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The Role of the Excited-State Geometry in the Photochemical Isomerization of Bis(glycinato) platinum (II)

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The mechanisms of the thermal and photochemical isomerizations of cis-Pt(gly)$_2$ *have been investigated. The thermal isomerization has been found to occur only in the presence of free glycine. On the contrary, the photoisomerization takes place both in the presence and in the absence of free glycine, with constant quantum yield (0.13). When the two isomerization reactions are carried out in the presence of labeled free glycine, the thermal isomerization leads to the formation of labeled* trans *isomer as well as to an extensive labeling of the starting* cis *form; whereas the photochemical isomerization occurs without any labeling of the two isomers. These results show that the thermal isomerization takes place by an* intermolecular *mechanism, whereas the photochemical isomerization must be an* intramolecular *process. A twisting mechanism is discussed for the photochemical isomerization. This mechanism is related to the recent spectroscopic evidence for tetrahedral stable conformations of some excited states of square planar complexes.*

Introduction

Two kinds of *cis→trans* isomerizations have been reported for Pt(gly)$_2$ (gly$^-$ = glycinato ion) : (1) an isomerization which occurs on prolonged heating of a saturated solution of *cis*-Pt(gly)$_2$ containing free glycine;[1] (2) an isomerization which is caused by the irradiation with light of 313 and 254 mμ of solutions of *cis*-Pt(gly)$_2$.[2] For the thermal isomerization an intermolecular mechanism has been proposed[1] involving HPt(gly)$_3$ and H$_2$Pt(gly)$_4$ as intermediate compounds. For the photochemical isomerization an intramolecular twisting mechanism has been suggested[2] which converts the excited states of the *cis* isomer into the *trans* form through the formation of an intermediate tetrahedral structure.

In order to obtain a better understanding of the mechanism of the photoisomerization, both the thermal and the photochemical isomerizations have been carried out in the presence and in the absence of labeled free glycine, and the results have been compared.

Experimental Section

Materials. *Trans*-Pt(gly)$_2$ was prepared according to Pinkard, *et al.*[3] For the *cis* isomer a method more advantageous than that of Pinkard was used: a solution containing K$_2$PtCl$_4$ (5 g.), glycine (5 g.) and a stoichiometric amount of NaOH was heated for about 30 minutes. The resulting pale yellow solution was concentrated to 20-30 ml. and made acid, yielding a white precipitate of H$_2$Pt(gly)$_4$.[1] The precipitate was filtered and dissolved in hot water. The crystallization of this solution yielded almost pure *cis*-Pt(gly)$_2$ that was then twice recrystallized from water.

Labeled (C^{14}) glycine was supplied by the Radiochemical Centre, Amersham (England), with a specific activity of 7.9 mc/mM. An amount corresponding to 0.5 mc (0.0048 g.) was mixed with 2.106 g. of non-labeled glycine and a 2.25×10^{-2} M stock solution was made.

Apparatus. The irradiation equipment for the 313 mμ radiations is the same as previously described[2] except for the use of an interference filter (Schott and Gen., $\lambda_{max} = 313$ mμ, $T_{max} = 24\%$, halfwidth = 12 mμ) instead of the glass-solution filter. The light intensity was measured by the ferric oxalate actinometer.[4]

Spectrophotometric measurements were performed with an Optica CF 4 NI spectrophotometer.

The activity measurements were carried out with a liquid-phase scintillation counter model 6850, Nuclear Chicago.

Procedures. For the experiments in the presence of labeled free glycine the procedure was as follows. Both the thermal and the photochemical isomerizations were carried out until a sufficient amount of the *trans* isomer was formed. Then a chromatographic separation of the reaction mixture was made, and activity measurements were performed on the various fractions. In order to rule out the possibility of some zero-time exchange, separations and counting have been made also on starting solutions containing *cis*-Pt(gly)$_2$ and glycine.

Thermal isomerization. An aqueous solution 1.5×10^{-3} M in *cis*-Pt(gly)$_2$ and 7.5×10^{-3} M in glycine was placed in a thermostated bath at 95°.[5] The reaction

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[1] L. M. Volshtein, M. F. Mogilevkina and G. G. Motyagina, *Russ. J. Inorg. Chem.*, 6, 564 (1961).

[2] V. Balzani, V. Carassiti, L. Moggi and F. Scandola, *Inorg. Chem.*, 4, 1243 (1965).

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

[4] C. G. Hatchard and C. A. Parker, *Proc. R. Soc.*, (A), 235, 518 (1956).

[5] This method is quite different from that of ref. 1 (see discussion).

was followed by spectrophotometric measurements[2] made on cooled samples of the solution.

Photochemical isomerization. 3 ml. of an aqueous solution 1.5×10^{-3} M in *cis*-Pt(gly)$_2$ and 7.5×10^{-3} M in glycine were placed in a 1 cm. spectrophotometric cell and irradiated at 25° with 313 mμ radiations. The reaction was followed spectrophotometrically.[2]

Chromatographic separation. The separation of *cis*-Pt(gly)$_2$, *trans*-Pt(gly)$_2$ and glycine from the reaction mixture was carried out on a column of Dowex 50 W×12 200/400 mesh resin. Percloric acid was added to 3 ml. of the reaction mixture in order to obtain 6 ml. of a solution 0.1 M in $HClO_4$. This solution was poured into the column. Tests on known mixtures of the two isomers and glycine showed that the following volumes of eluate had to be collected in order to separate the three components: 18 to 36 ml. of 0.1 N $HClO_4$ for the *trans* isomer, 36 to 60 ml. of 0.1 N $HClO_4$ for the *cis* isomer, 0 to 27 ml. of 4 N $HClO_4$ for the free glycine. The fraction 0 to 18 ml. of 0.1 N $HClO_4$ was used as a blank for the activity measurements. The elution of the two isomers was checked spectrophotometrically at 230 mμ. The presence of the glycine was controlled by the ninhydrin test[6] after neutralization of the solution. The chromatographic separation curve for an irradiated solution is reported in Fig. 1. The curve for a heated solution is qualitatively identical.

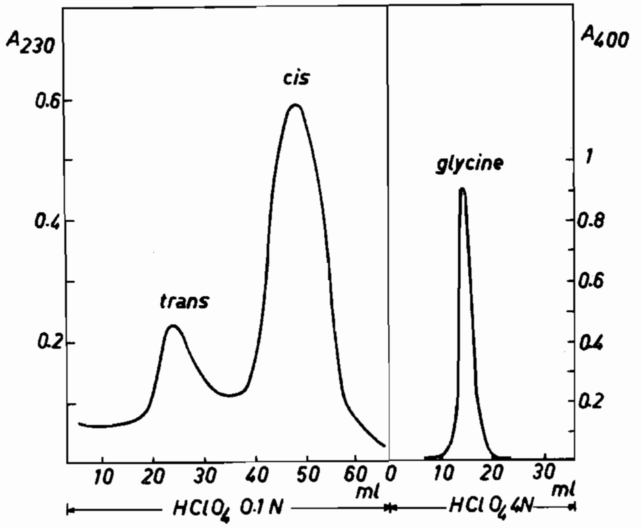

Figure 1. Chromatographic separation of *trans*-Pt(gly)$_2$, *cis*-Pt(gly)$_2$ and glycine.

Activity measurements. The various fractions were concentrated to 5 ml. except that one in 4 M acid which was concentrated only to 25 ml. All of the samples were prepared as follows: 0.3 ml. of the concentrated solution were mixed with 6 ml. of 95% ethanol, 20 drops of pure hyamine 2389 (BDH) and 8 ml. of the scintillating solution (5 g. of P.P.O. and 0.05 g. of P.O.P.O.P./liter of toluene). A higher per cent of scintillating solution should have given a higher counting efficiency, but the above conditions were imposed by solubility requirements. Each measured activity was corrected using the channels ratio quenching correction method. The activity of the glycine fraction was multiplied by a factor 5 in order to account for the difference in volume. All of the activity values were corrected for the activity of the blank fraction.

The experiments performed in the absence of free glycine were made under the same experimental conditions. The procedure was simplified because separation and counting were obviously unnecessary.

Results

(1) The heating of aqueous solutions of *cis*-Pt(gly)$_2$ did not cause any reaction, as shown by the invariance of the spectrum of the solution.

(2) The heating of solutions containing *cis*-Pt(gly)$_2$ and labeled free glycine caused the *cis*→*trans* isomerization reaction, as shown by the increase of the absorbance at 240 and 245 mμ (see the spectra of the *cis* and *trans* isomers in[2]). However, the agreement between the values for the *trans* isomer concentrations obtained from the 240 and 245 mμ spectral variations was not so good as for the photochemical runs. This indicates that in the thermal runs some other species were present together with the *cis* and *trans* isomers. The chromatographic separation of the reaction mixture confirmed that the *cis*→*trans* isomerization had occurred during the heating. The activity measurements showed that both the formed *trans* isomer and the remaining *cis* form were labeled. Accordingly, after the heating of the solution the free glycine exhibited a lower activity than that of the starting free glycine.

(3) As is already known,[2] the irradiation of aqueous solutions of *cis*-Pt(gly)$_2$ caused the *cis*→*trans* isomerization with quantum yield 0.13.

Table I. Comparison between the thermal and the photochemical isomerizations of *cis*-Pt(gly)$_2$

Type of experiment	Initial solution [c]		Final solution [c]		
	cis-Pt(gly)$_2$	glycine	*trans*-Pt(gly)$_2$	*cis*-Pt(gly)$_2$	glycine
thermal [a]	concentration = 1.50 activity = 0	concentration = 0	concentration = 0	concentration = 1.50	concentration = 0
thermal [a]	concentration = 1.50 activity = 0	concentration = 7.50 activity = 1260	concentration ~ 0.3 [d] activity = 24	concentration ~ 1.2 [d] activity = 217	concentration = 7.50 activity = 1070
photochemical [b]	concentration = 1.50 activity = 0	concentration = 0	concentration = 0.23	concentration = 1.27	concentration = 0
photochemical [b]	concentration = 1.50 activity = 0	concentration = 7.50 activity = 1250	concentration = 0.23 activity = 0	concentration = 1.27 activity = 0	concentration = 7.50 activity = 1250

[a] Heating at 95° for 100 hours. [b] Irradiation with 313 mμ radiations at 25° for 5 hours. [c] Concentration in $M\times10^3$, activity in $dpm\times10^{-2}$. [d] This value could be afftected by considerable experimental errors.

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(6) S. Moore and W. H. Stein, *J. Biol. Chem.*, *211*, 893 (1954).

(4) The irradiation of solutions containing *cis*-$\mathrm{Pt(gly)_2}$ and labeled free glycine caused the *cis*→*trans* isomerization with quantum yield 0.13 as in the previous case. The activity measurements performed after the chromatographic separation of the components of the irradiated solutions showed that neither the formed *trans* isomer nor the remaining *cis* form were labeled. Accordingly, the free glycine of the irradiated solution showed the same activity as the starting free glycine.

Typical results for the four types of experiments are summarized in Table I.

Discussion

Thermal isomerization. The thermal *cis*→*trans* isomerization of $\mathrm{Pt(gly)_2}$ had been already studied by Volshtein, *et al.*[1] Starting from a saturated solution of *cis*-$\mathrm{Pt(gly)_2}$ containing free glycine, they found that after prolonged heating a considerable amount of solid *trans*-$\mathrm{Pt(gly)_2}$ was formed. The ratio of the amounts of the two isomers in the solid phase was determined and the results obtained were interpreted on the basis of a mechanism involving the formation of $\mathrm{Pt(gly)_3^-}$ and $\mathrm{Pt(gly)_4^{2-}}$ as intermediate compounds.

Our results concerning the thermal reaction of *cis* $\mathrm{Pt(gly)_2}$ in the presence of labeled free glycine show that both the formed *trans* isomer and the remaining *cis* isomer were radioactive. This result could be explained by two different mechanisms:

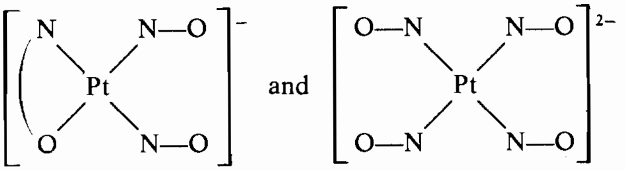
(1) The free glycine enters the starting *cis* isomer yielding some intermediate compound which in turn can give rise to the labeled *trans* and labeled *cis* isomers (intermolecular mechanism for the isomerization reaction):

$$\begin{array}{c} cis\text{-}\mathrm{Pt(gly)_2} + \mathrm{gly}^* \\ \downarrow \\ \left\{ \begin{array}{c} \text{intermediate compounds} \\ \text{containing labeled glycine} \end{array} \right\} \begin{array}{l} \nearrow\ cis\text{-}\mathrm{Pt(gly)_2}^* \\ \searrow\ trans\text{-}\mathrm{Pt(gly)_2}^* \end{array} \end{array}$$

(2) The isomerization reaction occurs by an intramolecular process and the two isomers undergo independent ligand exchange reactions:

$$\begin{tikzcd} cis\text{-}\mathrm{Pt(gly)_2} \arrow[r, "\text{intramolecular}", "\text{isomerization}"'] \arrow[d, shift left, "\mathrm{gly}^*"] & trans\text{-}\mathrm{Pt(gly)_2} \arrow[d, shift left, "\mathrm{gly}^*"] \\ cis\text{-}\mathrm{Pt(gly)_2}^* \arrow[u, shift left] & trans\text{-}\mathrm{Pt(gly)_2}^* \arrow[u, shift left] \end{tikzcd}$$

However our results, in accordance with the results of Volshtein, *et al.*,[1] also show that the thermal isomerization *needs* some free glycine to occur. Therefore, the intramolecular isomerization reaction required by the second mechanism can be ruled out. Moreover, also the following considerations are in contrast with the second mechanism. One can reasonably expect that the intermediate compounds for the ligand exchange reactions (as well as for the intermolecular isomerization reaction) are the compounds



($\mathrm{N{-}O^-}$ = glycinato ion) which have been studied by Volshtein, *et al.*[1,7,8] The formation of these compounds also agrees with the well known fact that: since the bond between platinum and amine nitrogen is particularly stable, the opening of the glycine rings of the original chelate compound occurs at the bond between the platinum and the carboxyl group.[1,9] Now, one can easily verify that: (a) the tris-glycinato complex, which will be labeled in different sites depending on the starting isomer, can either come back to the starting *non-labeled* isomer or lead to the labeled isomerized form (see, for example, Fig. 2, at the top); (b) the tetraglycinato complex, which except for the labeled sites will be identical for the two ligand exchange reactions, leads to the labeling of the starting isomer as well as to the formation of labeled isomerized form (see Fig. 2, at the bottom).

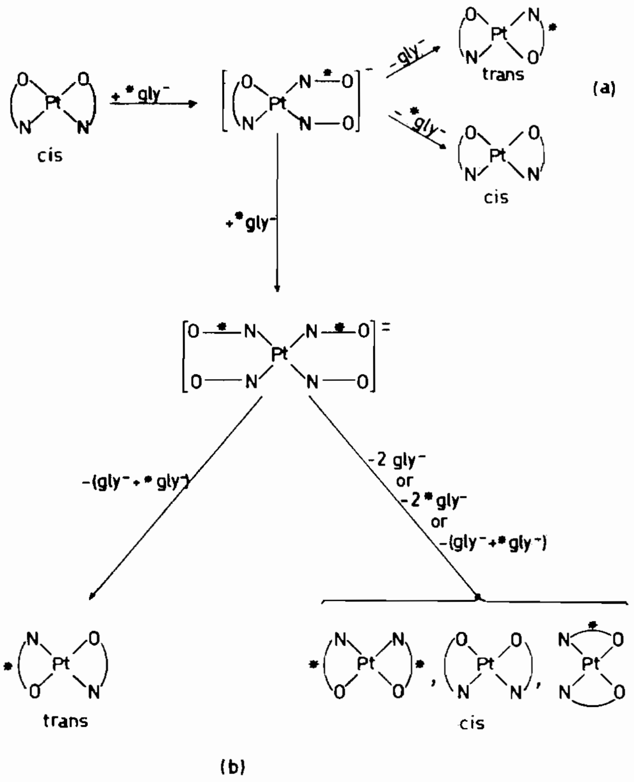


Figure 2. Possible paths for the ligand exchange and intermolecular isomerization reactions of *cis*-$\mathrm{Pt(gly)_2}$.

Thus, it appears that the ligand exchange reactions cannot occur without causing some isomerization, contrary to the requirements of mechanism 2 which, as a

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[7] L. M. Volshtein and G. G. Motyagina, *Russ. J. Inorg. Chem.*, *7*, 1294 (1962).

[8] L. M. Volshtein and G. G. Motyagina, *Russ. J. Inorg. Chem.*, *5*, 840 (1960).

[9] A. A. Grinberg, «An Introduction to the Chemistry of Complex Compounds», D. H. Bush and R. F. Trimble Jr. Editors, Pergamon Press, Oxford, p. 294 (1962).

consequence, can be definitely rule out. Therefore, *the mechanism of the thermal isomerization must be intermolecular.*

Although a quantitative or more detailed investigation of the thermal isomerization reaction is not the purpose of the present study, some other considerations can be drawn from our results. According to the above discussion on the nature of the tris- and tetra-glycinato complexes, two paths can reasonably be suggested for the *cis*→*trans* isomerization in the presence of labeled glycine (Fig. 2).[10] It can be noted that the path *a* (which includes only the tris-glycinato complex as intermediate) alone cannot account for the radioactivity found in the *cis* isomer. Therefore, the predominant path for the intermolecular isomerzation must be that involving the tetra-glycinato ion (path *b*). Quantitatively, on the basis of this mechanism, one should expect an activity value for the *trans* isomer higher than that reported in Table I. Experimental errors in the evaluation of the concentration of the *trans* isomer can account for this quantitative discrepancy. In fact, as it has been noted above, in the thermal runs the spectrophotometric method, which was used for determining the relative concentrations of the *cis* and *trans* isomers in the reaction mixture, did not work so well as in the photochemical runs, probably because of some interference from intermediate or secondary products.

Photochemical isomerization. The quantum yield of the photoisomerization being identical either with or without free glycine strongly suggests that the free glycine cannot play a determining role in the mechanism of this reaction. The lack of radioactivity in both the formed *trans* isomer and the remaining *cis* form after the photochemical isomerization in the presence of labeled glycine definitely rules out an intermolecular mechanism. Furthermore, this result suggests that also an intramolecular bond-cleavage mechanism cannot be effective. In fact, if some coordination sites were made available by the cleavage of some platinum-oxygen bonds, molecules of free glycine would coordinate to the central metal as they actually do during the thermal isomerization, and in this way labeled complexes would be produced.

Thus, *the photoisomerization not only must be intramolecular, but must also occur without any bond cleavage.* The previously proposed idea[2] of a molecular twisting mechanism is therefore confirmed definitively.

The role of the excited state geometry in the photoisomerization. Bearing in mind the close similarity of the spectra of most Pt(II) complexes,[12] the assignment of the bands of *cis*-Pt(gly)$_2$ could reasonably follow that recently given by Martin, *et al.*[13] for $PtCl_4^{2-}$. Thus, neglecting the lowering in symmetry, the band at 325 mμ ($\varepsilon_{max} = 27.5$) should correspond to the lowest two singlet→triplet transitions ($d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$) and the shoulder at about 250 mμ ($\varepsilon_{max} \sim 10^2$) to the first spin allowed transition ($d_{xy} \rightarrow d_{x^2-y^2}$). It has been recently stressed[14] that the ordering of the one-electron *d*-orbitals should depend on the bonding properties of the ligands. Assuming a different *d*-orbital ordering, however, should not affect the conclusions which will be reached.

According to the above discussion, the photoexcitation of the *cis* isomer would cause a molecular twisting leading to the *trans* isomer. It seems that the details of this type of distortion can be understood in the light of the recent spectroscopic suggestions about the geometry of the excited states of some square planar complexes.

Examining the polarized spectra of $Ni(CN)_4^{2-}$, Ballhausen, *et al.*[15] concluded that some of the excited states of the square planar structure have a pseudo-tetrahedral stable conformation. In a paper about the polarized spectra of $PtCl_4^{2-}$ Martin, *et al.*[13] made a detailed analysis of the energy levels including spin-orbit coupling. It was shown that the lowest square planar excited states (which arise by spin-orbit coupling from the lowest pure triplet states) correlate with the corresponding components of the $^3T_1$ tetrahedral ground state which lies at lower energy and which in turn correlates with the square planar ground state (see Fig. 5 in ref. 13). This means that the plot of the potential energy *versus* the angle ϑ of twisting (Fig. 3) of the two halves of the $PtCl_4^{-2}$ ion (a distortion corresponding to the β_{2u} normal vibration) should look something like Fig. 4. The states represented are the ground state and the lowest excited state (Γ_1-$^1(b_{1g}b_{1g})$ and Γ_1-$^3(b_{1g}b_{2g})$) in the square planar geometry.

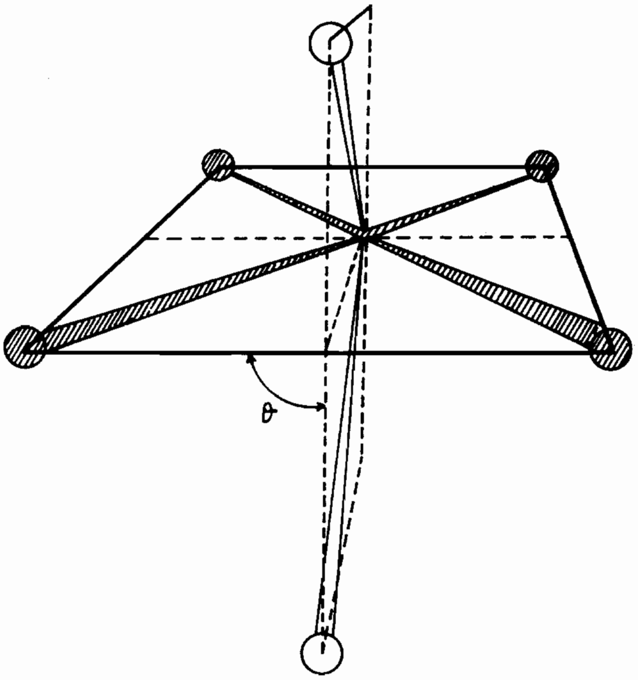

Figure 3. Schematic representation of the twisting of the two halves of a square planar complex.

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[10] Note that the scheme shows only overall stoichiometric mechanisms and nothing is meant about the particular mechanism by which each step occurs. Quite probably each elementary step will follow the general path of the substitution reactions of Pt(II) complexes, *i.e.* A or I mechanisms in Langford and Gray's notation.[11]

[11] C. H. Langford and H. B. Gray, «Ligand Substitution Processes», W. A. Benjamin, Inc., New York (1966).

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

[13] D. S. Martin, M. A. Tucker and A. Kassman, *Inorg. Chem.*, *4*, 1682 (1965).

[14] H. Basch and H. B. Gray, *Inorg. Chem.*, 6, 365 (1967).

[15] C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks and C. R. Hare, *Inorg. Chem.*, *4*, 514 (1965).

If these considerations can be extended to the case of $Pt(gly)_2$, the situation will be similar except for the 0° and 180° structures being no more identical (*i.e.*, if the 0° structure is the *cis* isomer, the 180° one will correspond to the *trans* isomer). From a picture like that of Fig. 4 it is easy to understand the possibility of a photochemical isomerization following the excitation of one isomer to its first excited state. In fact, the excitation of one isomer will lead to high vibrational levels of the excited state which, by vibrational relaxation, will deactivate to its 0-level, corresponding to a pseudo-tetrahedral structure. From there, intersystem crossing followed by vibrational relaxation can complete the deactivation, leading either back to the starting configuration or to the isomerized one.

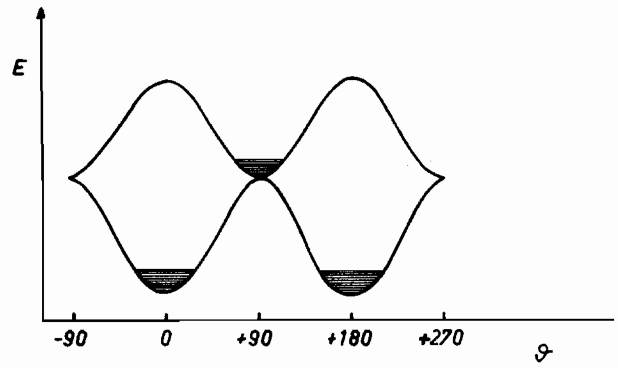

Figure 4. Potential energy curves for the $PtCl_4^{2-}$ ion as a function of the distortion angle ϑ. *Lower curve*: ground state; *upper curve*: lowest excited state.

Such a simple scheme suggests that both *cis*→*trans* and *trans*→*cis* photoisomerizations should be possible. An explanation of the observed lack of the *trans*→*cis* photoisomerization[2] could be as follows. Since in $Pt(gly)_2$ the two structures at 0° and 180° correspond to two different isomers the curves for the two states will be no longer symmetric. It might well be that this asymmetry causes the «intersystem crossing point» to be displaced towards one isomer, as compared to the maximum of the ground state. Tentatively, we hypothesize a situation like that of Fig. 5 (where the energetic differences have been overemphasized for purposes of clarity). In this case an energy barrier would be present between the «intersystem crossing point» and the *cis* configuration. Because of the high rates of the vibrational deactivation processes, even a small barrier could be sufficient to inhibit the conversion of the excited state to the *cis* configuration. As a consequence, the *trans*→*cis* isomerization would be prevented.

In the above discussion only the ground state and the first excited state have been considered. The *cis*→*trans* photoisomerization of $Pt(gly)_2$, however, was obtained irradiating in both the ligand field bands of the spectrum.[2] A simple explanation could be based on the assumption that higher excited states can deactivate completely to the lowest one, and then follow the above outlined path. This type of mechanism also accounts for the constant values of the quantum yield obtained at 313 and 254 mμ.

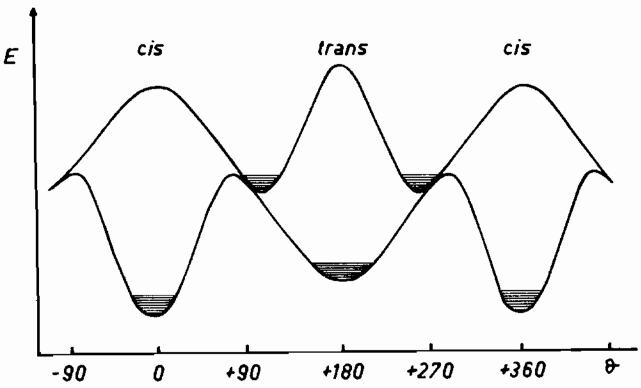

Figure 5. Possible situation for the potential energy curves of $Pt(gly)_2$ as a function of the distortion angle ϑ. *Lower curve*: ground state; *upper curve*: lowest excited state.

A complete deactivation of the higher excited states to the lowest one implies the assumption of high rates for the radiationless transitions between the excited states. Such an assumption has already been advanced for other coordination compounds (see, *e.g.*, the work of Schläfer on Cr(III) complexes[16]). In the case of platinum complexes the high spin-orbit coupling could become an important factor in determining the deactivation of the higher excited states to the lowest one. In fact, two main aspects of this coupling can be considered: (1) the increase in the number of energy states: the resulting level scheme shows considerably lower energy differences between the excited states as compared to the original one (see, *e.g.*, Fig. 5 in ref. 13); (2) the weakening of the spin selection rules caused by the mixing of states of different multiplicity. Both these factors should increase the rates of the radiationless transitions between the excited states.

Finally, it can be noted that the consideration of the diagram of Fig. 5 alone would require, in view of the lack of the *trans*→*cis* photoisomerization, a quantum yield of 1 for the *cis*→*trans* photoisomerization. It must be considered, however, that the deactivation of the excited state along coordinates other than that shown in Fig. 5 will not cause any permanent change in the geometry of the complex. The competition between these deactivation modes and the one which is responsible for the photochemical isomerization can account for the low quantum yield.

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(16) H. L. Schläfer, *J. Phys. Chem.*, 69, 2201 (1965), and references therein.