Titration of $[Nb_6Cl_{12}]^{2+}$ Solutions with I_2 and Fe^{3+}.—An aqueous solution (approximately 10^{-3} *M*) of $[Nb_6Cl_{12}]^{2+}$ was prepared by dissolving $Nb_6Cl_{14}\cdot 7H_2O$ in water. Aliquots of this solution were titrated using an aqueous solution of iron(III) ammonium sulfate and a methanol solution of iodine.

Polarographic Study of $[Nb_6Cl_{12}]^{2+}$ Oxidation.—Approximately 10^{-3} *M* solutions of $Nb_6Cl_{14}\cdot 7H_2O$ with 1 *M* $KClO_4$ as supporting electrolyte were used, with a standard calomel electrode (s.c.e.) as the reference electrode. An oxidation wave was found with $E_{1/2} = +0.426$ v. on the hydrogen scale; the maximum accessible potential is about 0.60 v.

Results and Discussion

Solutions of $[Ta_6X_{12}]^{2+}$ in which the ionized halide had been exchanged for nitrate or perchlorate proved to be unsuitable for quantitative studies of the oxidation. The nitrate solutions were unstable with respect to oxidation of $[Ta_6X_{12}]^{2+}$ by nitrate ion, and a perchlorate solution, evaporated to near dryness on a hot plate, detonated. Therefore, sulfate-exchanged solutions were chosen for study. Nitrate solutions of $[Nb_6Cl_{12}]^{2+}$ were also found to be unstable, decomposing to liberate Cl^-.

Direct titrations of the $[Ta_6X_{12}]^{2+}$ solutions were unsatisfactory because the disulfate which precipitated during the titration formed an impervious coating on the platinum electrode, producing erratic results. Indirect titrations allowed removal of this product by filtration and so were free of interference. However, direct titrations of the $[Nb_6Cl_{12}]^{2+}$ ion in the presence of Cl^- ion were carried out with both aqueous Fe(III) and methanolic I_2.

The titration of aged solutions (*ca.* 1 week) of $[Ta_6Cl_{12}]^{2+}$ and $[Ta_6Br_{12}]^{2+}$ with iron(III) gave Fe/Ta_6X_{12} ratios in the range of 1.90 to 1.81. However, on passing these solutions through a Jones reductor or titrating freshly prepared solutions Fe/Ta_6X_{12} ratios in the range 1.97 to 2.03 were obtained. Direct titrations of $[Nb_6Cl_{12}]^{2+}$ with methanolic iodine or aqueous iron(III) sulfate gave Fe/Nb_6Cl_{12} or $^1/_2I_2/Nb_6Cl_{12}$ ratios of 1.97 to 2.06.

These results for the freshly prepared or reduced solutions confirm the two-electron oxidation of $[Ta_6X_{12}]^{2+}$ and $[Nb_6X_{12}]^{2+}$. Since the titer of $[Ta_6X_{12}]^{2+}$ solutions which had been stored in air returned to the value expected of the two-electron oxidation after prior reduction with zinc, it is probable that a slow oxidation by oxygen is effective *via* reaction 1. Indeed, solutions of $[Ta_6X_{12}]^{2+}$ in methanol acidified with

$$[Ta_6X_{12}]^{2+} + {}^1/_2O_2 + H_2O = [Ta_6X_{12}]^{4+} + 2OH^- \qquad (1)$$

HCl were observed to oxidize rapidly in air with change of color from green to red. Addition of $SnCl_2$ to these oxidized solutions returned the familiar green color.

Evidence that all of the halogen is retained in the oxidized species is provided by the observation that no silver halide is precipitated when Ag^+ is added to the solution above the freshly oxidized sulfate derivatives. The analytical data of the oxidized sulfate derivatives confirm the X/Ta ratio of 2. However, the low sulfate analyses ($SO_4/Ta_6X_{12} \cong 1.75$) are not understood in view of the titration data which indicate complete oxidation to $[Ta_6X_{12}](SO_4)_2$. Further work on the oxidized derivatives of both $[Ta_6X_{12}]^{2+}$ and $[Nb_6X_{12}]^{2+}$ has been undertaken and will be reported at a later date.

The Oxidation Potential of the $[Nb_6Cl_{12}]^{2+}$ Ion.—Since iodine was observed to oxidize the ion $[Nb_6Cl_{12}]^{2+}$, and the standard potential for the half-cell $I^- = {}^1/_2I_2 + e^-$ is −0.535 v., the potential for $[Nb_6Cl_{12}]^{2+} = [Nb_6Cl_{12}]^{4+} + 2e^-$ must be appreciably more positive than −0.535 v. Moreover, since 0.535 v. lies between the potential of the polarographic oxidation wave and the highest potential applied polarographically, it is virtually certain that the oxidation wave corresponds to the two-electron oxidation of $[Nb_6Cl_{12}]^{2+}$ with $E_{1/2} = 0.426$ v. *vs.* H_2.

When 0.5 *M* potassium oxalate plus sufficient HCl to dissolve it is used as the supporting electrolyte, the oxidation wave appears at $E_{1/2} = 0.341$ v. *vs.* H_2. This indicates that the oxidation product is complexed by oxalate to a greater degree than is $[Nb_6Cl_{12}]^{2+}$.

CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

Isomers of the Dichlorobis(*l*-cyclohexanediamine)cobalt(III) Ion

BY ROBERT G. ASPERGER AND CHUI FAN LIU

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trans-1,2-Cyclohexanediamine (to be abbreviated chxn) was synthesized and resolved by Jaeger and co-workers.[1] The complexes of this ligand were investigated by Jaeger and co-workers,[2] and the results constituted an important part of a series of publications which were the foundation of stereospecificity of coordination compounds. The present study is concerned with the preparation of the two possible geometric isomers of the dichlorobis(*l*-cyclohexanediamine)-cobalt(III) ion. The preparation of this ion was reported by Jaeger and Bijkerk.[2a] They oxidized a 2:1 molar mixture of *l*-cyclohexanediamine and cobalt(II) chloride with hydrogen peroxide. The compound was described as a green viscous mass which was dried in a desiccator and used directly in further reactions. No analyses or optical rotation figures were available. Because of the green color of this compound it was assumed to have the *trans* configuration. Attempts were made during the present investigation to obtain the compound through Jaeger and Bijkerk's method.

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(1) (a) F. M. Jaeger and J. A. van Dijk, *Proc. Acad. Sci. Amsterdam*, **39**, 384 (1936); (b) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 12 (1937).

(2) (a) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 246 (1937); (b) F. M. Jaeger, *ibid.*, **40**, 2 (1937); (c) F. M. Jaeger and J. ter Berg, *ibid.*, **40**, 490 (1937); (d) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 116 (1937); (e) F. M. Jaeger and L. Bijkerk, *ibid.*, **40**, 316 (1937).

The green oil obtained corresponded closely to that described by them. Elemental analysis values of this substance did not correspond to those calculated for the desired compound. Careful fractional crystallization from ethanol revealed the inhomogeneity of this dried oil and no definite compound could be isolated from it. Therefore, a different approach was used for the synthesis of the compound. The carbonatotetraamminecobalt(III) ion was used as starting material. It was treated with 2 moles of *l*-cyclohexanediamine until no more ammonia was evolved. Treatment of the reaction mixture with concentrated hydrochloric acid yielded the desired product. This product gave the correct elemental analyses, showed *trans–cis* isomerization in ethanol, and formed other identifiable derivatives.

Reaction between *cis*[Co(*l*-chxn)$_2$Cl$_2$]Cl and *l*-cyclohexanediamine yielded the tris(*l*-cyclohexanediamine)-cobalt(III) ion, which was shown by elemental analysis and rotatory dispersion to be identical with that reported by Jaeger and Bijkerk.

Experimental

Reagents.—*trans*-1,2-Cyclohexanediamine sulfate was obtained from Aldrich Chemical Co., Milwaukee, Wis. The other compounds used were commercial reagent grade.

Microanalysis.—Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Rotatory Dispersion.—Rotatory dispersion measurements were carried out on a Keston polarimeter attachment on a Beckman DU spectrophotometer. The attachment was manufactured by the Standard Polarimeter Company, Hackensack, N. J.

Preparation of *d* and *l*-Cyclohexanediamine Dihydrochloride.[1b]—To 100 g. (0.471 mole) of racemic *trans*-1,2-cyclohexanediamine sulfate in aqueous solution was added 80.7 g. (0.471 mole) of barium hydroxide with stirring and heating on a steam bath for 30 min. After cooling to 10° in an ice bath the mixture was filtered through Celite No. 535. Then 70.7 g. (0.942 mole) of *d*-tartaric acid was added cautiously in small batches with cooling and stirring followed by heating on a steam bath for 10 min. Cooling the solution to 0° in a salt–ice bath yielded the levorotatory component. To the hot filtrate was added 38.0 g. (0.506 mole) of *d*-tartaric acid along with sufficient water to dissolve all solid materials. Then ethanol was added to the oil point followed by slow cooling and scratching to help induce crystallization. The solid product was removed from the ice-cold solution and recrystallized from minimal hot water using ethanol to precipitate the solid containing the dextrorotatory diamine. The optically active amines were separated from the tartaric acid by reduced pressure distillation from excess aqueous sodium hydroxide. The free amine was converted to the dihydrochloride by adding concentrated hydrochloric acid and allowing it to crystallize slowly over sulfuric acid. The pure optically active dihydrochloride salt, as well-defined crystals, was then mechanically separated from the feather-like aggregates of the racemic salt, which was present in small amount. The optical rotations of samples containing about 0.2 g./ml. were determined. The specific and molar rotation were found to be $[\alpha]^{25}\mathrm{D}$ ±15.8°; $[\mathrm{M}]^{25}\mathrm{D}$ ±29.6°.

Preparation of *trans*-[Co(*l*-chxn)$_2$Cl$_2$]Cl·$^1/_2$H$_2$O.—To 12.3 g. (0.0655 mole) of *l*-chxn·2HCl was added 5.48 g. (0.13 mole) of LiOH·H$_2$O in 130 ml. of water. To this solution was added 8.45 g. (0.0327 mole) of [Co(NH$_3$)$_4$CO$_3$]NO$_3$·$^1/_2$H$_2$O[3] followed by heating on a steam bath for 4.5 hr. After cooling to 10° in an ice bath the solution was filtered and concentrated hydrochloric acid was added dropwise with vigorous stirring during 0.5 hr. until effervescence stopped. This solution was then evaporated to dryness on a steam bath and triturated with a total of 200 ml. of acetone or until the filtrate was nearly colorless. The residue contained a mixture of both the *cis* and the *trans* isomers. The green *trans* isomer was dissolved in ethanol. The ethanol was removed on a steam bath by blowing air across it until the volume was one-fifth the original, then adding acetone to the oil point. On slow cooling green crystals of the product were deposited.

Anal. Calcd. for [CoC$_{12}$H$_{28}$N$_4$Cl$_2$]Cl·$^1/_2$H$_2$O: C, 34.3; H, 7.43; N, 13.3; Cl, 25.3. Found: C, 34.4; H, 7.34; N, 13.8; Cl, 24.8.

Preparation of *cis*-[Co(*l*-chxn)$_2$Cl$_2$]Cl.—The procedure was the same as that described above for the *trans* compound except, after the acetone extraction, the residue was digested with portions of alcohol on a steam bath until only a purple precipitate remained. The green alcoholic solutions were heated for 3 hr. on a steam bath during which time some conversion of the soluble green *trans* complex to the insoluble lavender *cis* complex took place. The solution was filtered and the filtrate reheated on a steam bath for 3 hr. This cycle was repeated until no more *cis* compound was precipitated, in which case the solution was evaporated to dryness on a steam bath followed by extraction of the residue with absolute alcohol and heating of the filtrate on a steam bath to induce additional *trans–cis* conversion. The total yield of *cis* is 9.02 g. or 75% of the theoretical.

Anal. Calcd. for [CoC$_{12}$H$_{28}$N$_4$Cl$_2$]Cl: C, 36.7; H, 7.2; N, 14.3; Cl, 27.0. Found: C, 36.8; H, 7.1; N, 14.2; Cl, 27.0.

In determining the optical rotation the compound was found to mutarotate to a stable value of $[\alpha]^{25}\mathrm{D}$ +203°, which probably was the rotation of the aquo–chloro complex.

Preparation of Some Derivatives. [Co(*l*-chxn)$_2$L-alanine]-Cl$_2$·3H$_2$O.—*cis*-[Co(*l*-chxn)$_2$Cl$_2$]Cl (0.514 g., 0.00131 mole) was dissolved in 10 ml. of H$_2$O by heating on a steam bath for 5 min. Then a solution of 0.054 g. (0.00131 mole) of LiOH·H$_2$O and 0.117 g. (0.00131 mole) of L-alanine dissolved in 2 ml. of H$_2$O was added. The pH was adjusted to 7.5–8.0 using dilute aqueous LiOH or HCl; H$_2$O was added to make the total volume 20 ml., and the solution was heated on a steam bath for 8 hr. in a glass-stoppered 25-ml. erlenmeyer flask. The solution was evaporated to dryness under moving air at room temperature, then triturated with 100 ml. of hot acetone. The residue was dissolved in the minimal amount of hot absolute alcohol and filtered through a warmed Hirsch funnel; the remaining pink residue was rinsed with 3 drops of hot alcohol. The filtrate was cooled to room temperature and filtered. Then the filtrate was reheated on a steam bath and ether added to the oil point. Cooling of the covered solution overnight yielded crude product which was recrystallized from hot absolute alcohol using ether and long standing.

Anal. Calcd. for C$_{15}$H$_{40}$N$_5$CoCl$_2$: C, 36.1; H, 8.05; N, 13.98. Found: C, 36.6, 36.8; H, 7.86, 7.88; N, 13.98.

[Co(*l*-chxn)$_2$L-alanine](ClO$_4$)$_2$·4H$_2$O.—To a hot saturated solution of [Co(*l*-chxn)$_2$L-alanine]Cl$_2$·3H$_2$O was added excess 70% HClO$_4$ followed by addition of acetone to the oil point. On standing at room temperature for 24 hr. the product was obtained by filtration.

Anal. Calcd. for C$_{15}$H$_{42}$N$_5$O$_{14}$CoCl$_2$: C, 27.5; H, 6.61; N, 10.7. Found: C, 27.3; H, 5.6; N, 10.9.

[Co(*l*-chxn)$_2$gly](HCO$_3$)$_2$ (gly = glycine).—*cis*-[Co(*l*-chxn)$_2$-Cl$_2$]Cl (1 g., 0.00254 mole) was dissolved in 10 ml. of water with warming, then passed through 15 ml. of Amberlite IRA-410 in the hydroxy form. The eluted compound was caught in an erlenmeyer flask containing 0.191 g. (0.00254 mole) of glycine and 0.106 g. (0.00254 mole) of LiOH·H$_2$O. The resulting solution was heated on a steam bath for 3 hr., then the pH was adjusted to 6.5–7.0 and the solution was evaporated to dryness under an air stream at room temperature. The resulting brick-red residue was triturated with two 100-ml. portions of hot acetone, then dissolved in 20 ml. of water and saturated with carbon dioxide during 2 hr. After evaporation of the solution the residue was recrystallized several times from hot methanol by adding ether

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(3) H. F. Waltson, "Inorganic Preparations," Prentice-Hall Inc., Englewood Cliffs, N. J., 1948, p. 91.

to the oil point, cooling slowly, and allowing to stand for a long time.

Anal. Calcd. for $C_{16}H_{34}N_5O_8Co$: C, 39.8; H, 7.1; N, 14.5. Found: C, 40.8; H, 7.4; N, 14.4.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE, UNIVERSITY OF BELGRADE,
AND INSTITUTE OF CHEMISTRY, TECHNOLOGY AND
METALLURGY, BELGRADE, YUGOSLAVIA

Study of the Reactions of Hexanitrocobaltates(III) with Amino Acids. II. Determination of the Configuration of Dinitrobis(glycinato)cobaltate(III) Ions[1,2]

BY M. B. ĆELAP, D. J. RADANOVIĆ, AND T. J. JANJIĆ

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In a previously published paper[1] we have undertaken a study of the reactions of hexanitrocobaltate(III) with amino acids. The first reaction we studied was that of glycine with potassium and sodium hexanitrocobaltate(III). In such a way the synthesis of a new class of complex compounds, dinitrobis(glycinato)-cobaltates(III) ($M^I[Co(H_2NCH_2COO)_2(NO_2)_2]$), was given.

The determination of the configuration of these coordination compounds is the subject of the present paper.

Experimental

(A) **Preparation of Potassium Dinitrobis(glycinato)cobaltate(III).**—This compound was prepared by the action of potassium glycinate on potassium hexanitrocobaltate(III) according to our procedure previously described.[1]

(B) **Preparation of Diastereoisomers of *d*-Cinchonine Dinitrobis(glycinato)cobaltate(III).**—The orange crystalline mixture of diastereoisomers was obtained by the action of *d*-cinchonine chlorohydrate dihydrate on potassium dinitrobis(glycinato)cobaltate(III). By fractional crystallization from hot water the corresponding diastereoisomers were obtained; yield of *d*-cinchonine *d*-dinitrobis(glycinato)cobaltate(III), 84%; yield of *d*-cinchonine *l*-dinitrobis(glycinato)cobaltate(III), 60%.

Anal. Calcd. for $C_{19}H_{23}ON_2[Co(H_2NCH_2COO)_2(NO_2)_2]$: Co, 9.92. Found for *d*-cinchonine *d*-dinitrobis(glycinato)cobaltate(III): Co, 9.95. Found for *d*-cinchonine *l*-dinitrobis(glycinato)cobaltate(III): Co, 9.74.

Solubility (g. in 100 ml. of aqueous solution at 23°): *d*-cinchonine *d*-dinitrobis(glycinato)cobaltate(III), 0.30 g.; *d*-cinchonine *l*-dinitrobis(glycinato)cobaltate(III), 1.96 g.

Optical Rotation.—*d*-Cinchonine *d*-dinitrobis(glycinato)cobaltate(III), $[\alpha]^{20}\text{D}$ +350° (0.1 g. in 100 ml. of aqueous solution); $[M]^{20}\text{D}$ +2081°; *d*-cinchonine *l*-dinitrobis(glycinato)cobaltate(III), $[\alpha]^{20}\text{D}$ −150° (0.1 g. in 100 ml. of aqueous solution); $[M]^{20}\text{D}$ −892°.

The measurements were carried out on a Franz Schmidt & Haensch, Berlin, Model S polarimeter.

(C) **Preparation of *d*- and *l*-Silver Dinitrobis(glycinato)-cobaltate(III).**—The optically active crystalline red silver salts were prepared by the double decomposition of the corresponding diastereoisomer with silver nitrate; yield ~80%.

Anal. Calcd. for $Ag[Co(H_2NCH_2COO)_2(NO_2)_2]$: Ag, 26.51. Found for the *d* form: Ag, 26.36. Found for the *l* form: Ag, 26.37.

Optical Rotation.—$[\alpha]^{20}\text{D}$ ±370° (0.1 g. in 100 ml. of aqueous solution); $[M]^{20}\text{D}$ ±1505°.

Solubility (g. in 100 ml. of aqueous solution at 23°): 0.19.

(D) **Reaction of *d,l*-Potassium Dinitrobis(glycinato)cobaltate(III) with Potassium Glycinate.**—To a hot solution of 3.38 g. (10 mmoles) of *d,l*-potassium dinitrobis(glycinato)cobaltate(III) in 20 ml. of water a solution of 1.5 g. (20 mmoles) of glycine and 1.0 g. (18 mmoles) of potassium hydroxide in 10 ml. of water was added. The mixture obtained was heated for 4 hr. on a boiling water bath with constant stirring. From the cold solution the crystalline β (red) isomer of tris(glycinato)cobalt(III) was slowly precipitated in the course of several days in about 20% yield.

This compound was identical with that of Winkler and Ley[3] prepared by dissolving cobaltic hydroxide in glycine solution. The identity was proved by infrared spectra and R_f values obtained.

(E) **Reaction of the β (Red) Isomer of Tris(glycinato)cobalt(III) with Potassium Nitrite.**—To a suspension of 6.0 g. (20 mmoles) of β (red) tris(glycinato)cobalt(III) in 30 ml. of water a solution of 13.6 g. (160 mmoles) of potassium nitrite in 15 ml. of water was added. The mixture was heated on a water bath for 5 hr. with constant stirring. The brown solution obtained was filtered from unreacted tris(glycinato)cobalt(III). After cooling 3 g. of brown crystalline potassium dinitrobis(glycinato)-cobaltate(III) was obtained. By evaporating the filtrate an additional amount of the substance was obtained. The total yield amounted to 4.3 g. (63.6%).

The compound isolated was identical with the one prepared in our previous work[1] by the action of potassium glycinate on potassium hexanitrocobaltate(III). This was proved by ultraviolet, visible, and infrared spectra and R_f values obtained by means of several solvent mixtures.

Discussion

As can be seen from the introduction, dinitrobis-(glycinato)cobaltates(III) could exist in five geometrical isomers. Two of them would contain the nitro groups in *trans* positions, while in the other three isomers the nitro groups would be in *cis* positions. The *cis* isomers could be resolved into optical antipodes, and the corresponding *trans* isomers would be symmetrical and optically inactive.

In order to establish the position of two nitro groups in the complex salts obtained, we have attempted to resolve them into optical antipodes. By fractional crystallization of the *d*-cinchonine salt we obtained two diastereoisomeric forms from which we prepared the optical antipodes in the form of the corresponding silver salts by double decomposition with silver nitrate. The molecular rotation for sodium light amounted ±1505°. Thus we proved that dinitrobis(glycinato)-cobaltates(III) contain two nitro groups in the *cis* positions.

This conclusion agrees with the fact that by the

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(1) First communication: T. J. Janjić, M. B. Ćelap, and P. Spevak, *Glasnik Hem. Drustva, Beograd*, **27**, 111 (1962).

(2) Presented at the Symposium on the Structure and Properties of Coordination Compounds, Bratislava (Czechoslovakia), Sept. 1964, and at the 11th National Meeting of the Serbian Chemical Society, Belgrade, Jan. 1965.

(3) H. Ley and H. Winkler, *Ber.*, **42**, 3900 (1909).