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

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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), $[\alpha]^{20}_D$ +350° (0.1 g. in 100 ml. of aqueous solution); $[M]^{20}_D$ +2081°; *d*-cinchonine *l*-dinitrobis(glycinato)cobaltate(III), $[\alpha]^{20}_D$ −150° (0.1 g. in 100 ml. of aqueous solution); $[M]^{20}_D$ −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.—$[\alpha]^{20}_D$ ±370° (0.1 g. in 100 ml. of aqueous solution); $[M]^{20}_D$ ±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).

action of potassium glycinate on *d,l*-potassium dinitrobis(glycinato)cobaltate(III) the β (red) isomer of tris(glycinato)cobalt(III) is obtained, which is possible only if the nitro groups are in the *cis* positions.

Besides, this reaction affords the possibility of determining the orientation of the glycine ligands in dinitrobis(glycinato)cobaltates(III) because only one of the three possible *cis* isomers of these salts could yield β (red) tris(glycinato)cobalt(III), *i.e.*, the 1,2,3-isomer of this compound,[4] which means that dinitrobis(glycinato)cobaltates(III) have the *cis,cis,cis* configuration.[5]

This conclusion was confirmed by opening of one of three rings of the 1,2,3- isomer of tris(glycinato)cobalt(III) by the action of potassium nitrite. This reaction gave a substance which was identical with potassium dinitrobis(glycinato)cobaltate(III) obtained through our reaction. The fact that the substitution of one of the glycine ligands with two nitro groups in the *cis* positions can yield only the above-mentioned isomer of dinitrobis(glycinato)cobaltate(III) can be taken as an additional proof that the configuration of our salts is *cis,cis,cis*.

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(4) The 1,2,3- configuration of the β (red) isomer of tris(glycinato)cobalt(III) was established by the following authors: F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955); K. Nakamoto, J. Fujita, M. Kobayashi, and R. Tsuchida, *J. Chem. Phys.*, **27**, 439 (1957); A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 5018 (1958).

(5) It was established the α (violet) 1,2,6- isomer of tris(glycinato)cobalt(III) cannot be transformed into the β (red) 1,2,3- isomer under the same experimental conditions, which proves that the β isomer is the primary product of the reaction described.

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A Study of β-Ferric Oxide Monohydrate Containing Excess Water

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Several workers[1-4] have shown that β-ferric oxide monohydrate requires an impurity in some of the interstitial positions. When the compound is prepared from ferric chloride or ferric fluoride, the impurity is chloride or fluoride ion. Bernal, *et al.*,[2] were unable to prepare the compound from solutions containing ferric ions and bromide ions because the bromide ion is too large for the interstitial positions.[4]

The Fe:Cl atomic ratios have often been reported in the range of about 5–45, while scant attention has been given to the water in excess of the structural water.[2,3] We have achieved a range of excess water from 0.8 to 0.01 mole of excess water per mole of $Fe_2O_3 \cdot H_2O$, along with Fe:Cl atomic ratios of about 7500. This has been done by varying the concentration of dilute aqueous ammonia used to wash the monohydrate from the ferric chloride hydrolysis. The influence of the amount of excess water on X-ray powder patterns, thermogravimetric curves, and magnetic susceptibility has been studied.

Experimental

The procedure of Weiser, *et al.*,[5] was used in the preparations of β-$Fe_2O_3 \cdot H_2O$. A constant rate of temperature rise was maintained for 8 hr. while the temperature rose to 80°. This temperature was maintained for 2 hr. The mixture was cooled rapidly to room temperature and allowed to stand 24 hr. Each product was washed in three stages, as shown in Table I. Throughout all stages, a centrifuge was necessary for separation. The products were dried at 110° in an electric oven for 24 hr. The dried products were stored in sealed vials placed inside a desiccator. Each was analyzed for iron and chlorine by standard procedures.

TABLE I

PREPARATION DATA AND RESULTS ON SEVERAL SYNTHESES OF β-FERRIC OXIDE MONOHYDRATE

Sample no.	Washing			% Fe	Excess H_2O per mole of $Fe_2O_3 \cdot H_2O$
	H_2O wash	Aq. NH_3[a] wash	Final H_2O wash		
1	3 × 144 ml.	None	None	58.44	0.8
2	2 × 144 ml.	1 × 572 ml. (0.01 *M*)	1 × 572 ml.	60.36	0.4
3	3 × 430 ml.	11 × 1720 ml. (0.01 *M*)	1 × 1720 ml.	61.19	0.27
4	2 × 144 ml.	11 × 572 ml. (0.01 *M*)	1 × 572 ml.	61.48	0.21
5	3 × 144 ml.	11 × 572 ml. (0.1 *M*)	2 × 572 ml.	62.53	0.05
6	3 × 144 ml.	11 × 572 ml. (0.2 *M*)	2 × 572 ml.	62.67	0.03
7	3 × 144 ml.	11 × 572 ml. (0.1 *M*)	2 × 572 ml.	62.77	0.01

[a] Molarity of aqueous ammonia in parentheses.

X-Ray powder diffractometer traces were run on several of the preparations. Zirconium-filtered Mo radiation of 0.70926 Å. wave length was used. Mackay[3] has reported 21 lines of the powder pattern for β-ferric oxide monohydrate, the strongest of which have the following *d* values in Å. and relative intensities in parentheses: 7.40 (10), 5.25 (4), 3.311 (10), 2.616 (4), 2.543 (8), 2.285 (4), 1.944 (6), 1.746 (4), 1.635 (10), 1.515 (4), 1.438 (8), 1.374 (4).

Thermogravimetric curves for samples 1, 3, and 7 were obtained with an apparatus similar to that of Loriers.[6] A 2 ml./sec. stream of dry helium was used in the apparatus. The rate of temperature rise was 1.4°/min. The quartz helix balance had a force constant of 1 mg./mm., and the extension of the helix was read to 0.005 mm. Sample weights of about 30 mg. were used.

Magnetic susceptibilities were measured by the Faraday method using a quartz helix from which the sample was suspended.[7] The apparatus was calibrated with a gaussmeter and with massive Pt and Re standards. Helium, at 1 atm., was used in the apparatus.

The gram susceptibility at zero reciprocal field (χ_∞) was obtained from a plot of apparent susceptibility *vs.* reciprocal field

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(6) J. Loriers, *Rev. Met.*, **49**, 807 (1952).

(7) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 14.