

# Kinetics and Mechanism of the Reaction of Platinum(II) Complexes with Thioglycolic Acid

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**Summary.** Complex formation of  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  and  $[\text{PtCl}_4]^{2-}$  with thioglycolic acid has been studied as a function of temperature (288.2–308.2 K) using spectrophotometry in 1.00 M aqueous perchloric acid; the statistically corrected corresponding second-order rate constants are  $k_1^{298} = 5.25 \times 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$  and  $0.624 \text{ M}^{-1} \cdot \text{s}^{-1}$ , respectively. The temperature dependence of the rate constants gives the following activation parameters:  $\Delta H_1^\ddagger = 34 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta S_1^\ddagger = -142 \pm 8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ ,  $\Delta H_1^\ddagger = 31 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta S_1^\ddagger = -133 \pm 6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for  $[\text{PtCl}_4]^{2-}$ . The negative values for the entropies of activation are consistent with an associative mode of activation. A LFER diagram observed for the complex formation of  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  with sulfur containing ligands support an A mechanism. The reactivity of sulfur-bonding ligands towards  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  follows the order  $\text{H}_2\text{O} < \text{Me}_2\text{SO} < \text{SHCH}_2\text{COOH} < \text{SCN}^- < \text{S}(\text{CH}_2)_4\text{O} < \text{Et}_2\text{S} < \text{S}(\text{CH}_2)_4\text{S} < \text{Me}_2\text{S} < \text{SC}(\text{NH}_2)_2$  ( $1:3:7.4 \times 10^3:4.8 \times 10^4:5.2 \times 10^4:6.8 \times 10^4:8.8 \times 10^4:1.3 \times 10^5:5 \times 10^5$ ). A trigonal bipyramidal transition state stabilized by hydrogen bonds between the entering thioglycolic acid and the leaving aqua or chloro ligand is suggested.

**Keywords.** Complexes; Mechanism; Platinum(II); Thiols.

## Kinetik und Mechanismus der Reaktion von Platin(II)-Komplexen mit Thioglycolsäure

**Zusammenfassung.** Die Komplexbildungsreaktionen von  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  und  $[\text{PtCl}_4]^{2-}$  mit Thioglycolsäure wurden in 1.00 M Perchlorsäure spektrophotometrisch als Funktion der Temperatur (288.2–308.2 K) untersucht; die entsprechenden statistisch korrigierten Geschwindigkeitskonstanten zweiter Ordnung wurden zu  $k_1^{298} = 5.25 \times 10^{-2}$  und  $0.624 \text{ M}^{-1} \cdot \text{s}^{-1}$  ermittelt. Die Temperaturabhängigkeit der Geschwindigkeitskonstanten liefert die folgenden Aktivierungsparameter:  $\Delta H_1^\ddagger = 34 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta S_1^\ddagger = -142 \pm 8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  für  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ ,  $\Delta H_1^\ddagger = 31 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta S_1^\ddagger = -133 \pm 6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  für  $[\text{PtCl}_4]^{2-}$ . Die negativen Werte für die Aktivierungsentropien stimmen mit einem assoziativen Aktivierungsverlauf überein. Ein LFER-Diagramm, das für die Komplexbildung zwischen  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  und schwefelhaltigen Liganden erstellt wurde, legt das Auftreten eines Mechanismus des Typs A nahe. Die Reaktivität von über Schwefel bindenden Liganden gegenüber  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  folgt der Reihe  $\text{H}_2\text{O} < \text{Me}_2\text{SO} < \text{SHCH}_2\text{COOH} < \text{SCN}^{2-} < \text{S}(\text{CH}_2)_4\text{O} < \text{Et}_2\text{S} < \text{S}(\text{CH}_2)_4\text{S} < \text{Me}_2\text{S} < \text{SC}(\text{NH}_2)_2$  ( $1:3:7.4 \times 10^3:4.8 \times 10^4:5.2 \times 10^4:6.8 \times 10^4:8.8 \times 10^4:1.3 \times 10^5:5 \times 10^5$ ). Es wird ein trigonal-bipyramidaler Übergangszustand vorgeschlagen, der durch Wasserstoffbrückenbindungen zwischen der eintretenden Thioglycolsäure und dem austretenden Aqua- oder Chloroliganden stabilisiert wird.

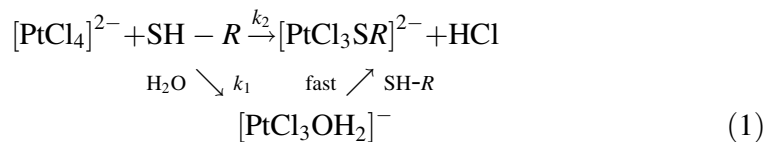
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## Introduction

Interactions between platinum(II) complexes and sulfur-bonding ligands are very important from a biological and bioinorganic point of view and have attracted considerable interest in recent years [1, 2]. Sulfur containing molecules have a high affinity for platinum [3]; examples of reactive biomolecules include cysteine, methionine, glutathione, and proteins. Some complexes of platinum(II) have been used as anticancer drugs [4, 6]. For instance, cisplatin (*cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]) is routinely used in chemotherapy and has been particularly successful in the treatment of testicular and ovarian cancer [7]. However, bonding between platinum(II) and sulfur containing compounds is very strong, and it is difficult to remove the platinum compound from the sulfur atom. Moreover, the binding of platinum(II) complexes to protein-bound sulfhydryl (thiol) groups is thought to be responsible for the observed toxic side-effects [8, 9].

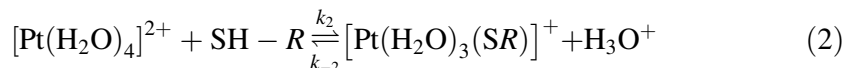
The present investigation attempts to obtain a better understanding of the interactions between platinum(II) complexes and thioglycolic acid as sulfur-bonding ligand. We report the kinetics and mechanism of the complex formation between relatively simple Pt(II) complexes, as tetrachloroplatinate(II) and tetraaquaplatinum(II), with thioglycolic acid in aqueous solution (Eqs. (1) and (2)).

Substitution reactions of square-planar d<sup>8</sup> metal complexes are generally accepted to proceed according to two parallel associative reaction paths [10]. One of them involves the rate-determining formation of a solvent-ligand complex (*k*<sub>1</sub> path in Eq. (1)) followed by rapid substitution of the coordinated solvent molecule. The other reaction involves direct nucleophilic attack by the entering ligand (*k*<sub>2</sub> path in Eq. (1)).



SH-R = thioglycolic acid (SHCH<sub>2</sub>COOH)

In the tetraaquaplatinum(II) complex, the situation is quite simple; only direct nucleophilic attack by the entering ligand takes place.



The kinetics of reactions (1) and (2) have been studied as a function of temperature in 1.00 M aqueous perchloric acid.

## Results and Discussion

The observed *pseudo*-first-order rate constants from the conventional kinetic experiments were obtained from a linear least square analysis of the first three half-lives and represent the average of two to five experiments. Figures 1 and 2 show the concentration dependence of *k*<sub>obsd</sub>. The rate constants are linearly dependent of the concentration of excess platinum(II) complexes. The second-order rate constants *k*<sub>2</sub>

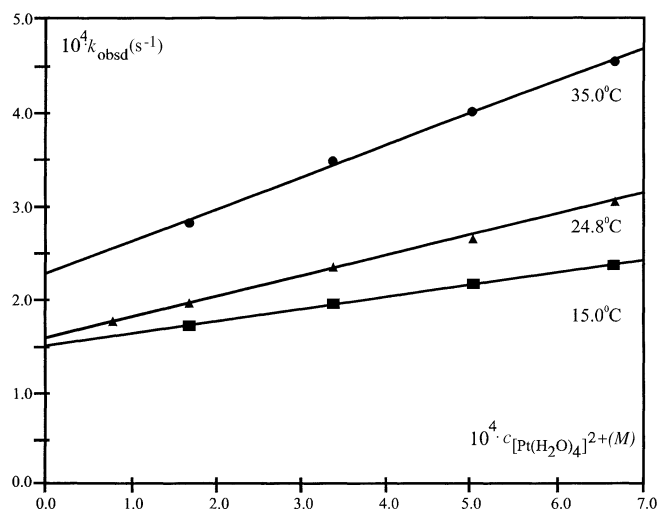


Fig. 1. Observed *pseudo*-first-order rate constants as a function of excess of  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$

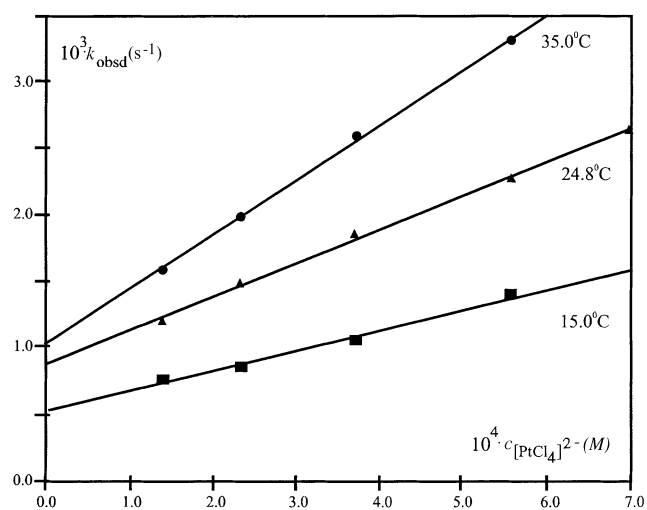


Fig. 2. Observed *pseudo*-first-order rate constants as a function of excess of  $[\text{PtCl}_4]^{2-}$

for formation of complexes were derived by fitting the  $k_{\text{obsd}}$  values to Eq. (3) according to the two-terms rate law for nucleophilic substitution at  $d^8$  metal complexes.

$$k_{\text{obsd}} = k_1 + k_2[\text{complex}] \quad (3)$$

One reaction involves direct nucleophilic attack by the entering ligand ( $k_2$ ), the other reaction involves the rate determining formation of a solvent-ligand complex ( $k_1$ ) [10].

The rate constants obtained at the three temperature allow the calculation of the corresponding enthalpies and entropies of activation through a fit to the *Eyring* equation [11]. Table 1 contains second-order rate constants ( $k_2$ ) and activation parameters. However, the close similarities between Pt(II) complexes (Table 1)

**Table 1.** Rate constants and activation parameters for reactions between platinum(II) complexes and thioglycolic acid in aqueous solution at 298 K

Complex	$k_2$ ( $M^{-1} \cdot s^{-1}$ )	$k_1$ ( $s^{-1}$ )	$\Delta H_1^\ddagger$ ( $kJ \cdot mol^{-1}$ )	$\Delta S_1^\ddagger$ ( $J \cdot K^{-1} \cdot mol^{-1}$ )
$[Pt(H_2O)_4]^{2+}$ <sup>a</sup>	$(5.25 \pm 0.01) \times 10^{-2}$	$(1.6 \pm 0.06) \times 10^{-4}$	34 ± 2	-142 ± 8
$[PtCl_4]^{2-}$ <sup>a</sup>	(0.62 ± 0.01)	$(8.7 \pm 0.03) \times 10^{-4}$	31 ± 2	-133 ± 6
$[Pt(dien)Cl]^+$ <sup>b</sup>	$(7.78 \pm 0.08) \times 10^{-3}$	$(1.2 \pm 0.04) \times 10^{-4}$	20 ± 2	-118 ± 8
$[Pt(terpy)Cl]^+$ <sup>c</sup>	$(5.70 \pm 0.12) \times 10^{-2}$	$(2.0 \pm 0.08) \times 10^{-4}$	-	-

<sup>a</sup> Statistically corrected rate constants; values refer to 1.00 M perchloric acid; errors quoted are standard deviations; <sup>b</sup> Ref. [14]; <sup>c</sup> Ref. [13]

with respect to their reactions with thioglycolic acid strongly suggest that the activation processes are very similar. The activation entropies listed in Table 1 have large negative values which is compatible with an associative A mechanism.

Tetrachloroplatinate(II) is more reactive than tetraaquaplatinum(II) in spite of the tetraqua complex being the smallest metal ion of platinum(II) and sterically unhindered. This difference in reactivity could be explained by the higher *trans*-effect of the chloro ligand in  $[PtCl_4]^{2+}$  compared to the water in  $[Pt(H_2O)_4]^{2+}$ . The chloro ligand has a 350 times larger *trans*-effect compared to coordinated water [12]. However, the *cis*-effect and the leaving group effect are operative as well. A comparison of  $[Pt(terpy)Cl]^+$  (*terpy* = 2,2':6',2''-terpyridine) and  $[Pt(dien)Cl]^+$  (*dien* = 1,5-diamino-3-azapentane) shows that the platinum(II) *terpy* complex is more reactive [13, 14]. The difference in reactivity between these two complexes can be explained by the peculiar coordination geometry of the aromatic terpyridine ligand [15].

Second-order rate constants  $k_2$  for the formation of complexes between  $[Pt(H_2O)_4]^{2+}$  and various ligands are given in Table 2 and shows the usual strong dependence of the rate on the nature of the entering ligand. In other words, the large spread in  $k_2$  values supports an associative activation according to an A mechanism in which formation of the transition state involves bond formation between the incoming ligand and the complex. Moreover, this large sensitivity of the reaction rate to the  $\sigma$ -donor properties of the entering ligands is as expected for an associative mode of activation. From Table 2 it can also be seen that thioglycolic acid is a relatively good entering ligand for the tetraaquaplatinum(II) complex.

Undissociated thiols (HSR) may be expected to behave like thioethers ( $RSR_1$ ) taking into account the different electronic and steric peculiarities of H as compared to  $R_1$ . A comparison of thioglycolic acid and other sulfur-bonding ligands ( $Me_2SO$  excluded due to its ambidentate nature) shows that the latter, for instance thioethers [16–18], are better nucleophiles than thioglycolic acid. However, the difference in nucleophilicity between thiols and thioethers towards platinum(II) complexes could be explained by different steric and electronic structures of the sulfur atom [19–21].

The transition state of reactions (1) and (2) probably involves a proton. The reaction leads to deprotonation of the thioglycolic acid; the reaction product is the thiolate complex  $[PtCl_3(SR)]_2$ .

**Table 2.** Rate constants for formation ( $k_2$ ), aquation ( $k_{-2}$ ), and stability constants ( $K_2$ ) of  $[\text{Pt}(\text{H}_2\text{O})_3\text{L}]^{(2-z)+}$  in aqueous solution at 298 K<sup>a</sup>

$L^{n-}$	$k_2$ ( $M^{-1} \cdot s^{-1}$ )	$k_{-2}$ ( $s^{-1}$ )	$K_2 = k_2/k_{-2}$ ( $M^{-1}$ )	Ref.
H <sub>2</sub> O	$2.80 \times 10^{-5b}$	$3.9 \times 10^{-4}$	1	[30]
Cl <sup>-</sup>	$2.66 \times 10^{-2}$	$2.8 \times 10^{-7}$	$9.50 \times 10^4$	[22]
Br <sup>-</sup>	$2.11 \times 10^{-1}$	$1.1 \times 10^{-6}$	$1.92 \times 10^5$	[22]
I <sup>-</sup>	7.7	$8.0 \times 10^{-5}$	$9.62 \times 10^4$	[31]
SCN <sup>-</sup>	1.33	–	–	[22]
Me <sub>2</sub> SO	$8.4 \times 10^{-5}$	–	$>10^7$	[12]
Me <sub>2</sub> S	3.6	$6.6 \times 10^{-6c}$	$5.45 \times 10^5$	[18]
Et <sub>2</sub> S	1.92	–	–	[18]
S(CH <sub>2</sub> ) <sub>4</sub> O	1.47	$3.6 \times 10^{-6c}$	$4.08 \times 10^5$	[18]
S(CH <sub>2</sub> ) <sub>4</sub> S	2.48 <sup>d</sup>	–	–	[18]
SC(NH <sub>2</sub> ) <sub>2</sub>	13/9	–	$>10^7$	[23]
SHCH <sub>2</sub> COOH	$2.10 \times 10^{-1}$	$1.6 \times 10^{-1}$	$1.31 \times 10^3$	This work

<sup>a</sup> All values refer to 1.00 M perchloric acid; <sup>b</sup> estimations based on the observed first-order exchange rate constant divided by an assumed concentration of water of 55 M; <sup>c</sup> calculated from stability constants; <sup>d</sup> per S:  $0.31 M^{-1} \cdot s^{-1}$

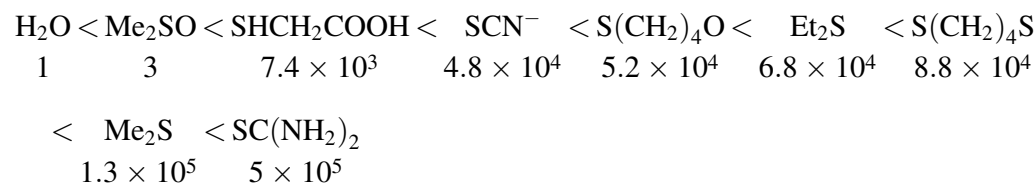
**Table 3.** <sup>1</sup>H NMR shifts ( $\delta$ , ppm) relative to internal TMS

	$\delta(\text{CH}_2)$	$\delta(\text{SH})$
Thioglycolic acid	3.35	2.63
$K_2[\text{PtCl}_3(\text{SR})]$	3.55	–

For the reaction between  $[\text{Pt}(\text{terpy})\text{Cl}]^+$  and different thiols, the same mechanism has been suggested [13]. However, deprotonation of the products  $[\text{Pt}(\text{terpy})(\text{HSR})]^{2+}$  has been observed, and the reaction leads to the thiolate complexes  $[\text{Pt}(\text{terpy})(\text{SR})]^+$  as well [13].

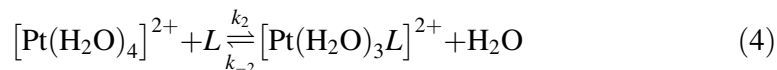
Table 3 contains the <sup>1</sup>H NMR spectroscopic data for the free thioglycolic acid and for the complex  $K_2[\text{PtCl}_3(\text{SR})]$  which is the reaction product. It can be seen that the chemical shift of the CH<sub>2</sub> group of thioglycolic acid is shifted downfield when it is coordinated to platinum. Furthermore, there is no signal of the SH group in the spectrum of the complex  $K_2[\text{PtCl}_3(\text{SR})]$ . Clearly, this is an evidence for the deprotonation of the thioglycolic acid when it is coordinated to platinum.

A comparison of the rate constants in Table 2 for the reactions of tetra-aquaplatinum(II) complexes with sulfur-bonding ligands [12, 18, 22, 23] gives as a first approximation the following entering ligand order for water as a leaving ligand:



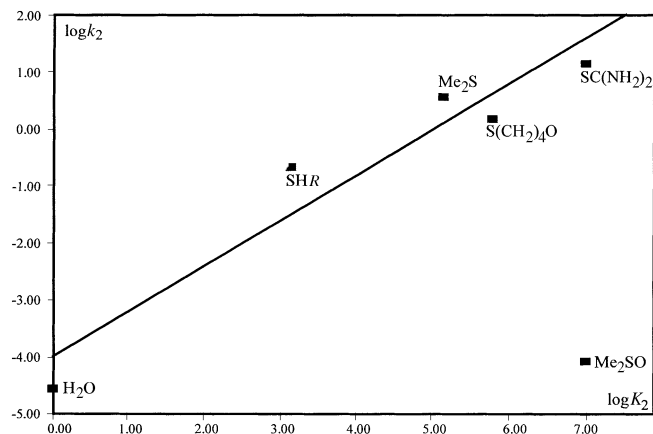
The sequence of reactivity is in excellent agreement with the order of electron density on the sulfur atom. Hence, electronic effects of the substituents  $R$  and  $R_1$  have an obvious influence on the reactivity.

In Fig. 3, a linear free energy relationship (LFER) diagram is shown for a collection of ligand substitution reactions according to Eq. (4) where all ligands involved are sulfur-bonding, neutral, and monodentate.



The straight line indicates that all sulfur-bonding ligands react *via* the same mechanism. The slope is 0.79, indicating that the activated complex and the products closely resemble another. The closer to unity the value of the slope, the more dominant the bond-making contribution; and a value of 0.79 might be indicative of a rather strongly associative mode of activation, although not a limiting associative one [24]. Further support for this conclusion is obtained from the fact that there seems to exist a certain spread of  $k_{-2}$  values (cf. Table 2), indicating some effect of the leaving ligand on the rate of reaction. The large deviation of dimethyl sulfoxide from the linear plot may probably be attributed to a different reaction mechanism.  $\text{Me}_2\text{SO}$  and other sulfoxides are in general poor entering ligands in reactions with platinum(II) and palladium(II) complexes [25–27]. This is rather surprising, since ligands coordinating *via* sulfur atoms (as shown by crystal structures of platinum(II) complexes [25–27]) are generally also good entering groups [18]. It has been suggested that the rate-determining step in the  $\text{Me}_2\text{SO}$  reaction, is the formation of an oxygen-bonded intermediate, followed by a rapid intramolecular isomerization to the thermodynamically more stable sulfur-bonded complex [25–27]. This two-step procedure might account for the low value of rate constants.

The LFER shown in Fig. 3 could be very useful, for instance to extrapolate rate or stability constants as well as to detect mechanistic deviations (as in the case of  $\text{Me}_2\text{SO}$ ). A linear relation between  $\log k_2$  and  $\log K_2$  observed for the complex



**Fig. 3.** Linear free energy relationship between rate constants ( $\log k_2$ ) and stability constants ( $\log K_2$ ) for reactions of  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  with sulfur-bonding ligands; values from Table 2

formation of  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  with those sulfur-bonding ligands supports an A mechanism.

## Materials and Methods

### *Chemicals and solutions*

Potassium tetrachloroplatinate(II) (Johnson and Matthey) was used directly. A solution of tetra-aquaplatinum(II) perchlorate (*ca.* 10 mM) in 1.00 M perchloric acid (Baker, p.a.) was prepared from  $\text{K}_2[\text{PtCl}_4]$  (Johnson and Matthey) and  $\text{AgClO}_4$  (G. F. Smith) as described previously [32]. The metal concentration was determined spectrophotometrically from the absorbance at 275 nm, where the molar absorptivity of  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  is  $56.5 \text{ M}^{-1} \cdot \text{cm}^{-1}$ . The concentration of perchloric acid was determined potentiometrically. The ionic strength was 1.00 M with perchloric acid (Baker, p.a.) as supporting electrolyte. At the low *pH* used, hydrolysis of the complex is negligible. The spectra were identical to those reported earlier [32]. Ligand stock solutions were prepared shortly before use from freshly distilled thioglycolic acid (Merck, p.a.) and diluted with 1.00 M perchloric acid. Under this experimental conditions, thioglycolic acid was protonated. All solutions were flushed with nitrogen to remove dissolved oxygen. Water was double distilled from quartz vessels.

### *Kinetic measurements*

The reactions were sufficiently slow to be followed spectrophotometrically by measuring the changing of absorbance at suitable wavelengths as a function of time. The kinetics were followed using a Varian Super-Scan 3 double-beam spectrophotometer equipped with water thermostatted cells. All reactions were started by mixing equal volumes of reactants in the cell and recording the change of absorbance at 240 nm. The kinetic measurements were performed between 288 and 308 K using a large excess of platinum(II) complexes (at least ten-fold excess) to obtain *pseudo*-first-order rate conditions. Attempts to study the reactions by use of excess of ligands were unsuccessful because of disturbance from subsequent formation of higher complexes. The *pseudo*-first-order rate constants,  $k_{\text{obsd}}$ , were determined graphically from a plot of  $\ln(A_\infty - A_t)$  vs. time [11] ( $A_t$  and  $A_\infty$  are the absorbances of the reaction mixture at time  $t$  and at the end of the reaction, respectively, usually after 10 half-lives) or from a non-linear least-squares fit of the experimental data to Eq. (5) with  $A_0$ ,  $A_\infty$ , and  $k_{\text{obsd}}$  as the parameters to be optimized. Rate constants were accurate within 5%.

$$A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{\text{obsd}}t) \quad (5)$$

### *NMR measurements*

NMR spectra were obtained with a Varian Gemini 200 MHz spectrometer equipped with a 5 mm probe for  $^1\text{H}$  NMR measurements  $\text{DMF-d}_7$  (Merck); chemical shifts ( $\delta$ ) are reported in ppm relative to *TMS*. The reaction product potassium trichloro(thioglycolate)platinate(II),  $\text{K}_2[\text{PtCl}_3(\text{SR})]$ , was isolated, and its  $^1\text{H}$  NMR spectrum was recorded.

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