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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. XIII.
Photochemical Behavior and Electronic Spectra of Some d^8 Glycinato Complexes[1]

BY VINCENZO BALZANI, VITTORIO CARASSITI, LUCA MOGGI, AND FRANCO SCANDOLA

Received December 8, 1964

The photochemical behavior of *trans*-Ni(gly)$_2$·2H$_2$O, *trans*-Pd(gly)$_2$, and *cis*- and *trans*-Pt(gly)$_2$ has been studied. *trans*-Ni(gly)$_2$·2H$_2$O, *trans*-Pd(gly)$_2$, and *trans*-Pt(gly)$_2$ are not appreciably photosensitive to excitation in d–d bands. *trans*-Pd(gly)$_2$ and *trans*-Pt(gly)$_2$ are decomposed as a consequence of the excitation in electron-transfer bands. *cis*-Pt(gly)$_2$ when excited in d–d bands changes into the *trans* isomer. The quantum yields of this photoreaction are 0.12 ± 0.01 at 254 mμ and 0.13 ± 0.01 at 313 mμ. For this photoisomerization an intramolecular mechanism is suggested involving the formation of a tetrahedral intermediate. The ultraviolet spectra of *cis*- and *trans*-Pt(gly)$_2$ are discussed on the basis of the photochemical data.

Introduction

The present work deals with the photochemical behavior of the tetracoordinated square-planar glycinato complexes of some d^8 metal ions: Ni(II), Pd(II), Pt(II).

The aims pursued by our research group through systematic studies of the photochemistry of the coordination compounds[2] are as follows: (1) to arrive at general correlation between the structure and composition of the complex and its photochemical behavior; (2) to study the relationship between the wave length of the exciting radiation and the type of the consequent chemical reaction, in order to contribute to the interpretation of the electronic spectrum of the complex; and (3) to study the kinetics of the possible secondary thermal processes which follow the photoexcitation.

Experimental

Materials.—*trans*-Ni(gly)$_2$·2H$_2$O[3] was prepared according to Stosick.[4] X-Ray analysis indicates that two glycinato ions coordinate to the metal by forming a *trans* square-planar structure.[4] The *cis* isomer is not known.

trans-Pd(gly)$_2$ was prepared according to Pinkard, *et al.*[5] Although the *cis* isomer of this complex has also been reported,[5] Saraceno, *et al.*,[6] observed, on the basis of the infrared spectra, that the different fractions crystallizing from the solution are all similar and can be identified with the *trans* isomer. Also, our ultraviolet spectra of the various fractions are all identical.

cis- and *trans*-Pt(gly)$_2$ were prepared by the method of Pinkard, *et al.*,[5] separated by means of the great difference of solubility, and twice recrystallized from water. The infrared spectra of the compounds so obtained agree with those reported in the literature.[6]

Apparatus.—The irradiation equipment consists of a source, filters, diaphragm, and reaction cell, all in line along an optical axis. The reaction cell is a closed spectrophotometer cell (thickness 1 cm.), thermostated at 25 ± 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 of required wave lengths was isolated as follows: **254 mμ.**—Source: Hanau NN 15/44 low-pressure mercury vapor lamp; filter[7]: 2 cm. of a solution containing 321 g. of NiSO$_4$·7H$_2$O and 56 g. of CoSO$_4$·7H$_2$O/l. Extraneous transmission (~4%) was between 297 and 313 mμ. The source, the filter, and the cell were placed close together. **313 mμ.**—Source: Hanau Q 400 mercury vapor lamp; filter: 1 cm. of a 0.02% solution of K$_2$CrO$_4$ in 0.05 *N* NaOH + 2 mm. of Chance glass OX 1. Extraneous transmission (~13%) was between 302 and 366 mμ. In this case the filter and the reaction cell lie about 50 cm. from the source, and the light is focused by a quartz lens. **365 mμ.**—Source: Hanau Q 81 mercury vapor lamp; filter: 4 cm. of 10% w./v. CuSO$_4$·5H$_2$O in 0.01 *N* H$_2$SO$_4$ + 2 mm. of Chance glass OX 1. Extraneous transmission (~4%) was between 334 and 408 mμ. The general arrangement is similar to that of the previous case.

The light intensity was always measured by means of the uranyl oxalate actinometer.[8] The intensities incident on the

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[1] For the previous paper in this series see V. Carassiti, G. Condorelli, and L. L. Condorelli-Costanzo, *Ann. chim.* (Rome), **55**, 329 (1965).

[2] V. Carassiti and V. Balzani, *ibid.*, **50**, 630 (1960); A. Bertoluzza, V. Carassiti, and A. M. Marinangeli, *ibid.*, **50**, 645 (1960); V. Carassiti and V. Balzani, *ibid.*, **50**, 782 (1960); V. Carassiti, A. M. Marinangeli, and V. Balzani, *ibid.*, **50**, 790 (1960); V. Carassiti and V. Balzani, *ibid.*, **51**, 518 (1961); V. Balzani and V. Carassiti, *ibid.*, **51**, 533 (1961); V. Balzani, A. Bertoluzza, and V. Carassiti, *Bull. soc. chim. Belges*, **71**, 821 (1962); V. Balzani, V. Carassiti, and L. Moggi, *Ann. chim.* (Rome), **54**, 251 (1964).

[3] gly = glycinato ion.

[4] A. J. Stosick, *J. Am. Chem. Soc.*, **67**, 365 (1945).

[5] F. W. Pinkard, E. Sharratt, and W. Wardlaw, *J. Chem. Soc.*, 1012 (1934).

[6] A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 5018 (1958).

[7] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

[8] G. S. Forbes and L. J. Heidt, *J. Am. Chem. Soc.*, **56**, 2363 (1934).

reaction cell were in all cases of the order of 1 × 10^{-6} einstein/min.

Spectrophotometric measurements were performed with an Optica C.F.4 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 photoreactions were followed quantitatively at selected wave lengths by periodic measurements of the absorbance of the irradiated solutions. Light intensity measurements were performed before and after each experiment.

Results

Spectra.—The *trans*-$Ni(gly)_2 \cdot 2H_2O$ spectrum, as reported by Maki,[9] consists of d–d absorption bands at 370 mμ (ϵ 6.8), 620 mμ (ϵ 4.2), 1005 mμ (ϵ 6.1), and shoulders at 750 and 1150 mμ. Moreover, a strong absorption due to parity-allowed transitions is also present below 240 mμ.

The *trans*-$Pd(gly)_2$ spectrum, as reported by Jørgensen,[10] shows a d–d band at 325 mμ (ϵ 245) and a strong absorption below 260 mμ.

The spectra of the *cis*- and *trans*-$Pt(gly)_2$ isomers are reported in Figure 1. These spectra have not been discussed previously.

Thermal Stability.—The solutions of the complexes examined are thermally stable at the temperature of the experiments. In particular, with the *cis*- and *trans*-$Pt(gly)_2$ isomers, no isomerization occurs even after prolonged boiling of the solution.

Photochemical Behavior. *trans*-$\mathbf{Ni(gly)_2 \cdot 2H_2O}$.—Irradiation at 365 mμ of a 0.1 *M* solution of this complex did not bring about any alteration in the absorption spectrum, not even after long periods. No irradiation at 254 and 313 mμ was attempted because these wave lengths do not correspond to absorption bands.

trans-$\mathbf{Pd(gly)_2}$.—Irradiation of ~10^{-3} *M* solutions at 254 mμ, corresponding to the intense band probably due to electron-transfer transitions, brings about the decomposition of the complex and a concomitant formation of a dark precipitate of palladous oxide which makes any quantitative evaluation impossible. By contrast, the complex is completely insensitive to the radiation of 313 mμ corresponding to the d–d band.

cis-$\mathbf{Pt(gly)_2}$.—Irradiation at 254 and 313 mμ leads to a change in the spectrum of aqueous solutions (~2 × 10^{-3} *M*) of this complex. The absorbance greatly increases at wave lengths longer than 250 mμ, and two isosbestic points are present at about 255 and 280 mμ (curves a, b, and c in Figure 2); evidently the *trans* isomer is formed. After sufficiently long periods crystals separate from the solution. The infrared spectra confirm that they are crystals of the *trans* isomer, which is less soluble than the *cis* isomer. Once the precipitation has begun, continued illumination of the solution causes a decrease of absorbance in the whole spectrum (curve d in Figure 2). From the variation of the absorbance in the range 240–250 mμ, during the period preceding precipitation, it is possible to follow the photoisomerization quantitatively. The nonlinear plot of absorbance *vs.* time (Figure 3) is due to the progressive decrease in the number of photons absorbed by the reagent. The data required to establish the proportion of the incident light absorbed by the reagent and the product are (1) the ϵ values of the reagent and the product at the wave length of excitation, and (2) the transmittance values of the solution at the wave length of excitation at various times during the experiment. Knowing these data it is possible to verify, by means of a numerical integration, that the photoreaction rate depends only on the number of photons absorbed by reagent per unit time.

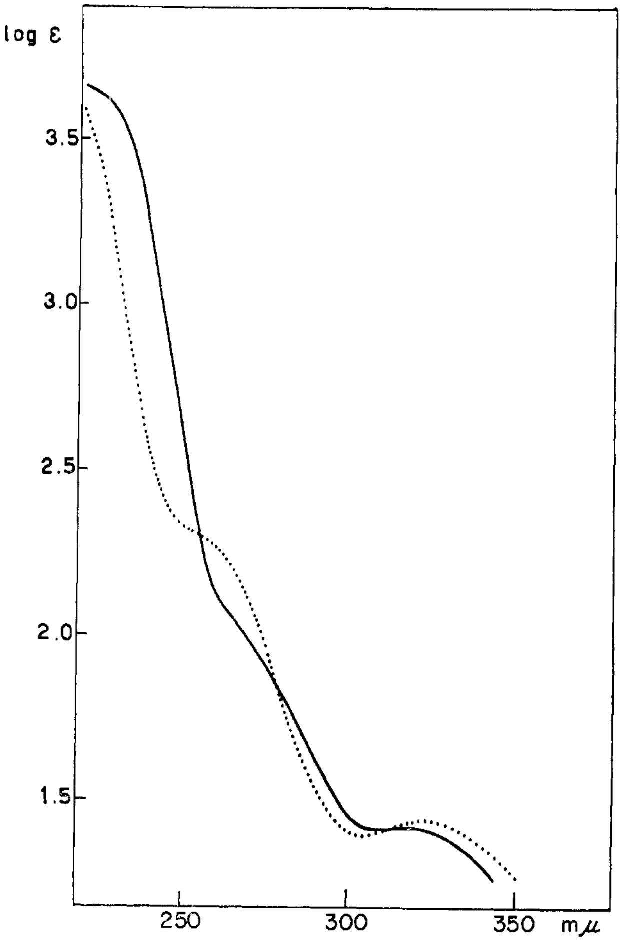

Figure 1.—Electronic absorption spectra of: ……, *cis*-bis(glycinato)platinum(II); ———, *trans*-bis(glycinato)platinum(II).

The quantum yield of the *cis* → *trans* isomerization of $Pt(gly)_2$ is 0.12 ± 0.01 for light of 254 mμ wave length and 0.13 ± 0.01 for 313 mμ light.

trans-$\mathbf{Pt(gly)_2}$.—Irradiation at 254 mμ, for periods comparable to those during which *cis* → *trans* isomerization is observed, does not produce appreciable variation in the solution spectrum; after much longer periods a black precipitate is formed which is soluble in hydrochloric acid.

Irradiation at wave lengths >280 mμ produced no detectable change in the absorption spectrum.

Discussion

The most interesting experimental results are those with the *cis* → *trans* isomerization of $Pt(gly)_2$, and

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[9] G. Maki, *J. Chem. Phys.*, **29**, 162 (1958).

[10] C. K. Jørgensen, Contract No. DA-91-508-EUC-247 with European Research Office, U. S. Department of the Army, Frankfurt am Main.

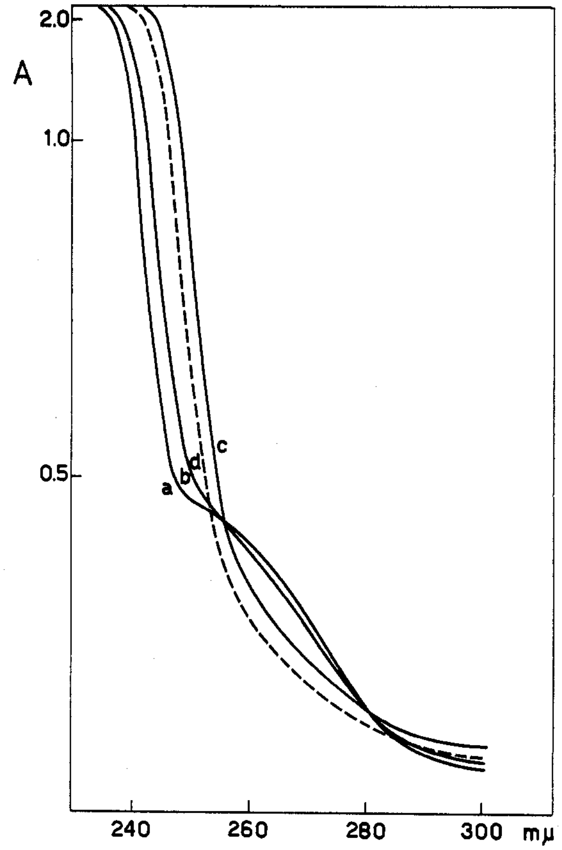

Figure 2.—Spectral variations of a 2×10^{-3} *M* solution of *cis*-bis(glycinato)platinum(II) irradiated at 254 mμ.

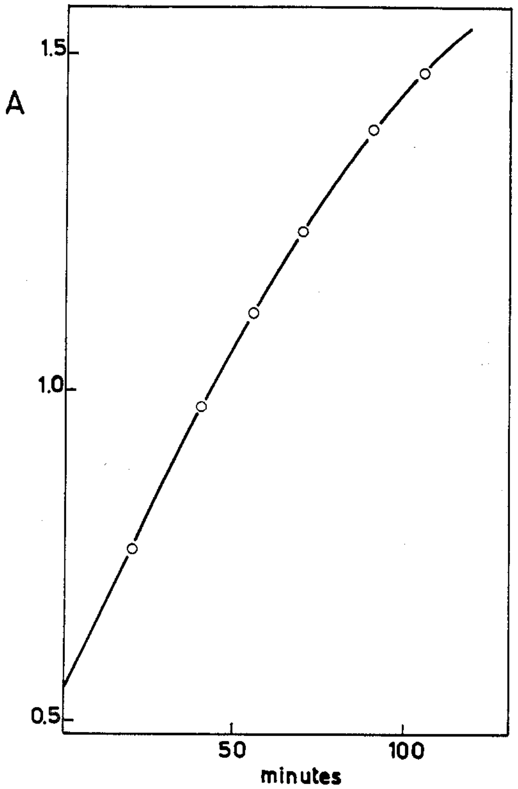

Figure 3.—Plot of absorbance at 240 mμ *vs.* time for a 1.4×10^{-3} *M* solution of *cis*-bis(glycinato)platinum(II); irradiation at 254 mμ.

therefore the following discussion will be mainly concerned with them.

Spectra of ***cis*****- and** ***trans*****-Pt(gly)$_2$.**—The electronic absorption spectra of Pt(gly)$_2$ (Figure 1) show a band at 325 mμ in the *cis* isomer (ϵ 27.5) and at about 320 mμ (ϵ 26) in the *trans* isomer. These bands, because of their low intensity, are certainly due to d–d transitions. The shoulders at about 250 mμ in the *cis* isomer and at about 270 mμ in the *trans* isomer are due to other d–d bands (ϵ of the order of 10^2) partially hidden by more intense bands which attain maxima below 240 mμ. Since glycinato ion does not absorb in this spectral range, the latter bands are probably electron-transfer bands.

The local symmetry determining the splitting of the d orbitals of the central ion is C_{2v} for the *cis* isomer and D_{2h} for the *trans* isomer. In complexes of these symmetries the degeneracy of the d orbitals is completely removed. The Pt^{2+} ion (d^8 electronic configuration) in a diamagnetic complex having one of the above mentioned structures may undergo four singlet–singlet and as many singlet–triplet electronic transitions. It is to be considered that, owing to the relatively high spin–orbit coupling in platinum, singlet–triplet transitions may give rise to relatively intense bands.

As far as the assignments of the individual bands in the square-planar complexes of Pt(II) are concerned, substantial differences of opinion still exist. According to Chatt, *et al.*,[11a] and Fenske, *et al.*,[11b] the band at higher wave length with a molar absorptivity of the order of 10 is due to one or more d–d singlet–triplet transitions and the successive d–d bands with ϵ of the order of 10^2 correspond to singlet–singlet transitions. While this assignment is generally accepted for the bands of the second type, according to Gray, *et al.*,[12a] and Martin, *et al.*,[12b] the band of the first type is due to the first singlet–singlet transition.

It has been observed[11] that the replacement of one or more coordinated groups in a square-planar complex of Pt(II) does not substantially modify the characteristics of the spectrum, but only leads to a shifting toward the high or low wave length values, depending on whether the new coordinated group generates a stronger or weaker field than that of the original group. In fact the spectrum of Pt(gly)$_2$ is very similar to that of $Pt(NH_3)_4^{2+}$,[9a] with a shift toward high wave length values, according to the position of the glycinato ion and NH_3 in the spectrochemical series.[13]

As far as assignment of the d–d bands in *cis*- and *trans*-Pt(gly)$_2$ is concerned, the shoulders at about 250 and 270 mμ undoubtedly can be assigned to a singlet–singlet transition. But for the band at about 320 mμ the same problem arises as previously discussed; that is, whether this band must be attributed to a singlet–singlet transition or to a singlet–triplet one.

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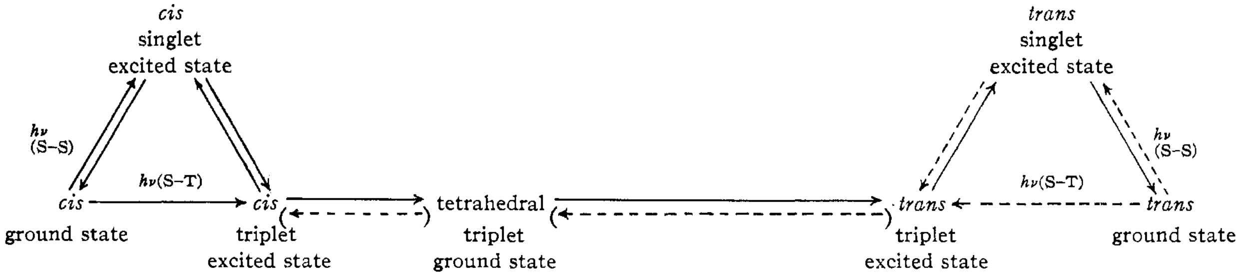
[11] (a) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958); (b) R. F. Fenske, D. S. Martin, and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

[12] (a) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963); H. B. Gray, communication to the Eighth International Conference on Coordination Chemistry, Vienna, Sept. 1964; (b) D. S. Martin and C. A. Lenhardt, *Inorg. Chem.*, **3**, 1368 (1964).

[13] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p. 109.

Scheme I

Mechanism of *cis–trans* Photoisomerization of Bis(glycinato)platinum(II)[a]



[a] ——→, *cis* → *trans* isomerization; - - - - - - - - →, *trans* → *cis* isomerization; hν(S–S), singlet–singlet excitation; hν(S–T), singlet–triplet excitation.

Mechanism of the Photoisomerization.—*cis* → *trans* thermal isomerization in Pt(II) complexes is not a very common phenomenon, and it seems to occur only in the presence of an excess of one of the ligands.[14] Therefore an intermolecular mechanism has been suggested, which implies the formation of a trigonal bipyramidal intermediate compound.[14] An intermolecular mechanism has also been suggested for the thermal isomerization of Pt(gly)$_2$ (both *cis* → *trans* and *trans* → *cis*) which occurs after prolonged boiling of the complex in an aqueous solution of glycine.[15] However, we have observed that, in the absence of free glycine, no thermal isomerization is possible. Since the photochemical isomerization we have studied takes place in the absence of free glycine and only from the *cis* to the *trans* isomer, it is thought that the latter isomerization follows a completely different mechanism and therefore must be an intramolecular reaction.

The most probable intramolecular mechanism for the *cis* → *trans* isomerization of a square-planar complex is the one involving a tetrahedral intermediate compound. This mechanism is in accordance with the nature of the excited states reached by irradiation. In the case of the *cis* isomer, the exciting radiations promote an electron to the highest d orbital σ^* ($x^2 - y^2$); a destabilization of the planar structure may result and a tetrahedral structure may be favored over the square-planar one. Since the ground state of a tetrahedral complex of this type is a triplet state, it is logical to think that the passage to the tetrahedral structure occurs more probably from a triplet excited state of the square-planar structure (Scheme I).[16]

Haake and Hylton[17] also have put forward a hypothesis of this type for the photochemical isomerization of $Pt(P(C_2H_5)_3)_2Cl_2$, though they did not exclude an intermolecular photochemical mechanism similar to that of thermal isomerization. In our case we can conclude that the mechanism is certainly an intramolecular one. Owing to the above-mentioned reasons, we think that Scheme I represents the most probable intramolecular mechanism for the photochemical isomerization of Pt(II) complexes.

Conclusions.—Apart from the mechanism of the photoisomerization we can expect that the excitation in a triplet band leads to greater quantum yields than the excitation in a singlet band. From the spectrum of *cis*-Pt(gly)$_2$ it can be seen that excitations at 313 and 254 mμ correspond, respectively, to the d–d band which is doubtful in assignment and to a singlet–singlet d–d band.[18] The experimental results show that the quantum yield is, within experimental error, equal at the two excitation wave lengths. This suggests that both the radiations at 254 and 313 mμ lead to excited states of the same nature; as a consequence we can conclude that in *cis*-Pt(gly)$_2$ the weaker band at 325 mμ is due to the first singlet–singlet transition. If, as is probable, in Pt(gly)$_2$ the ordering of the three most antibonding d orbitals is that proposed for $PtCl_4^{2-}$ by Martin, *et al.*,[12b] then the band at 325 mμ and the shoulder at 250 mμ in the *cis* isomer correspond, respectively, to $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1B_2$ transitions. In the *trans* isomer the corresponding transitions are: $^1A_g \rightarrow {}^1A_g$, $^1A_g \rightarrow {}^1B_{1g}$.

This result shows that a careful photochemical study of a complex by excitation corresponding to its various absorption bands may contribute to the interpretation of its spectrum.

As far as the photochemical behavior of the *trans* forms is concerned, we find that the Ni(II) and Pd(II) complexes, existing only in the *trans* form, are completely insensitive to the photonic excitation in d–d bands. The fact that no *trans* → *cis* isomerization has been found in Pt(gly)$_2$ confirms the general photochemical stability of the *trans* structures of these complexes when excited in d–d bands. These structures also have a common photochemical behavior after excitation in electron-transfer bands. This type of excitation in fact leads to the decomposition of *trans*-Pd(gly)$_2$ and *trans*-Pt(gly)$_2$.[19]

Finally, on the basis of the suggested mechanism for

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[14] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1960, pp. 249–254.

[15] L. M. Volshtein, M. F. Mogilevkina, and G. G. Motyagina, *Zh. Neorgan. Khim.*, **6**, 1105 (1961); L. M. Volshtein and I. O. Volodina, *ibid.*, **7**, 2685 (1962).

[16] In Scheme I we also consider the possibility of the *trans* → *cis* isomerization. We will discuss later the absence of this process.

[17] P. Haake and T. A. Hylton, *J. Am. Chem. Soc.*, **84**, 3774 (1962).

[18] Though in this spectrum there is a partial overlap between electron-transfer and d–d bands, we can consider that the 254 mμ radiations cause almost exclusively d–d transitions.

[19] Note that, unlike in the *cis* isomer, in the *trans* isomer the 254 mμ radiations cause almost exclusively electron-transfer transitions.

the *cis* → *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 reasons. 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 Complexes[1]

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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 mμ wave length, which corresponds to electron-transfer bands, whereas they are only slightly photosensitive to excitation in d–d bands. Irradiation at 254 mμ leads to the decomposition of the complexes, with production of Co(H$_2$O)$_6$$^{2+}$ 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 mμ 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 K$_2$SO$_4$. 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 mμ radiations.[1] The set used to isolate the 546 mμ radiation was the following. The source was a Hanau Q 400 high-pressure mercury vapor lamp; the filter[6] consisted of 2 cm. of 10% w./v. CuSO$_4$·5H$_2$O in 0.01 *N* H$_2$SO$_4$, 1 cm. of a solution containing 50 ml. of CuCl$_2$·2H$_2$O (1000 g. in 1 l. of water) and 50 ml. of 3 *M* CaCl$_2$, and 2 cm. of a solution containing 15 g. of K$_2$Cr$_2$O$_7$ in 1 l. of water. Extraneous transmission (~7%) was between 525 and 557 mμ. The general arrangement is that previously described for the 365 mμ 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 mμ was measured by means of a uranyl oxalate actinometer,[7] and at 546 mμ 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 mμ). 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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(1) For the previous paper in this series see V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, **4**, 1243 (1965).

(2) H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909); H. Ley and H. Winkler, *ibid.*, **45**, 372 (1912); H. Ley and K. Ficken, *ibid.*, **50**, 1123 (1917).

(3) V. Carassiti and M. Claudi, *Ann. chim.* (Rome), **50**, 581 (1960).

(4) I. Lifschitz, *Proc. Accad. Sci. Amsterdam*, **39**, 1192 (1936).

(5) (a) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955); (b) V. Carassiti and A. M. Marinangeli, *Ann. chim.* (Rome), **50**, 593 (1960).

(6) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

(7) G. S. Forbes and L. J. Heidt, *J. Am. Chem. Soc.*, **56**, 2363 (1934).