can be seen that these values are very similar to k_{10}, ΔH_{10}^*, and ΔS_{10}^*, respectively, given in Table III, providing additional evidence for the view that the rates of complex formation are controlled primarily by the rate of loss of a coordinated water molecule from the cation.[4,12,16]

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Oxalate Exchange in the Bisoxalatoplatinate(II) Ion

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The kinetics of the exchange between bisoxalatoplatinate(II) ion and free oxalate have been examined in weakly acidic aqueous medium. Under the conditions employed (25°, pH 3.6–6.8, ionic strength = 0.17–0.55) the exchange proceeds very slowly according to the two-term rate law: oxalate exchange rate = $k_1[\mathrm{Pt(C_2O_4)_2}^{-2}] + k_2[\mathrm{Pt(C_2O_4)_2}^{-2}][\text{oxalate}]$. Both rate constants are essentially independent of hydrogen ion concentration; k_1 is also independent of ionic strength while k_2 increases with increasing ionic strength. Typical values for the constants at 25° are: pH 4.7 (oxalate buffer), ionic strength = 0.170, $k_1 = 1.6\ (\pm 0.2) \times 10^{-9}$ sec.$^{-1}$, $k_2 = 4.6\ (\pm 0.3) \times 10^{-7}\ M^{-1}$ sec.$^{-1}$. The results are interpreted in terms of a mechanism involving intermediates containing monodentate oxalate ligands.

Many workers[3] have investigated substitution reactions of monodentate ligands in square complexes. In general these reactions have been found to exhibit a combination of first- and second-order rate behavior, considerable evidence existing to imply that the first-order term involves solvent participation. Also, exchange reactions between free and coordinated oxalate have been reported for various metal complexes.[4–9] To the best of our knowledge, however, this is the first reported kinetic study of oxalate exchange in a square complex.

Experimental

(A) **Materials.**—Potassium bisoxalatoplatinate(II) dihydrate was prepared by the reaction of potassium hexachloroplatinate(IV) (J. Bishop and Co.) with excess oxalate.[10] The resultant salt was recrystallized three times from distilled water, washed with absolute alcohol, and dried at 70°. Portions of the salt were analyzed for carbon and hydrogen by the usual procedure, the residue being heated in a stream of carbon dioxide and weighed as platinum plus potassium carbonate.[11] The potassium content of a solution of the salt was estimated by passing measured volumes through Dowex 50W-X8 ion-exchange resin in the H^+ form and titrating the effluent solution with standard sodium hydroxide using methyl red as an indicator. A typical analysis is given. *Anal.* Calcd. for $K_2Pt(C_2O_4)_2 \cdot 2H_2O$: K, 16.11; Pt, 40.20; C, 9.89; H, 0.82. Found: K, 15.89; Pt, 40.6; C, 10.12; H, 0.94. For the exchange experiments the potassium salt was quantitatively converted into the more soluble sodium salt by treatment of an aqueous solution at 80° with Dowex 50W-X8 cation-exchange resin in the sodium form.

Sodium oxalate with a carbon-14 activity of ~1.7 μcuries per mg. was obtained from International Chemical and Nuclear Corporation. Water was obtained by heating ordinary distilled water with $KMnO_4$ and NaOH and redistilling in a Barnstead S-1 apparatus. All other materials employed were of reagent grade.

(B) **Preparation of Exchange Solutions.**—Reactant solutions were prepared by mixing appropriate volumes of sodium bisoxalatoplatinate(II) solution, 0.050 *M* oxalate solution[12] with a carbon-14 activity of ~0.5 μcurie per ml., sodium nitrate solution (for ionic strength adjustment), and distilled water. In some cases inactive oxalate solution and/or a phosphate buffer solution was also added. The reaction was studied at three different pH values, namely, 3.6, 4.7, and 6.8. In the first two cases it was possible to use the active oxalate solution as a buffer, and it was ascertained by pH measurements on similar but inactive solutions that variation of the uncomplexed oxalate concentration (from 1×10^{-3} to 2×10^{-2} *M*) in the various exchange solutions did not change the pH by more than ±0.1 unit. For the highest pH it was necessary to buffer the exchange solutions by the addition of an appropriate phosphate solution. For more strongly acidic conditions (pH <3) we were unable to obtain consistent kinetic results, and it was also visually apparent that a reaction other than oxalate exchange was taking place; possibly polymerization of the bisoxalatoplatinate(II) ion.[13] Reactant solutions were stored in the dark at a temperature of 25.00 ± 0.05°.

(C) **Exchange Procedure and Calculations.**—In a given experimental run the amount of exchange was determined by duplicate determinations after three periods of time, usually ~100, 200, and 300 hr. Quenching was achieved by adding an aliquot of the reactant solution to an equal volume of 10% potassium chloride solution and cooling to 0°. Under these conditions potassium bisoxalatoplatinate(II) dihydrate is precipitated in 2–3 hr.[14] The precipitate was filtered and washed with ice-cold

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[1] Supported by the National Science Foundation under Grant G11283.

[2] Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[3] See, for example: (a) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954); (b) D. Banerjea, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **79**, 4055 (1957); (c) A. A. Grinberg, *Russ. J. Inorg. Chem.*, **4**, 139 (1959); (d) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962); (e) S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

[4] F. A. Long, *J. Am. Chem. Soc.*, **61**, 570 (1939).

[5] D. R. Llewellyn and A. L. Odell, *Proc. Australian At. Energy Symp.*, 623 (1958).

[6] D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962).

[7] F. A. Johnson and E. M. Larsen, *ibid.*, **1**, 159 (1962).

[8] F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).

[9] K. V. Krishnamurty and G. M. Harris, *ibid.*, **64**, 346 (1960).

[10] P. Pascal, "Traité de Chemie Minérale," Masson et Cie., Paris, 1928, p. 672.

[11] Analyses by S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

[12] Oxalate concentrations refer to the total concentrations of all uncomplexed oxalate species in solution.

[13] K. Krogmann and P. H. Dodel, Proceedings of the 7th International Conference on Coordination Chemistry, 1962, p. 67.

[14] Analysis of a carefully dried precipitate confirmed the formula $K_2Pt(C_2O_4)_2 \cdot 2H_2O$. This result and observations that spectra of solutions of the platinum complex remain essentially constant for 1 or 2 weeks, both in the presence and absence of phosphate buffer, support the view that aquation is unimportant and that no significant amounts of phosphate become incorporated in the coordination sphere of the platinum.

TABLE I[a]

	Sample 1	Sample 2
Sample weight, mg.	1.99	1.38
Measured activity, counts min.$^{-1}$	296.8	228.6
Background, counts min.$^{-1}$	23.6	23.6
Apparent specific activity, counts mg.$^{-1}$ min.$^{-1}$	137.3	148.3
Correction for sample wt., counts mg.$^{-1}$ min.$^{-1}$	+11.0	−3.0
Correction for activity at zero time, counts mg.$^{-1}$ min.$^{-1}$	−2.0	−2.0
Corrected specific activity, counts mg.$^{-1}$ min.$^{-1}$	146.3	143.3
Percentage exchange of *one* ligand of complex	*0.559*	*0.547*

[a] pH 4.7, ionic strength = 0.550, 25.0°, $[Pt(C_2O_4)_2^{-2}]$ = 0.00291 *M*, [oxalate*] = 0.00407 *M*, exchange time 183 hr. 100% exchange for *one* ligand of complex ≡ 26,200 counts mg.$^{-1}$ min.$^{-1}$.

water. One or two mg. of the separated bisoxalatoplatinate(II) salt was then dissolved in hot water, and the solution was evaporated to dryness on a stainless steel planchet, care being taken to obtain a uniform deposit.

After heating at 110° for 2 hr., the deposit was weighed as the anhydrous salt and the activity was measured by means of a gas-flow proportional counter at a tube potential at 1450 volts. The dehydration process was confirmed by the fact that the weight of a 50-mg. sample of $K_2Pt(C_2O_4)_2 \cdot 2H_2O$ decreased by ~8% when treated in the above manner and did not vary with further heating. All weighings were performed in triplicate, after reheating of the planchets before each reweighing, and the weights were found to be consistent with the average to within ±0.03 mg. (planchet weight = 2–3 g.; sample weight = 1–2 mg.).

The active oxalate content for each sample was estimated by comparison with standard samples of potassium bisoxalatoplatinate(II) prepared from oxalic acid containing a known proportion of active oxalate. Standard samples of active potassium oxalate, employed as a secondary standard, were found to agree with the activities of theoretically similar active complex samples to within 2%. This confirmed that there had been no large isotope effect in the preparation of the active potassium bisoxalatoplatinate(II).

A series of samples was prepared containing a constant amount of active potassium bisoxalatoplatinate(II) and varying amounts of the inactive salt in order to obtain total sample weights through the range 0.75–2.5 mg. From the apparent activities of these samples an empirical expression was obtained relating the recorded activity to the total sample weight, *viz.*

$$\frac{\text{specific activity at sample weight of } x \text{ mg.}}{\text{specific activity at sample weight of 1.5 mg.}} = 1.22 - 0.145x$$

The above equation enabled the apparent specific activities of samples of known weights to be corrected to values which would be expected if the samples had been 1.50 mg. and contained similar amounts of active oxalate. This treatment reduced the errors caused by self-absorption and self-scattering in comparing the activities of samples of different weight.

Because less than 2% of the complexed oxalate exchanged within the time of the studies, the exchange rate could be calculated directly from the activity of the sample. When reactant solutions were quenched immediately after mixing the reactants (*i.e.*, at zero time) the amount of exchange observed was about 3% of that found for a typical solution after 100 hr. at 25°. Also, repeated recrystallization of a sample of the active salt obtained from a typical exchange experiment had no significant effect upon its measured activity. The two preceding observations indicate how it was possible to follow the reaction with a reasonable degree of accuracy in spite of the small total amount of exchange.

TABLE II[a]

Time, hr.	% exchange (of one ligand)	Exchange rate × 10^5 [b]
69	0.095	1.38
69	0.116	1.68
163	0.223	1.37
163	0.261	1.60
235	0.327	1.37
235	0.366	1.56

[a] pH 3.6, ionic strength = 0.170, 25.0°, $[Pt(C_2O_4)_2^{-2}]$ = 0.00291 *M*, [oxalate*] = 0.00651 *M*. [b] Moles of oxalate per mole of complex per hour.

Table I illustrates the method of calculating the amount of exchange for a typical pair of duplicate samples obtained from a reaction solution.

To obtain the rate of exchange corresponding to specific reaction conditions (concentrations of reactants, ionic strength, etc.), a set of such duplicate results was obtained for each of three reaction times. The average rate was then calculated from the six values so obtained. A typical set of such data is shown in Table II.

Results

Rates of exchange, calculated in accord with the method described above, are given in Table III for varying values of pH, ionic strength, and oxalate concentration. For each of series I through V of Table III the results can be described by a rate equation of the type given in eq. 1. This relationship is demon-

$$\text{oxalate exchange rate} = \{k_1 + k_2[\text{oxalate}]\}[Pt(C_2O_4)_2^{-2}] \quad (1)$$

strated by Fig. 1 in which the results for series I have

TABLE III[a]

Series	pH	Ionic strength	Oxalate concn., 10^3 *M*	Rate of exchange[f]
I	3.6[b]	0.170	1.86	7.3
			3.72	10.1
			6.51	15.1
			9.29	20.7
			12.12	22.9
II	4.7[c]	0.170	2.04	7.5
			2.71	9.8
			4.07	14.7
			10.84	24.0
			16.26	31.7
III	6.8[d]	0.170	1.16	8.8
			2.91	9.5
			5.82	15.8
			12.23	19.9
			17.46	25.6
IV	4.7[c]	0.550	2.04	11.1
			4.07	22.6
			8.14	30.0
			12.21	43.5
V	4.7[e]	0.550	2.04	11.9
			4.07	19.8
			8.14	32.4
			12.21	47.0

[a] $[Pt(C_2O_4)_2^{-2}]$ = 0.00291 *M*, 25.0°. [b] Free oxalate from 60% sodium oxalate, 40% oxalic acid. Rest of ionic strength from complex and sodium nitrate. [c] Free oxalate from 90% sodium oxalate, 10% oxalic acid. Rest of ionic strength from complex and sodium nitrate. [d] 0.1 *M* in phosphate buffer. [e] 0.05 *M* in phosphate. Rest of ionic strength from reactants and sodium nitrate. [f] Moles of oxalate per mole of complex per hour × 10^6.

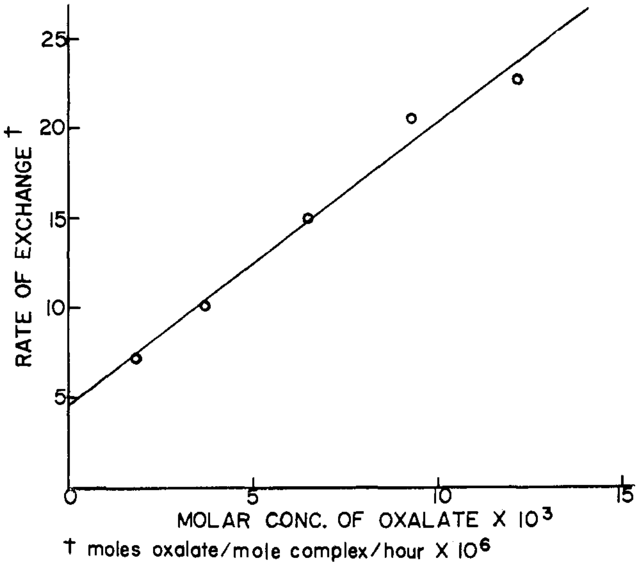

Fig. 1.—Dependence of exchange rate on concentration of oxalate: pH 3.6, ionic strength = 0.170, 25.0°, complex concentration = 2.91 × 10^{-3} *M*.

TABLE IV

Series	k_1, sec.$^{-1}$ × 10^9	k_2, M^{-1} sec.$^{-1}$ × 10^7
I	1.31(0.22)^a	4.36(0.26)
II	1.64(0.22)	4.59(0.28)
III	2.20(0.22)	2.86(0.17)
IV	2.05(0.24)	8.09(0.53)
V	1.50(0.24)	9.40(0.65)

^{a} Values in parentheses refer to standard deviations obtained as described in text.

been plotted. For each series the constants in the rate expression were calculated from the slope and intercept of the graph. Table IV summarizes these results, which have been transformed into more usual units.

For each series the least-squares standard deviations were calculated for both the slope and the intercept. However, since these standard deviations were obtained from only five pieces of data (for series I, II, and III) or four pieces of data (for series IV and V), a value calculated for a given constant could not be expected to be particularly significant. Consequently, the standard deviations obtained for the five series were averaged (weighted averages based on the number of pieces of data used). The average deviation for a slope was 7% of the measured slope, while that for an intercept was 0.22 × 10^{-9} sec.$^{-1}$. These values were then used, with modification where the constants were obtained from four rather than five pieces of information (values quoted in Table IV). From the average difference between the recorded activities of duplicate samples (see Table I) it is possible to calculate the standard deviation of the distribution from which the samples were drawn.[15] Using this result the standard deviation of k_2 was calculated to be ~5% by routine statistical methods, which is in satisfactory agreement with the value obtained from the mean of the least squares plots.

Further evidence for the two-term rate law was obtained by studying the dependence of the apparent exchange rate on the *active* uncomplexed oxalate concentration at a constant *total* uncomplexed oxalate concentration. Under these conditions the contribution of the first-order term should be proportional to the ratio of the active: total free oxalate concentrations, whereas the contribution of the second-order term should be proportional to the active free oxalate concentration.[16] Consequently a plot of the apparent exchange rate against the active free oxalate concentration at constant total free oxalate concentration should be linear and pass through the origin. Experimentally this was found to be the case at a pH of 3.5, ionic strength of 0.170, and 25°, as is shown in Fig. 2.

A final check of the rate law was obtained by studying the dependence of the exchange rate on the complex ion concentration. If both terms in the rate expression are first order with respect to this concentration, the *specific* initial rate of exchange should be independent of the total bisoxalatoplatinate(II) concentration. This is shown to be the case in Table V.

TABLE V^{a,b}

Concn. of complex, 10^3 *M*	Rate of exchange^c
1.20	6.2(±0.6)
2.91	5.8(±0.6)
6.00	6.6(±0.7)

^{a} pH 4.7, ionic strength = 0.170, 25.0°, [oxalate*] = 0.00407 *M*. ^{b} The unusual units are necessary because concurrent first- and second-order reactions are taking place. ^{c} Moles of oxalate per mole of complex per second, ×10^9.

Discussion

The experimental data for oxalate exchange are consistent with the two-term rate law given by eq. 1. Deviations from this rate law would clearly be expected at very low oxalate concentrations, however, since the expression predicts exchange in the absence of free oxalate.

From Table III it is seen that the rate constants, at constant ionic strength, are essentially independent of hydrogen ion concentration through the observed pH range of 3.6–6.8. The differences between the rate constants at pH 6.8 and those at the two other pH values are small (although statistically significant)

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[15] W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 12.

[16] Assuming the first-order reaction is of S$_N$1 type, the following general mechanism would apply

$$\text{M–ligand} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \text{M} + \text{ligand}$$

$$\text{M} + \text{ligand}^* \underset{k_2}{\overset{k_2'}{\rightleftharpoons}} \text{M–ligand}^*$$

If k_1 is the rate-determining step and isotope effects are small, the observed initial exchange rate is given by

$$\text{rate} = \frac{k_1[\text{M–ligand}][\text{ligand}^*]}{[\text{ligand}] + [\text{ligand}^*]}$$

Similar reasoning applied to an S$_N$2 type reaction results in an observed initial exchange rate proportional to [M–ligand][ligand*].

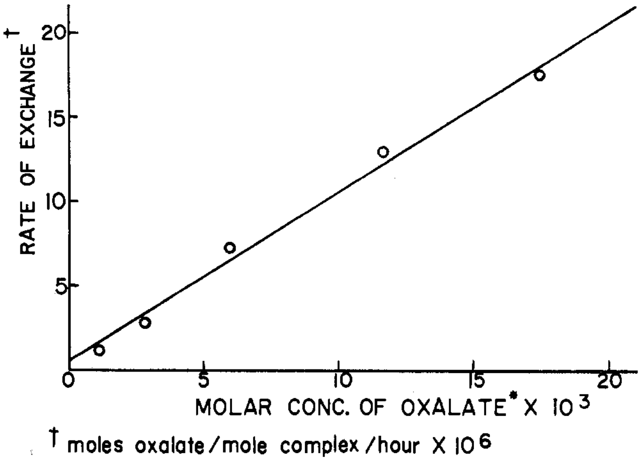

Fig. 2.—Dependence of apparent exchange rate on active free oxalate concentration at constant total free oxalate concentration: pH 3.5, ionic strength = 0.170, 25.0°, complex concentration = 2.91×10^{-3} *M*, total oxalate concentration = 5.0×10^{-2} *M*.

and it is possible that these small differences are caused by the electrostatic inequivalences of phosphate buffer and sodium nitrate as background electrolytes.

Because of the limited solubility of sodium bisoxalatoplatinate(II) it was not possible to vary greatly the ionic strengths of the exchange solutions. Nevertheless, the data in Table IV show k_1 to be essentially independent of ionic strength, and k_2 to be significantly increased when the ionic strength is increased from 0.17 to 0.55. The observation that addition of 0.05 *M* phosphate at pH 4.7 has no significant effect on the exchange rate implies phosphate does not play an important role in the exchange at that pH. Extrapolation of this result to a pH of 6.8, where different ionic species are present, would, however, be dangerous.

The results of this investigation are consistent with the mechanistic outline shown in Fig. 3. It is assumed that the axial positions about the platinum will be occupied by water molecules or by "free" ends of oxalate which are coordinated singly in equatorial positions. The observed kinetic behavior can be satisfactorily explained if intermediate I forms in small concentrations through the pre-equilibrium reaction 1 ($k_1'' >> k_2'$) and reacts through rate-determining reactions 2 and 3 to form very small concentrations of intermediates II and III ($k_1'' > k_2'$ and k_3'; $k_2'' > k_2'$; $k_3'' > k_3'$). Reaction 4, involving direct bimolecular reaction of the complex with oxalate, could possibly add to reaction 2 in contributing to the second-order term.

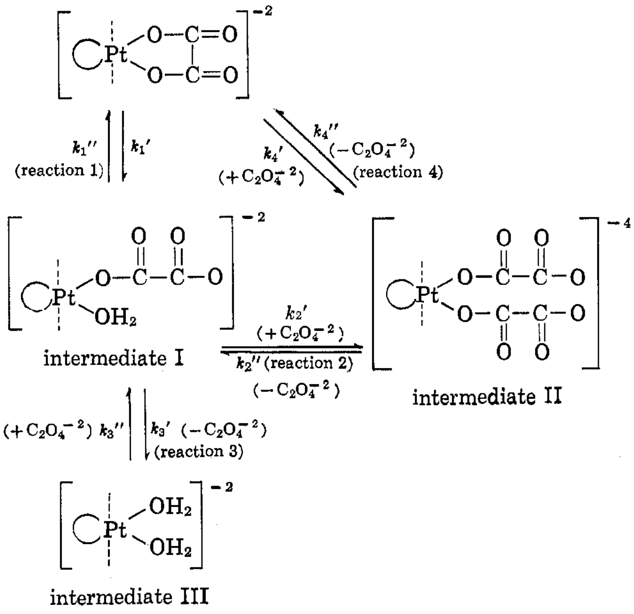

Fig. 3.—Outline of possible mechanism for exchange process.

The postulation of intermediates containing monodentate oxalate is entirely plausible because stable monodentate oxalatoplatinum(II) compounds have been prepared.[17] Also, such intermediates have been proposed for oxalato complexes of chromium(III) and rhodium(III) to explain observations on racemization and aquation, and exchange of oxalate and oxygen.[5,6,8,9] One might suppose hydrogen ion would assist a one-ended dissociation of oxalate for platinum, as was found to be the case for chromium(III) and rhodium(III), but the limited range over which we could vary acidity made it impossible to test rigorously for such an effect. On the other hand, an intermediate of type I, stabilized by protonation, could well be of importance in the hydrogen ion catalyzed polymerization of $Pt(C_2O_4)_2^{-2}$ ion observed by Krogmann and Dodel,[13] since such an intermediate would be expected to polymerize more readily than the chelated $Pt(C_2O_4)_2^{-2}$ ion. Any tendency of intermediate I to protonate would be reduced, however, by accommodation of the "free" end of the oxalate in an axial position about the platinum. Our mechanistic interpretation implies $C_2O_4^{-2}$ and $HC_2O_4^-$ are not markedly different in their reactivity toward intermediate I. On electrostatic grounds this feature is not unreasonable, since $C_2O_4^{-2}$ should maintain a greater cationic atmosphere than $HC_2O_4^-$.

The rates of substitution reactions in platinum(II) complexes can vary over a very wide range, from reactions that are too fast to measure by conventional techniques to extremely slow reactions—the slowest to have been kinetically investigated being that studied herein. The major features influencing these substitution rates are now fairly well understood.[3,18] Thus, it has been shown that substitution is enhanced if the group *trans* to that being replaced is high in the "*trans* sequence of ligands" and if the external reagent is high in the same *trans* sequence.[3b] Measurement of the rate at which oxalate replaces chloride in *trans*-$Pt(NH_3)_2Cl_2$ indicates that oxalate should have a slightly smaller *trans* effect than ammonia. This low position of oxalate in the sequence is to be expected since oxalate, like hydroxide and water, cannot readily accept electrons from the 5d-orbitals of the platinum. This feature, together with the fact that our concern

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(17) V. I. Goremykin and K. I. Gladyshevskaya, *Compt. rend. acad. sci. URSS*, **28**, 625 (1940).

(18) See F. Basolo and R. G. Pearson in: (a) "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958. Chapter 4; (b) *Advan. Inorg. Chem. Radiochem.*, **3**, 46 (1961); (c) *Progr. Inorg. Chem.*, **4**, 381 (1962).

TABLE VI

FIRST- AND SECOND-ORDER RATE CONSTANTS FOR AQUEOUS SOLUTION AND 25°

	k_1, sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$
$Pt(C_2O_4)_2^{-2}$–$C_2O_4^{-2}$	10^{-9}	4×10^{-7}
trans-$Pt(NH_3)_2Cl_2$–$C_2O_4^{-2}$	$\sim 10^{-5}$	$\sim 7 \times 10^{-3}$
Systems summarized by Gray[3d]	10^{-4}–10^{-5}	10^{-1}–10^{-4} [a]

[a] Excluding OH^-, which is a very weakly biphilic reagent.

is with oxalate as a bidentate ligand, can account for the extremely low rates observed.

It is of interest to compare the first- and second-order rate constants for the oxalate–bisoxalatoplatinate(II) exchange with values obtained under similar conditions for substitution of monodentate groups in platinum(II) complexes. Table VI summarizes our values, those obtained by Banerjea, *et al.*,[3b] for oxalate replacement of a chloride in *trans*-$Pt(NH_3)_2Cl_2$, and those accumulated by Gray[3d] for monodentate substitution in a series of complexes (where the group *trans* to that being replaced was ammonia, a secondary amine, or chloride). Both the constants for the bisoxalatoplatinate(II) exchange are of the order of 10^{-4} times the average constants quoted by Gray. The observations can be explained in terms of the mechanism we have proposed, considered to proceed through reactions 1, 2, and 3, if ~0.01% of the bisoxalatoplatinate(II) ion is in the form of intermediate I and this is as reactive as one of the above monodentate platinum(II) complexes.

The proposed mechanism requires that intermediate III react rapidly with free oxalate. There is considerable evidence in the literature[3b,3d,19,20] to indicate that aquoplatinum(II) complexes react rapidly enough with ligands to be intermediates in reactions exhibiting first-order behavior, and it is reasonable to assume that diaquo complexes are at least equally reactive. The invariance of k_1 with ionic strength does seem to rule out the possibility that the first-order term corresponds to a rate-determining nucleophilic attack of the complex by nitrate ion. Our results give no information on whether the first-order term (equivalent to equilibrium between intermediates I and III in the mechanism) involves solvent participation or proceeds by SN1-type elimination of oxalate from intermediate I. However, the arguments of Gray and Olcott[19] favoring solvent participation in exchange reactions involving complexes of the type Pt(dien)X are probably relevant in the case of the oxalate–bisoxalatoplatinate(II) exchange. From Debye–Hückel considerations reactions between ions of similar sign of charge would be expected to be accelerated by increasing ionic strength. This could explain why the second-order reaction (for which we proposed reaction 2 and/or reaction 4 to be rate-determining) is accelerated by increases in ionic strength.

(19) H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

(20) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **80**, 536 (1958).

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Imidazole Complexes of Nickel(II), Copper(II), Zinc(II), and Silver(I)

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The site of complex formation of the imidazole molecule has been determined to be the pyridine nitrogen by comparing data on the N-methylimidazole complex with the imidazole complex of Ag(I). The preparation and characterization of a dual system of imidazole and imidazolate complexes is presented for Ni(II), Cu(II), Zn(II), and Ag(I). Total heats of formation of these complexes have been determined.

Introduction

The bonding of imidazole with transition metal ions is of interest because of this ligand's close relationship with biological systems of a more complex nature involving histidine residues. The literature contains free energy data obtained by potentiometric studies on these systems.[1–4] These data indicate that imidazole forms some of the most stable complexes of all heterocyclic-N ligands. This is corroborated by the high acid association constant of imidazole. Although the acidity of the hydrogen bound at the pyrrole nitrogen[5] in the imidazole ring (hereafter referred to as the "pyrrole hydrogen") is very weak, with a pK_a value of 14.52,[6] metal imidazolates were known as early as 1877.[7,8] The formation of the compound $Hg(C_3H_3N_2)(ClO_4) \cdot H_2O$ was reported by Brooks and Davidson.[9] Martin and Edsall[10] reported that Cu(II) and Ni(II) induced the ionization of the pyrrole hydrogen in glycyl- and his-

(1) J. T. Edsall, G. Felsenfeld, D. S. Goodman, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **76**, 3054 (1954).

(2) B. L. Mickel and A. C. Andrews, *ibid.*, **77**, 5291 (1955).

(3) A. C. Andrews, T. D. Lyons, and T. D. O'Brien, *J. Chem. Soc.*, 1776 (1962).

(4) W. L. Koltun, R. N. Dexter, R. E. Clark, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **80**, 4188 (1958).

(5) The imino nitrogen in the imidazole ring is referred to as the "pyrrole nitrogen" and the other nitrogen the "pyridine nitrogen." This nomenclature is rather arbitrary.

(6) H. Walba and R. W. Isensee, *J. Org. Chem.*, **21**, 702 (1956).

(7) G. Wyss, *Ber.*, **10**, 1365 (1877).

(8) A. Windaus and F. Kopp, *ibid.*, **38**, 1166 (1905).

(9) P. Brooks and N. Davidson, *J. Am. Chem. Soc.*, **82**, 2118 (1960).

(10) R. B. Martin and J. T. Edsall, *ibid.*, **82**, 1107 (1960).