

the *cis* \rightarrow *trans* photoisomerization of Pt(gly)₂, in order to explain the lack of the inverse photochemical process, it might be thought that one of the steps of the inverse isomerization is improbable for energetic rea-

sons. Such critical steps may be either the passage from the *trans* triplet excited state to the tetrahedral intermediate state or the passage from the tetrahedral state to the *cis* triplet excited state.

CONTRIBUTION FROM THE ISTITUTO CHIMICO DELL'UNIVERSITÀ, CENTRO NAZIONALE DI CHIMICA DEI COMPOSTI DI COORDINAZIONE ED ELEMENTO-ORGANICI DEL C.N.R., SEZIONE IV, FERRARA, ITALY, AND THE ISTITUTO CHIMICO "G. CIAMICIAN" DELL'UNIVERSITÀ, CENTRO NAZIONALE DI CHIMICA DELLE RADIAZIONI E DEI RADIOELEMENTI DEL C.N.R., SEZIONE III, BOLOGNA, ITALY

Photochemistry of Coordination Compounds. XIV. Electron Transfer and d-d Excitation in Cobalt(III)-Amino Acid Complexes¹

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The photochemical behavior of the following complexes has been studied: α -tris(glycinato)cobalt(III), β -tris(glycinato)cobalt(III), α -tris(alaninato)cobalt(III), α -tris(valinato)cobalt(III), α -tris(glutamato)cobalt(III)³⁻, and β -tris(glutamato)cobalt(III)³⁻. The solutions of these complexes are very photosensitive (quantum yields 0.16–0.33) to light of 254 and 313 m μ wave length, which corresponds to electron-transfer bands, whereas they are only slightly photosensitive to excitation in d-d bands. Irradiation at 254 m μ leads to the decomposition of the complexes, with production of Co(H₂O)₆²⁺ ions, amino acids, and amino acid oxidation products. The photochemical behavior of the complexes does not substantially depend on the type of coordinated amino acid or on the geometrical configuration of the complexes. The quantum yield at 254 m μ increases slightly with temperature and is practically independent of the H⁺ concentration of the solution. The nature of the excited states is correlated with their chemical behavior. A mechanism is proposed which interprets the photochemical decomposition as results from excitation at an electron-transfer band.

Introduction

Our researches on the photochemistry of coordination compounds aim at correlating photochemical reactivity with theoretical predictions based on the electronic absorption spectra.¹ In this paper we examine the photochemical behavior of the following complexes: α -tris(glycinato)cobalt(III), β -tris(glycinato)cobalt(III), α -tris(alaninato)cobalt(III), α -tris(valinato)cobalt(III), α -tris(glutamato)cobalt(III)³⁻, and β -tris(glutamato)cobalt(III)³⁻. In these complexes the electron-transfer bands are distinct from the d-d bands; consequently excitation with suitable radiation makes it possible to study the chemical behavior of the different excited states.

Experimental

Materials.— α - and β -tris(glycinato)cobalt(III) and α -tris(alaninato)cobalt(III) were prepared according to Ley, *et al.*² α -Tris(valinato)cobalt(III) was prepared according to Carassiti and Claudi.³ α - and β -tris(glutamato)cobalt(III)³⁻ ions were obtained in solution starting from the corresponding Pb salts,⁴ through a double decomposition reaction with K₂SO₄. The α forms (violet) are fairly soluble in water, whereas the β forms (red) are slightly soluble; they correspond, respectively, to the *trans* (1,2,6) and the *cis* (1,2,3) isomers which are possible for M(AB)₃ octahedral complexes. On the basis of a ligand field interpretation of their electronic absorption spectra the assignment of the *trans* configuration to the α form and of the *cis* configuration to the β form has been made.⁵

Apparatus.—The general irradiation equipment is the one previously described with regard to the 254, 313, and 365 m μ radiations.¹ The set used to isolate the 546 m μ radiation was the following. The source was a Hanau Q 400 high-pressure mercury vapor lamp; the filter⁶ consisted of 2 cm. of 10% w./v. CuSO₄·5H₂O in 0.01 N H₂SO₄, 1 cm. of a solution containing 50 ml. of CuCl₂·2H₂O (1000 g. in 1 l. of water) and 50 ml. of 3 M CaCl₂, and 2 cm. of a solution containing 15 g. of K₂Cr₂O₇ in 1 l. of water. Extraneous transmission (\sim 7%) was between 525 and 557 m μ . The general arrangement is that previously described for the 365 m μ radiation.¹ The photochemical reaction was carried out in a closed spectrophotometer cell (thickness 1 cm., capacity 3 ml.). This cell was thermostated to 0.2°. The slit limiting the light beam, having almost the same width as that of the window of the reaction cell, was placed just in front of the cell. The light intensity at 254, 313, and 365 m μ was measured by means of a uranyl oxalate actinometer,⁷ and at 546 m μ by means of a ferric oxalate actinometer.⁶ The number of einsteins/minute striking the reaction cell was of the order of 1×10^{-6} at all wave lengths used. Absorption spectra were measured by an Optica CF4-NI spectrophotometer, which makes possible both manual measurements and automatic recording.

Procedures.—Preliminary experiments verified the lack of induction periods and post-photochemical effects. The kinetics of the photoreactions was followed spectrophotometrically at the maximum of the visible absorption band (520–540 m μ). The reactions were carried out with $\sim 5 \times 10^{-3}$ M solutions. The light intensity measurements were performed before and after each experiment.

Results

Thermal Stability.—It has already been noted that the Co(III)-amino acid complexes are stable with re-

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TABLE I
 QUANTUM YIELDS FOR THE PHOTOCHEMICAL DECOMPOSITION OF COBALT(III)-AMINO ACID COMPLEXES IN ACID SOLUTIONS

Cobalt(III) compd. ^a	H ₂ SO ₄ , N	Temp., °C.	λ of excitation, mμ			
			254	313	365	546
α-Tris(glycinato)	10 ⁻³	25	0.20
α-Tris(glycinato)	10 ⁻²	25	0.23
α-Tris(glycinato)	10 ⁻¹	25	0.25	0.25	~1 × 10 ⁻³	≪10 ^{-3b}
α-Tris(glycinato)	4	25	0.24	0.27	~1 × 10 ⁻³	...
α-Tris(glycinato)	10 ⁻¹	50	0.31
α-Tris(glycinato)	10 ⁻¹	75	0.35
β-Tris(glycinato)	10 ⁻¹	25	0.17	0.19	~1 × 10 ⁻³	≪10 ^{-3b}
α-Tris(alaninato)	10 ⁻¹	25	0.31	0.21	~1 × 10 ⁻³	≪10 ^{-3b}
α-Tris(valinato)	10 ⁻¹	25	0.33	0.16	1 × 10 ⁻²	≪10 ^{-3b}
α-Tris(valinato)	10 ⁻¹	50	0.44
α-Tris(valinato)	10 ⁻¹	75	0.47	≪10 ^{-3b}
α-Tris(glutamato) ³⁻	10 ⁻¹	25	0.33	0.28	≪10 ^{-3b}	≪10 ^{-3b}
β-Tris(glutamato) ³⁻	10 ⁻¹	25	0.31	0.21	~1 × 10 ⁻³	≪10 ^{-3b}

^a The solutions of the complexes are ~5 × 10⁻³ M. ^b This entry means that, if a photodecomposition occurs, it has a quantum yield lower than the sensitivity of our experimental method.

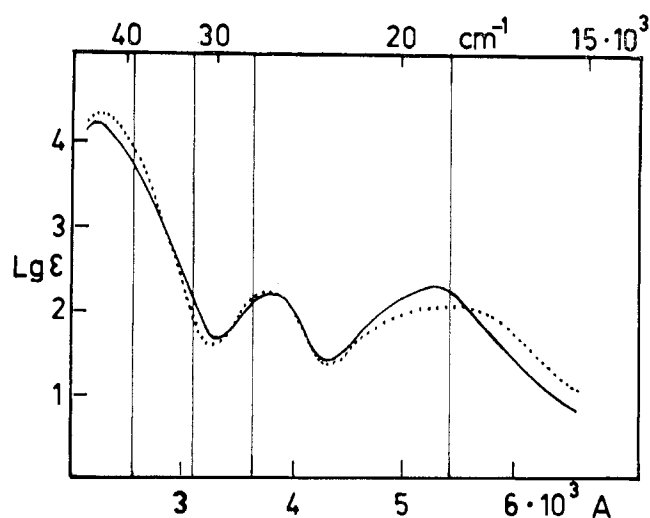


Figure 1.—Electronic absorption spectra of tris(glycinato)-cobalt(III) complexes: dotted line, *trans* isomer; full line, *cis* isomer. Vertical lines correspond to the nearly monochromatic exciting radiations (extraneous transmissions are reported in the Experimental section).

spect to acid hydrolysis, so that they can be dissolved in concentrated acids without undergoing any alteration.^{5b} We have verified that solutions of these complexes remain unaltered, at 25°, for a time longer than that employed for the photochemical reactions. For experiments carried out at higher temperatures corrections were made for simultaneous thermal reactions.

Photochemical Behavior.—The electronic absorption spectra of the complexes studied are all very similar^{5b}; we report here, as an example, only the spectra of the α and β forms of the tris(glycinato)cobalt(III) complex (Figure 1). In this figure the vertical lines correspond to the λ values used for the excitation. On irradiation of aqueous solutions of these complexes with light of 254 and 313 mμ complete decomposition occurs, as shown by the disappearance of their characteristic color. The final spectrum coincides with that of the Co(H₂O)₆²⁺ ion.⁸ For the photoreactions at 254 mμ, in which the absorption of light is essentially

(8) If the solution is not sufficiently acid, the bis(glycinato)cobalt(II) complex can be obtained instead of the Co(H₂O)₆²⁺ ion; see L. E. Maley and D. P. Mellor, *J. Australian Sci. Res.*, **2**, 579 (1949).

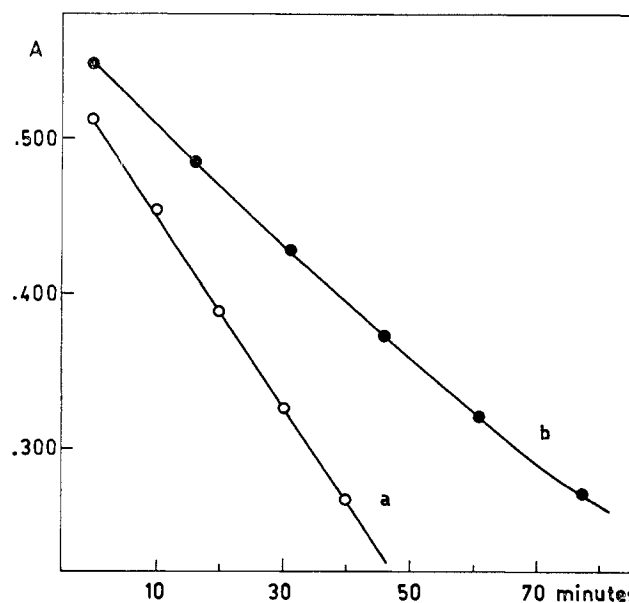


Figure 2.—Plots of absorbance vs. time for the photochemical reaction at 25° of α-tris(glycinato)cobalt(III): a, excitation with 254 mμ radiation; b, excitation with 313 mμ radiation.

complete during the time of the experiment, the absorbance of the solution decreases linearly with time (curve a in Figure 2). The quantum yield can be calculated from the slope of the absorbance vs. time plots. With light of 313 mμ, our experimental conditions were such that the absorption of light decreased as the reaction proceeded, so that the decrease of the absorbance with time was not linear (curve b in Figure 2). Therefore the quantum yields were calculated by means of a numerical integration. The values of the quantum yields for the excitation at 254 and 313 mμ are reported in Table I; the experimental error in these values is no more than ±10%. Irradiations at 365 mμ also lead to decomposition of the complexes; in this case, however, the quantum yield is much lower and only an approximate evaluation of its magnitude is possible (Table I). Irradiations at 546 mμ lead to no detectable variation in the absorption spectrum of the solutions. In order to evaluate the influence of the reaction conditions on the quantum yield some experiments were made in various acid solutions and at

served that upon irradiating the Co(III) acidopentammine complexes at wave lengths where electron-transfer and d-d bands partially overlap, both photoreactions occur. Since with irradiation of the Co(III)-amino acid complexes in pure d-d bands (λ 546 $m\mu$) no appreciable reaction occurs, it is thought that the d-d excitation does not contribute to quantum yields at every wave length. Therefore the photodecomposition following the irradiations at 313 and 365 $m\mu$ can be attributed to the partial electron-transfer character of the absorption. Thus the overlap between the electron-

transfer and d-d bands is probably more accentuated in α -tris(valinato)cobalt(III),^{5b} in accordance with the quantum yields obtained for this complex.

Finally, according to the proposed mechanism, which regards the photodecomposition as a direct consequence of the radial redistribution of the electronic charge caused by the excitation, the quantum yield is wholly independent of the H^+ concentration and is also almost independent of the temperature, the type of coordinated amino acid, and the steric arrangement of the complex.

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Complexes of Trivalent Lanthanide and Actinide Ions. I. Outer-Sphere Ion Pairs

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Stability constants have been measured for the mononitrate complexes of Ce(III), Pm(III), Eu(III), Tb(III), Tm(III), and Am(III) by a solvent-extraction technique. These stability constants as well as the enthalpy and entropy data for MNO_3^{2-} indicate that these are outer-sphere ion pairs. It is proposed that these data can be interpreted in terms of a general model of lanthanide complexing in which the effect on the hydration sphere about the cation is the dominant effect.

Introduction

The sequence of stabilities of lanthanide complexes as a function of atomic number has been of interest for a number of years. Attempts to correlate this sequence with various properties of the lanthanide ions have been less than successful. A major reason for this difficulty has been the lack of sufficiently complete thermodynamic data. Although values of the enthalpy and entropy of complexation have been published in the past few years,¹⁻⁶ considerable disagreement exists in interpretation of the observed data. This is to be attributed partially to the relative complexity of the chelate systems studied. We have begun examination of simpler systems to minimize this difficulty. In previous publications^{7,8} the thermodynamic values for the formation of MCl^{2+} and $MS-CN^{2+}$ have been reported. In this paper the results of a study of the nitrate complexes are reported. In the next paper, we report the thermodynamic parameters for the formation of propionate and isobutyrate systems.⁹

Peppard and his co-workers¹⁰ have measured the first

stability constants for several trivalent lanthanide nitrates and obtained values only half as large as those reported by Russian chemists.¹¹ Recently Bansal, Patil, and Sharma¹² have reported first stability constants for Eu(III) and Am(III) nitrates which were smaller than Peppard's. Second step constants for these same ions were also given in this last paper. However, thus far no data have been reported on the enthalpy and entropy changes in formation of these complexes.

Experimental

Materials.—Ce¹⁴⁴, Pm¹⁴⁷, Eu¹⁵²⁻¹⁵⁴, and Am²⁴¹ were obtained from the Oak Ridge National Laboratory as carrier-free isotopes. Tb¹⁶⁰ and Tm¹⁷⁰ were obtained by the neutron irradiation of Tb₂O₃ and Tm₂O₃ at the University of Florida reactor. All isotopes were dissolved in 1 *M* HClO₄.

The extractant, dinonylnaphthalenesulfonic acid (referred to as HD), was obtained from the R. T. Vanderbilt Co., Inc., as a 38.2% solution in *n*-heptane. It was analyzed according to the procedure described previously⁷ and found to be approximately 0.8 *M*.

All acids were reagent grade, diluted to volume, and standardized to a phenolphthalein end point with standard NaOH. The aqueous and organic solutions were pre-equilibrated with each other prior to use.

Procedure.—The procedure followed that of the earlier report.⁷ Whenever possible, the aqueous phase was prepared to contain at least 7000 counts/min. per ml. for each radioisotope. The concentration of HD was varied from approximately 10^{-2} *M* to 6×10^{-5} *M*. The total ionic strength of the aqueous phase

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