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Kinetics of the Reaction of the Dinitrooxalatoplatinate(II) Ion with Thiocyanate

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The reaction of $Pt(NO_2)_2C_2O_4^{2-}$ with SCN^- in water takes place in at least three steps and gives $Pt(SCN)_4^{2-}$ as a final product. Two intermediate products were isolated and identified as *cis*-$PtC_2O_4(NO_2)_2SCN^{3-}$ and *trans*-$PtC_2O_4(SCN)_2NO_2^{3-}$, in which the oxalato ligand appears to be unidentate. The rate constants and the activation parameters were measured and support the assumption that this reaction takes place with a ring-opening mechanism.

To begin examination of the mechanism of substitution reactions of the $Pt(C_2O_4)^{2-}$ complex with mono-[1] or bidentate ligands,[2] the $Pt(NO_2)_2C_2O_4^{2-} + SCN^-$ reaction was studied.

The intermediates of these reactions are the first examples of complexes containing unidentate oxalato groups, which have been often postulated in many reaction mechanisms involving planar or octahedral oxalato complexes.[3,4] Another peculiarity of these reactions is that in the presence of the unidentate oxalato ligand the kinetic equation exibits a first-order contribution (solvent path) greater than the reagent-dependent path, despite the small H_2O reactivity.

It was therefore of interest to confirm the ring-opening mechanism and the stability of the unidentate oxalato group also in a complex containing a good trans-activating ligand.

Experimental Section

Materials. The $K_2Pt(NO_2)_2C_2O_4$ complex was prepared following literature methods[5] and examined by elementary analysis and by ir spectrophotometry (Table I). All other chemicals were Erba RP reagents, recrystallized twice from conductivity water.

Anal. Calcd for $K_2Pt(NO_2)_2C_2O_4{\cdot}2H_2O$: Pt, 39.90; C, 4.90; N, 5.72; H, 0.82; K, 15.97. Found: Pt, 39.73; C, 5.0; N, 5.7; H, 0.82; K, 15.87.

Spectrophotometry Measurements. The absorption spectra taken at suitable intervals during the reaction under examination are shown in Figure 1 and indicate that the reaction occurs in three consecutive steps. Spectrum A corresponds to that of the initial $K_2Pt(NO_2)_2C_2O_4$ complex, which reacts very quickly to give spectrum B. The second and third steps correspond to the spectrum changes B → C and C → D, respectively.

The first step of the reaction was followed by using a Durrum "stopped-flow" spectrophotometer at 280 nm; the second and the third were investigated with a Hilgher-Watts Uvispek H700 spectrophotometer at 297 nm. In the last method the initial amount of $K_2Pt(NO_2)_2C_2O_4$ was introduced and weighed directly in a 2-cm optical cell as a concentrated solution of known titer. KSCN was added, after thermostating, by means of a microsyringe. The first reading was taken after a time interval corresponding to about 6 half-lives of the first step (A → B).

During the second (B → C) and third steps (C → D), the optical density, OD, initially decreases (at 297 nm) reaching a minimum value after about 12 min and then slowly increases (Figure 2).

Reaction Products. The reaction intermediates (B and C) were isolated from the reaction mixture by fast cooling and addition of $Pt(NH_3)_4Cl_2$ at the end of the respective product-forming steps. The intermediates give microcrystalline yellow precipitates, whose ir data are reported in Table I. It was impossible to obtain these compounds with other cations, leading to simpler ir spectra. The elemental analysis of two precipitates give the following results.

Anal. for intermediate B. Calcd for $[Pt(NH_3)_4]_3[PtC_2O_4(NO_2)_2SCN]_2{\cdot}3H_2O$: Pt, 57.1; C, 4.2; N, 14.7; S, 3.75; H, 2.5. Found: Pt, 56.7; C, 4.30; N, 14.95; S, 3.85; H, 2.6.

Anal. for intermediate C. Calcd for $[Pt(NH_3)_4]_3[PtC_2O_4(SCN)_2NO_2]_2{\cdot}3H_2O$: Pt, 56.27; C, 5.53; N, 14.53; S, 7.39; H, 2.44. Found: Pt, 56.67; C, 5.60; N, 14.00; S, 7.20; H, 2.5.

The final product of the reaction was isolated and analyzed with the same method and corresponds to $Pt(NH_3)_4Pt(SCN)_4$.

In order to obtain further information on the reaction mechanism, the nitrite ions developed during the reaction were estimated by the nitritometric method (sulfanilic acid and α-naphthylamine.[6] The optical density of the orange dye was measured at 520 nm. At the end of the first step of the reaction no traces of NO_2^- ion were detected, whereas after the end of the second and the third step the concentration of NO_2^- developed was the same as and twice the initial $K_2Pt(NO_2)_2C_2O_4$ concentration, respectively.

Kinetic Results. All kinetics have been run in an excess of SCN^- (in the range 10^{-2}–10^{-1} *M*) with respect to the reagent complex (3×10^{-4} *M*).

The rate constants, k'_{obsd}, for the first step of the reaction (A → B, Figure 2) were measured at 280 nm and evaluated graphically by standard methods. The experimental infinity value remained constant because at this wavelength the OD changes of the second step are negligible. The rate constants' reproducibility, as judged by many duplicated runs, is within 5%.

The k'''_{obsd} values for the third step of the reaction (C → D) was similarly calculated, by neglecting the first part which was still influenced by the previous step. The reproducibility in this case is about ±3%.

The rate constants for the first and the third steps show a linear dependence upon the thiocyanate ion concentration, $k_{obsd} = k_1 + k_2[SCN^-]$.[4] The k_1 and k_2 values (which are related to the via-solvent and via-SCN paths, respectively), evaluated from six to eight kinetic runs for each step or temperature, are reported in Table II. The k_1 values are very small. However, while for the first step this value is zero within experimental error, for the third step it is significant, despite the large error (±15%).

The k''_{obsd} values were calculated by applying the least-squares method to the well-known equations for consecutive first-order reactions.[7] A set of variables, k''_{obsd}, ϵ_B, and ϵ_C, was determined for each kinetic run (ϵ_B and ϵ_C are the molar absorptivities of the final products of the first and second steps, respectively).

A confirmation of the reliability of this calculation is given by the reproducibility of the ϵ_B and ϵ_C values, obtained for nine kinetics runs at various SCN^- concentrations: $\epsilon_B = 1230 \pm 70$ and $\epsilon_C = 1020 \pm 50$. The maximum variation of the rate constant is only 20%, $k''_{obsd} = (2.2 \pm 0.2) \times 10^{-3}$ sec^{-1}, despite the great change in thiocyanate concentration. Therefore, the SCN path, if present at all, is very small compared to the solvent path.

Discussion

Table I gives the ir spectrum of the $K_2Pt(NO_2)_2C_2O_4$ complex, which, to the best of our knowledge, is unknown in the literature. The observed bands are assigned by comparison with the frequencies reported for $PtC_2O_4(NH_3)_2$,[8] $K_2Pt(C_2O_4)_2$,[9] and *cis*- and *trans*-dinitro complexes of Pt(II).[10,11] The two sharp and quite distinct bands at 850 and 842 cm^{-1} and the presence of an additional band at 1350 cm^{-1} are characteristic of *cis*-dinitro complexes of Pt(II).[11]

The ir spectra of the two intermediates (Table I) are very similar, both because the two compounds have the same ligands and because some spectral regions characteristic of C_2O_4 and NO_2 groups (1600–1300 and 850–800 cm^{-1}) are complicated by the superposition of the Pt–NH_3 bands. However some bands are characteristic and sufficient to determine the structure of the intermediates. In both spectra the peak at 2115 cm^{-1} is single and sharp, in accordance with the presence of only one SCN ligand in the intermediate B and two SCN ligands in trans position for the intermediate C.[12] In the two compounds the peaks assigned to antisymmetric stretching (1620–1600 cm^{-1}) of –COO have frequencies markedly lower than those of the bidentate oxalato complexes (1700–1750

Table I. Infrared Spectral Data (cm^{-1}) (KBr Pellets)

$K_2Pt(NO_2)_2Ox$	*cis*-$[Pt(NH_3)_4]_3$-$[PtOx(NO_2)_2SCN]_2$	*trans*-$[Pt(NH_3)_4]_3$-$[PtOx(SCN)_2NO_2]_2$	Assignments	Ref
	2115 s	2115 s	ν_s(SCN)	12
1705 s, 1680 s, 1667 s			ν_{as}(C=O)	8, 9
1610 s	1610 s, 1440 sh, 1385 s	1610 s, 1440 sh, 1385 s	ν_{as}(C=O) + $\delta(NH_3)$	1, 2, 13
1425 s, 1400 s	1340, 1320, 1290	1320, 1290	$\nu(NO_2)$	10, 11
1380 s			ν_s(C–O) + ν(C–C)	8, 9
1350 s, 1325 s			$\nu_s(NO_2)$	10, 11
1250 m, 900 m-w	900 m	900 m	ν_s(C–O) + δ(O–C=O)	8, 9
850 s, 842 s			$\delta_s(NO_2)$	10, 11
815 s			δ(O–C=O) + ν(Pt–O)	8, 9
	850 sh, 835 m, 812 sh	830 m, 812 sh	$\delta(NH_3)$ + $\delta(NO_2)$ + δ(O–C=O) + ν(Pt–O)	10, 11
	760 s	760 s	δ(O–C=O) + ν(Pt–O)	
568 m			ν(Pt–O) + ν(C–C)	8, 9
475 m			Ring def + δ(O–C=O)	10, 11
Not identified	560 w, 510 w	510 w	ν(Pt–N)	2

Table II. k_1 (sec^{-1}) and k_2 ($sec^{-1}\ M^{-1}$) Values for the Three Steps of the Examined Reaction, at Various Temperatures in Water at $I = 0.1\ M^a$

		First Step		
Temp, °C	25.0	30.0	35.0	40.0
k_1'	0.0	0.0	0.0^2	0.0^2
$k_2'\ ^b$	3.65	4.45	5.35	6.35
		Second Step		
Temp, °C	24.9			
$10^3k_1''$	2.2			
		Third Step		
Temp, °C	24.9	34.2	39.7	44.1
$10^3k_1'''$	0.02	0.04	0.04	0.04
$10^3k_2'''\ ^c$	1.13	2.80	4.83	7.65
$10^3k_1'''\ ^d$		0.01		
$10^3k_2'''\ ^d$		4.75		

[a] For the first step the cation present in the reaction mixture is Na^+; for second and third steps the cation is K^+. [b] For k_2' $\Delta H^\ddagger = 6.3 \pm 0.1$ kcal/mol and $\Delta S^\ddagger = -35 \pm 2$ eu. [c] For k_2''' $\Delta H^\ddagger = 19.5 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -11 \pm 2$ eu. [d] In the presence of $[Ba^{2+}] = 0.05\ M$.

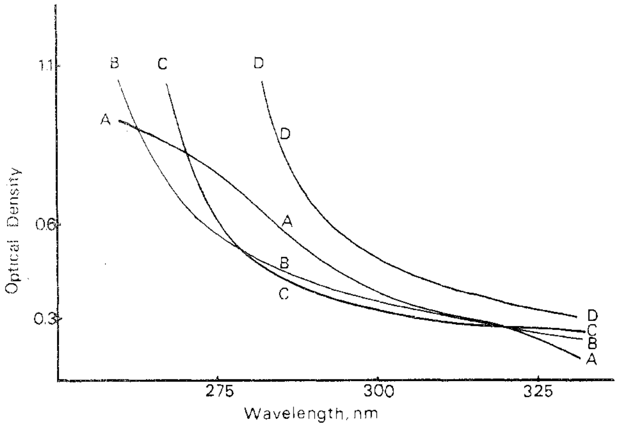


Figure 1. Absorption spectra: (A) of the initial complex, $3 \times 10^{-4}\ M$; (B) at the end of the first step; (C) at the end of the second step; (D) after 2 hr of reaction with KSCN 0.1 *M* at 25°.

cm^{-1})[9] and almost equal to that of ionic oxalate (1600 cm^{-1}).[13] This is in agreement with the frequencies found in other unidentate oxalato complexes[1,2] of Pt(II). Finally the intermediate B shows, as expected for *cis*-dinitro complexes, a strong band at 1350 cm^{-1} [10] and two Pt–N stretching vibrations at 560 and 510 cm^{-1}.[10] The trans intermediate C has no band at ca. 1350 cm^{-1} and only one band, as expected, at 510 cm^{-1} for the Pt–N vibration.

On the basis of the analytical data of the two intermediates, the nitrometric analysis, and the rate constants, the total reaction takes place according to Scheme I (the *k*'s refer to a temperature of 25°). In the first step of the reaction, as in other $Pt(C_2O_4)_2^{2-}$ reactions,[1-3] the ring opening occurs practically without the usual first-order contribution due to solvent. The very low, undetectable value of k_1' (Table II) can be attributed either to the small nucleophilicity of H_2O or to the high probability of the unimolecular ring closure, which competes with the entering nucleophile in displacing the H_2O molecule (bimolecular process).

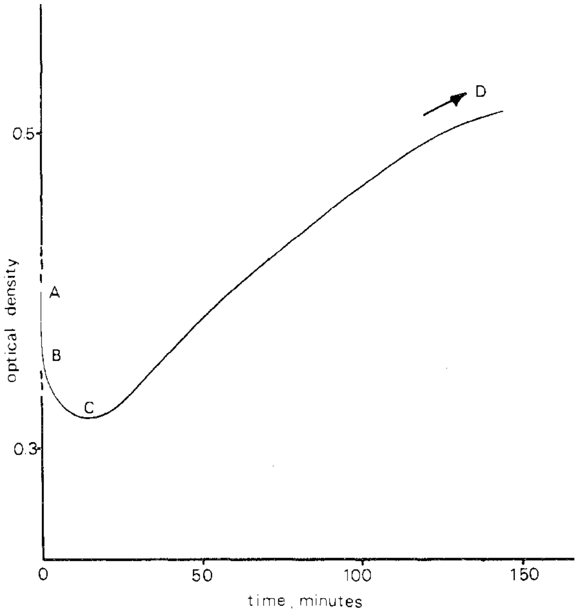


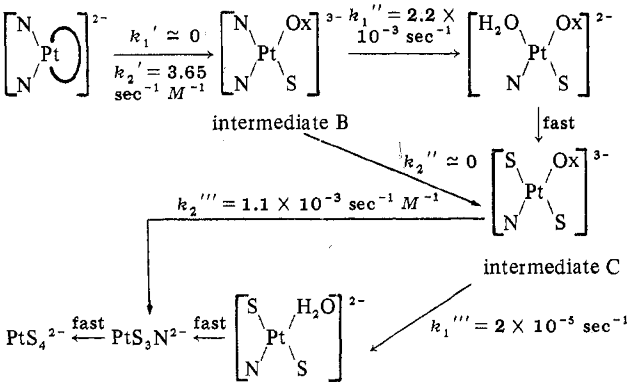
Figure 2. Absorbance changes with time, at 297 nm. Symbols and reaction conditions are the same as reported in the caption to Figure 1.

It is interesting to compare the first step of this reaction with that of $Pt(C_2O_4)_2^{2-}$ + SCN^-, in which the kinetic parameters corresponding to the opening of the oxalato ligand are $k_{SCN} = 6.35 \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 25°, $\Delta H^\ddagger = 13$ kcal/mol, and $\Delta S^\ddagger = -24$ eu.

The rate constat k_2' (Table II) is 500 times greater than k_{SCN} and this is largely due to the decrease in $\Delta H^\ddagger$, depending on the difference in the trans effect $NO_2 \gg C_2O_4$, which compensates the strong decrease in $\Delta S^\ddagger$. The entropies of activation appear always to be negative for the reactions of Pt(II) complexes and to depend very little on solvent effects. It is probable, therefore, that the decrease in $\Delta S^\ddagger$ can be due to the increased bond order (interactions) between Pt and NO_2 ligand[4,14] in the transition state.

For the second step of the reaction it is found that k_2'' is negligible even at the highest [SCN] studied. This result, which is unusual for reactions of Pt(II) complexes, is reminiscent of the kinetic data found for the second step of the bis(oxalato)platinate(II) reaction with thiocyanate.[1] In the

Scheme I



N = NO$_2$; S = SCN; Ox = monodentate C$_2$O$_4$; ◯ = bidentate C$_2$O$_4$

next case, the hypothesis under examination was that of a stabilization of the activated complex due to the formation of a hydrogen bridge between the entering H_2O molecule and the "free" end of the unidentate oxalato. This reaction mechanism is similar to that proposed for some substitution reactions of octahedral amino complexes and has been named S$_N$2FS[15] (where the entering water molecule is hydrogen bonded both to a leaving group and to an inert amine group) or to the "anchoring effect", invoked to explain the kinetic behavior of the bidentate amine as entering groups in Pt(II) complexes.[16]

For the third step of the reaction, where $k_1''' \ll k_2'''[\mathrm{SCN}]$, two mechanisms are possible: (1) the oxalato ligand substitution precedes NO_2 (eq 1); (2) the NO_2 ligand is the first group to leave, followed by C_2O_4 in an even faster reaction. The second mechanism is less probable, because, in the presence of the unidentate oxalato ligand, it should lead to the same kinetic results of the second step, i.e., $k_1''' > k_2'''[\mathrm{SCN}]$. On the contrary in mechanism (1) the entropy values also appear to support the mechanism proposed in Scheme I. In the third step $\Delta S^{\ddagger}$ is higher than in the first, despite the increased charges of the anion reagents. This result is in agreement with that of the $Pt(C_2O_4)_2^{2-} + SCN^-$,[1] where the opening process of the bidentate ring (first step) has a much more negative $\Delta S^{\ddagger}$ than that of the substitution reaction of the unidentate oxalato group (second step).

In Table II the kinetic salt effect of the Ba^{2+} ion is also reported, confirming the results obtained in other Pt(II) reactions.[1,2,17] The specific character of these results can be explained by two different mechanisms. In the first, similar to that postulated for the electrophilic catalysis, the cations interact with the Pt(II) anions, through the elongated z axis.[18] By removing d valence orbital electrons, the metal can then more readily accept the bonding electrons from the entering nucleophile. Another explanation is that the cation electrophilic attack takes place on the coordinated oxalato group, causing in this case Pt–O bond rupture.[1] It is probable that both mechanisms are present, because on the substitution reaction of Pt(II) complexes the bond-making and the bond-breaking processes are equally important.

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Registry No. $Pt(NO_2)_2C_2O_4^{2-}$, 54516-14-2; *cis*-$[Pt(NH_3)_4]_3[PtOx(NO_2)_2SCN]_2$, 54531-59-8; *trans*-$[Pt(NH_3)_4]_3[PtOx(SCN)_2NO_2]_2$, 54531-61-2; SCN^-, 302-04-5; $C_2O_4^{2-}$, 338-70-5; NO_2^-, 14797-65-0.

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Notes

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Five-Coordinate Copper(II) Complexes. Synthesis and Properties of $[Cu(tren)L]^{2+}$ Cations

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The presence in solution of five-coordinate copper(II) complexes of the type $[Cu(tren)X]^{n+}$ (n = 1 or 2; tren = 2,2',2''-triaminotriethylamine) has been previously suggested.[2] However, such complexes have not been isolated except in the case of [Cu(tren)NCS]SCN.[3] A trigonal-bipyramidal structure has been deduced for the latter complex from X-ray diffraction studies.[4]

We now report the synthesis and characterization of some complexes of the type $[Cu(tren)L]Y_2$ (L = amine ligand; Y^- = BPh_4^- or ClO_4^-) (Table I), prepared by two different general procedures. By the first method (A) the complexes have been obtained by the reaction (at room temperature in 2% $NaHCO_3$ aqueous solution) of equimolar ratios of a copper(II) salt (sulfate or chloride) and the tetradentate and the monodentate amine ligands. The immediate color change of the solution from light to very deep blue indicated that a very fast reaction had taken place. The products were easily precipitated from the solution by adding $NaBPh_4$. By the second method (B)

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