cis*-dinitrobis(trimethylenediamine)cobalt(III) complex. In addition, on the basis of CD spectra of enantiomers, Δ absolute configuration[2] was tentatively assigned to the $(-)_{546}$ enantiomer with the dominant negative Cotton effect.

Introduction

In our previous papers[3] we have initiated an investigation of the effects of chelate ring size and of geometrical configuration on the position of absorption maxima in the electronic spectra of transition metal octahedral complexes. For the purpose of that study we have synthesized a number of coordination compounds of cobalt(III) containing five-membered and/or six-membered aminoacidato and/or diamine chelate rings in addition to the coordinated nitro groups.

Among others, we prepared two isomers (cis and trans) of dinitrobis(trimethylenediamine)cobalt(III) ion which were previously described by Kawaguchi and Kawaguchi.[1] Our trans isomer is indeed identical with the *trans*-$[Co(tn)_2(NO_2)_2]^+$ ion of Kawaguchi and Kawaguchi. However, our *cis*-$[Co(tn)_2(NO_2)_2]^+$ isomer appears to be different from the product which was assigned as the cis isomer by Kawaguchi and Kawaguchi. In order to resolve this ambiguity we describe in this paper the synthesis of both of the isomers, their geometrical configurations, and the absolute configurations of the enantiomers of *cis*-$[Co(tn)_2(NO_2)_2]^+$ ion.

Experimental Section

Paper chromatography was performed by the ascending method on Whatman No. 1 paper (3 × 30 cm) in a glass cylinder (50 × 22 cm) which was equilibrated for 1 hr prior to immersion of paper strips. The solvent path was ca. 20 cm. Chromatograms were detected with ammonium sulfide. Optical rotation was measured with a Perkin-Elmer 141 MC polarimeter. Electronic absorption spectra were recorded on a Perkin-Elmer 137/UV spectrophotometer. The aqueous solutions were 3×10^{-3}, 3×10^{-4}, and 3×10^{-5} *M* for the measurements in visible, near-uv, and uv regions, respectively. Infrared spectra were measured on a Perkin-Elmer Model 337 Infracord spectrophotometer using the potassium bromide disk technique. Circular dichroism was recorded on a Roussel-Jouan Dichrographe Model 182.

Preparation of *trans*-Dinitrobis(trimethylenediamine)cobalt(III) Nitrite, *trans*-$[Co(tn)_2(NO_2)_2]NO_2$.[4] To a solution of 8.08 g (0.02 mol) of $Na_3[Co(NO_2)_6]$ in 15 ml of water was added 3.36 ml (0.04 mol) of trimethylenediamine (99%, sp gr 0.89). The mixture was heated on a boiling water bath for 1/2 hr and then was filtered while hot. From the filtrate, which was allowed to cool at room temperature for about 2 hr, yellow-brown crystals precipitated off and were suction filtered, washed with ethanol and ether, and air-dried, yielding 2.4 g. The filtrate was concentrated under an airstream and the filtration procedure above was repeated to give a second yield of 3.45 g. The total yield was 5.85 g (85% based on cobalt). The material was recrystallized from water at 80°C, and its purity was checked by paper chromatography using two solvent systems. Anal. Calcd for $CoC_6N_7O_6H_{20}$: C, 20.87; N, 28.40; H, 5.84. Found: C, 20.66; N, 28.08; H, 5.72.

Preparation of *cis*-Dinitrobis(trimethylenediamine)cobalt(III) Chloride, *cis*-$[Co(tn)_2(NO_2)_2]Cl$. To a solution of 6.4 g (0.02 mol) of $[Co(tn)_2CO_3]Cl{\cdot}H_2O$[7] in 15 ml of water was added 2.76 g (0.04 mol) of $NaNO_2$ and 4.8 ml of 50% acetic acid. The mixture was heated at 55°C for 1/4 hr whereupon the solution changed color from red-violet to brown-red with the liberation of CO_2 and then cooled under the water stream. After standing of the mixture at ambient temperature for about 2 hr, yellow-brown crystals precipitated and were suction filtered, washed with ethanol and ether, and air-dried, yielding 3.1 g. The filtrate was concentrated to two-thirds of the initial volume in a vacuum evaporator at 50°C and was allowed to cool at room temperature overnight. In this way a second yield of 2 g was obtained. The total yield was 5.1 g (76% based on cobalt). The combined material was recrystalized from water at 50°C. The purity of the material was checked by paper chromatography using two solvent systems. Anal. Calcd for $CoC_6N_6O_4H_{20}Cl$: C, 21.53; N, 25.11; H, 6.02. Found: C, 21.47; N, 25.02; H, 6.38.

Preparation of Diastereoisomers of *cis*-Dinitrobis(trimethylenediamine)cobalt(III) $(+)_{589}$-*cis*(*NO_2*),*trans*(*N*)-Dinitrobis(glycinato)cobaltate(III), $[Co(tn)_2(NO_2)_2][Co(gly)_2(NO_2)_2]$. Diastereoisomer I. A suspension of 3.26 g (0.008 mol) of finely powdered $(+)_{589}$-*cis*(*NO_2*),*trans*(*N*)-$Ag[Co(gly)_2(NO_2)_2]$[8-10] in 15 ml of water was added to 2.68 g (0.008 mol) of *cis*-$[Co(tn)_2(NO_2)_2]Cl$ in 20 ml of water at ambient temperature. The mixture was agitated mechanically for about 3 hr. After removing AgCl (by suction filtration) the filtrate was maintained in a refrigerator overnight. In this way 0.66 g of the less soluble diastereoisomer (I) was obtained. The crystalline tobacco-colored diastereoisomer I was filtered off and the filtrate was concentrated to half of the initial volume in the vacuum evaporator at 50°C and again left overnight in a refrigerator. The second yield of 1.16 g was obtained. The total yield of diastereoisomer I was 1.82 g (38%). The material was recrystallized to constant optical rotation from water at 50°C; $[\alpha]^{20}_{546}$ +490° (*c* 0.1 in water). Anal. Calcd for $Co_2C_{10}N_{10}O_{12}H_{28}$: C, 20.07; N, 23.41; H, 4.72. Found: C, 20.23; N, 23.17; H, 4.82.

Diastereoisomer II. From the remaining filtrate (after isolation of diastereoisomer I), which was concentrated to two-thirds of the initial volume on the vacuum evaporator and allowed to cool in refrigerator for about 4 hr, precipitated 0.64 g of the material which was removed by suction filtration. It consisted of a mixture of diastereoisomers I and II. The remaining filtrate was evaporated to dryness under an airstream at ambient temperature yielding 1.92 g (40%) of the more soluble diastereoisomer (II), which was recrystallized to constant optical rotation from water at 50°C; $[\alpha]^{20}_{546}$ +540° (*c* 0.1 in water). Anal. Calcd for $Co_2C_{10}N_{10}O_{12}H_{28}$: C, 20.07; N, 23.41; H, 4.72. Found: C, 20.19; N, 23.22; H, 4.80.

Isolation of Enantiomers of *cis*-Dinitrobis(trimethylenediamine)cobalt(III) Chloride. A solution of 1 g of diastereoisomer (I or II) in 10 ml of water was placed on an anion-exchange column (Dowex 1X4, 200–400 mesh, Cl^- form, 1 × 8 cm) and eluted with water. The eluate was evaporated to dryness at ambient temperature and the remaining solid was recrystallized from water at 50°C. In this way the enantiomer with $[\alpha]^{20}_{546}$ −22° (*c* 0.1 in water) was recovered from diastereoisomer I, and the enantiomer with $[\alpha]^{20}_{546}$ +22° (*c* 0.1 in water) was recovered from diastereoisomer II. Anal. Calcd for $CoC_6N_6O_4H_{20}Cl$: C, 21.53; N, 25.11; H, 6.02. Found for $(+)_{546}$ enantiomer: C, 21.87; N, 25.08; H, 6.03. Found for $(-)_{546}$ enantiomer: C, 21.63; N, 25.00; H, 6.08.

Cis–Trans and Trans–Cis Isomerizations. Five hundred milligrams of the cis or trans isomer of dinitrobis(trimethylenediamine)cobalt(III)

Table I. Characterization of the Isomers of Dinitrobis(trimethylenediamine)cobalt(III) Ion

	Absorption max^a				R_f values	
Isomer	λ_1	log ϵ_1	λ_2	log ϵ_2	I^b	II^c
Cis isomer	451	2.30	330	3.67	0.82	0.36
Trans isomer	446	2.24	350	3.49	0.70	0.22

^{a} Wavelengths are given in nm. ^{b} Solvent system: acetone, 75 ml; water, 20 ml; nitric acid (sp gr 1.42), 5 ml. ^{c} Solvent system: 2-propanol, 75 ml; water, 20 ml; nitric acid (sp gr 1.42), 5 ml.

chloride was dissolved in 10 ml of water. The solutions of cis and trans isomers were heated at 80°C for the period of 7 hr and then chromatographed on paper strips using the solvent mixture containing acetone (Table I, solvent system I). In both cases chromatograms showed two bands with R_f values identical with the corresponding R_f values of pure cis and trans isomers which were chromatographed simultaneously. Equilibrium mixtures were subsequently applied on Dowex 50WX4 (200–400 mesh) columns (1 × 15 cm) in K^+ form, and eluted with 0.2 N KCl. Both equilibrium mixtures yielded two fractions which were completely separated and eluted in the order trans, cis. The configuration of the corresponding isomers of dinitrobis(trimethylenediamine)cobalt(III) was proved by electronic absorption and ir spectra.

Results and Discussion

Two geometrical isomers of dinitrobis(trimethylenediamine)cobalt(III) ion were synthesized in high yields (ca. 80%). One of them was obtained by the action of trimethylenediamine on sodium hexanitrocobaltate(III), and the other, by the action of sodium nitrite and acetic acid on carbonatobis(trimethylenediamine)cobalt(III) chloride. Geometrical configurations of the isomers were determined by optical resolution of the latter isomer[11] which was, therefore, assigned the cis configuration on the basis of symmetry considerations. This assignment is supported by the results of paper chromatography (Table I) showing R_f(cis) > R_f(trans) with two solvent systems—in conformity with the rule of Stefanović and Janjić.[12] The assignment of geometrical configurations is further supported by the electronic absorption spectra (Table I); i.e., the position of the "second band" (of $^1A_{1g} \rightarrow {}^1T_{2g}$ parentage), which is superimposed with a nitro-specific band, is found to be in accordance with the empirical rules set forth by Shimura[13] and further detailed by us.[3]

As already mentioned in the Introduction, the properties of our trans isomer are in agreement with those of the trans isomer described by Kawaguchi et al.[5] which was obtained from *trans*-dichlorobis(trimethylenediamine)cobalt(III) chloride and sodium nitrite. For example, the absorption maxima and molar extinction coefficients (for methanol solutions) are almost identical. However, in the case of the cis isomer, the electronic absorption spectrum of Kawaguchi's isomer is entirely different from the spectrum of our cis isomer and admittedly very similar to the spectrum of the trans isomer. This unlikely result was pointed out already by Kawaguchi and Kawaguchi.[1] Not being able to discriminate between cis and trans isomers on the basis of the electronic absorption spectra, Kawaguchi and Kawaguchi[1] resorted to the ir spectra of their isomers in order to determine geometrical configurations. Basing their analysis on the findings of Hughes and McWhinnie,[14] who have studied the effect of geometrical configurations on ir spectra of *cis*- and *trans*-dinitrobis(ethylenediamine)cobalt(III) complexes, Kawaguchi and Kawaguchi[1] assigned the cis configuration to the isomer showing the more complex ir spectrum.

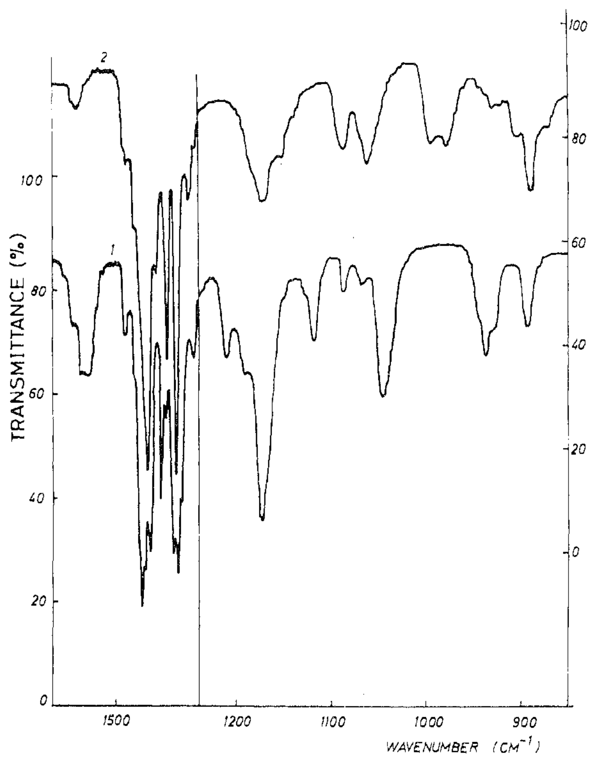

Figure 1. Ir spectra of the cis(NO_2) isomer of dinitrobis(trimethylenediamine)cobalt(III) chloride before (1) and after (2) deuteration.

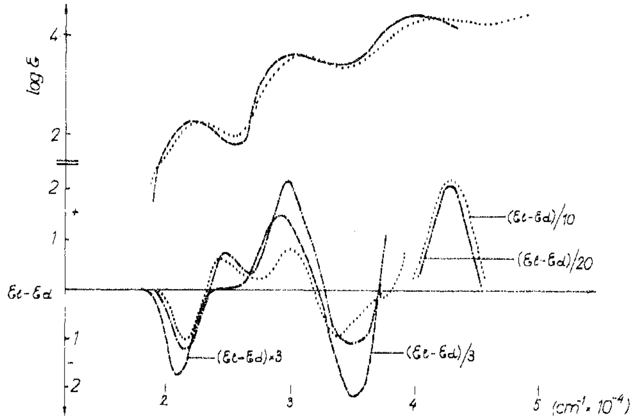

Figure 2. Circular dichroism spectra ($\epsilon_l - \epsilon_d$) (and absorption spectra (log ϵ)) of Δ-$(+)_{589}$-*cis*-dinitrobis(*l*-propylenediamine)cobalt(III) iodide (· · · · · ·),[19] Δ-$(-)_{589}$-*cis*-dinitrobis(ethylenediamine)cobalt(III) perchlorate (– · – · – · –),[20] and $(-)_{546}$-*cis*-dinitrobis(trimethylenediamine)cobalt(III) chloride (- - - -).

Along with cis(NO_2) and trans(NO_2) compounds, Kawaguchi and Kawaguchi[1] described also the cis isomer of nitronitritobis(trimethylenediamine)cobalt(III) complex. This isomer has virtually positions of absorption maxima and corresponding molar absorptivities (measured in MeOH solution) identical with those of our cis isomer. Furthermore, our cis isomer also exhibits a strong ir band at 1170 cm^{-1} which was, according to Kawaguchi and Kawaguchi,[1] indicative of the presence of the nitrito ligand in their compound. For this reason we have pursued study of linkage isomerism of our compounds. We have, therefore, measured ir spectra of our cis isomer before and after N-deuteration and we found that the band at 1170 cm^{-1} looses approximately half of its intensity on deuteration (Figure 1). This might imply that the band at 1170 cm^{-1} is not due solely to the ONO vibration and that it might contain superposed NH_2 vibration. Another possibility might be that the band at 1170 cm^{-1} is due only to the NH_2 vibration which shifts to 980 cm^{-1} upon deuteration. The remaining band of reduced intensity at 1170 cm^{-1} in the deuterated compound would then be due to the shift of a band originally located at 1600 cm^{-1}. The $\bar{\nu}$(NH)/$\bar{\nu}$(ND) ratio for both bands (i.e., 1600 and 1170 cm^{-1}) is within the limits of the values found by Baldwin[15] for diamine complexes of trivalent cobalt. It is unlikely that the remaining band at 1170 cm^{-1} is due to the incomplete deuteration because of the fact that the other NH bands after deuteration almost completely disappeared.

This result supports our assumption that our cis isomer is a dinitro complex. This is further substantiated by heating aqueous solutions of our cis and trans isomers at 80°C for 7 hr. In both cases, such a treatment (as revealed by paper chromatography) resulted in an equilibrium mixture consisting of about 80% trans and 20% cis isomer. The isomers were recovered from the equilibrium mixtures by ion-exchange column chromatography and subsequently identified by electron and ir spectra. This analysis confirmed that the cis isomer obtained by the isomerization (i.e., from the equilibrium mixture initially consisting of pure trans isomer) was identical with the cis isomer that remained after equilibration (i.e., from the equilibrium mixture initially consisting of pure cis isomer) and that both samples of cis isomer exhibited strong ir bands at 1170 cm^{-1}. Since the cis isomer in the former case resulted from the isomerization (at 80°C for 7 hr) of the trans isomer, which is undoubtedly a dinitro compound,[16] we conclude that our cis isomer is also a dinitro compound although its ir spectrum contains a strong band at 1170 cm^{-1}. It is well known that nitrito complexes undergo facile isomerization into the corresponding nitro complexes[17] and therefore it is very unlikely that the reverse process takes place in above example, namely, that the *trans*-dinitro isomer is converted into the *cis*-nitronitrito isomer by prolonged heating. Finally, the above experiments show that the band at 1170 cm^{-1} does not disappear from the ir spectrum of the cis isomer which was subject to prolonged heating unless the isomerization into the trans form takes place.

As evident from above, we have undoubtedly isolated both of the isomers of dinitrobis(trimethylenediamine)cobalt(III) ion, and we have unambiguously assigned their geometrical configurations (by the resolution of one of the isomers into enantiomers). This result is consistent with the electronic absorption spectra and R_f values of our isomers. Therefore, we think that Kawaguchi and Kawaguchi were mistaken when they claimed that they have isolated the cis isomer of $[Co(tn)_2(NO_2)_2]^+$ ion.

Finally, in this work we have determined the absolute configurations of the enantiomers of *cis*-dinitrobis(trimethylenediamine)cobalt(III) ion on the basis of their CD spectra. The assignment of absolute configurations was accomplished by correlation of the corresponding Cotton effect signs of our enantiomers with that of the (+)-*cis*-dinitrobis(*l*-propylenediamine)cobalt(III) ion of which a molecular and crystal structure determination was done by Barclay et al.[19] As shown in Figure 2, the enantiomer which is levorotatory at 546 nm and has a negative dominant Cotton effect, is assigned $\Delta(MC_2)$ absolute configuration.

Acknowledgment. Thanks are due to Dr. Gunner Borch (The Technical University of Denmark) for the CD spectra and S. R. Niketić for invaluable help in the preparation of the manuscript.

Registry No. *trans*-$[Co(tn)_2(NO_2)_2]NO_2$, 31188-10-0; *cis*-$[Co(tn)_2(NO_2)_2]Cl$, 56488-46-1; $[Co(tn)_2(NO_2)_2][Co(gly)_2(NO_2)_2]$, diastereoisomer I, 56498-53-4; diastereoisomer II, 56498-55-6; $[Co(tn)_2(NO_2)_2]Cl$, enantiomer I, 56498-56-7; enantiomer II, 56498-57-8; $(+)_{589}$-*cis*(NO_2),*trans*(*N*)-$Ag[Co(gly)_2(NO_2)_2]$, 56498-58-9.

References and Notes

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