Rates and Mechanisms of Substitution Reactions of Platinum Dithiolato-complexes

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Kinetics and mechanisms of substitution reactions of square-planar platinum(II) dithiolato-complexes $[Pt(S{-}S)_2]^{2-}$ [$S{-}S^{2-}$ = $(NC)_2C{:}CS_2^{2-}$ (cet), $S(NC)C{:}C(NC)S^{2-}$ (ct), $NO_2CH{:}CS_2^{2-}$ (net), $S(O)C{:}C(O)S^{2-}$ (dta), $NC{-}N{:}CS_2^{2-}$ (cimd), and $NC(Ph)C{:}CS_2^{2-}$ (npet)], with both uni- and bi-dentate nucleophiles have been studied in aqueous solution. The reactions are second order, first order in substrate and first order in nucleophile. Activation parameters have been measured for a number of the reactions. The results permit a comparison of the reaction mechanisms and relative reactivities of dithiolato-complexes of nickel, palladium, and platinum.

THE rates and mechanisms of substitution reactions of four-co-ordinate planar complexes of d^8 metal ions in their dipositive oxidation states have been extensively studied during the past decade.[1-3] Most of the work is concerned with results for platinum(II) systems, while results for palladium(II) and nickel(II) are much less numerous. There may be a number of reasons for this. Reactions of palladium(II) and nickel(II) complexes are quite rapid and usually require the use of flow methods to study the kinetics. Furthermore, there are few known square-planar complexes of nickel(II). As a result there are very little data available by which it is possible to

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[1] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., John Wiley & Sons, New York, 1967.

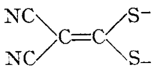
[2] F. Basolo, *Advances in Chemistry Series*, 1965, **49**, 81.

[3] L. Cattalini, *Progr. Inorg. Chem.*, 1970, **13**, 263.

compare rates and mechanisms of substitution reactions of square-planar complexes of nickel(II), palladium(II), and platinum(II).

Dithiolato-complexes of these metals have been shown to be planar[4,5] and provide a suitable basis for a comparison. Some results for nickel(II) and palladium(II) systems have already been reported.[6,7] This work has now been extended to platinum(II) and in order to gain further insight into the intimate details of the reaction mechanisms of square-planar substitution reactions, in particular those of dithiolato-complexes, activation parameters have been measured for a number of the reactions studied.

Most of the results for platinum(II) complexes so far reported concern reactions in which unidentate ligands are replaced by unidentate ligands. Very little information is available concerning the mechanisms by which bidentate ligands displace uni- and bi-dentate ligands and *vice versa*. Present indications are that the mechanisms may be considerably modified in such cases.[8,9] This work is also concerned with elucidating the details of the mechanisms of such reactions. The structures of the ligands used in this study are shown below.



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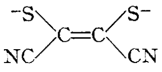

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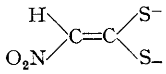

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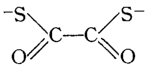

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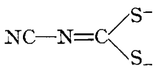

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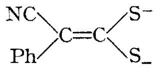

(npet)

EXPERIMENTAL

The ligands were prepared as previously described.[6,7] The metal complexes were prepared by reacting aqueous solutions of $K_2[PtCl_4]$ with the appropriate ligand in a molar ratio of 1 : 2. Addition of an excess of tetramethylammonium chloride resulted in precipitation of the complex. The purity of the ligands was checked by spectrophotometric titration with an aqueous solution of nickel(II) which had been previously standardized with EDTA. Cyanide-ion solutions were standardized by titration with standard silver(I) nitrate.

U.v. and visible spectra were recorded on a Unicam SP 800 spectrophotometer equipped with a constant-temperature cell holder, scale expander, and chart recorder. The kinetics were also measured using this instrumentation. The ionic strength was maintained constant at 0·1M using sodium perchlorate as the inert electrolyte. All the reactions were run under pseudo-first-order conditions with the ligand present in an excess. The substrate concentration was usually $2{\cdot}5 \times 10^{-5}$M. In order to obtain the concentration dependence of the rate constants, the reactions were studied at from five to ten concentrations of an excess of nucleophile.

The substitution reactions with bidentate nculeophiles were monitored at wavelengths which gave large absorbance changes. This was usually a wavelength at which the substrate had an absorption maximum. The reactions between the complexes $[Pt(S{-}S)_2]^{2-}$ and cyanide ion were monitored at wavelengths which were isosbestic points with respect to $[Pt(S{-}S)(CN)_2]^{2-}$ and $[Pt(CN)_4]^{2-} + S{-}S^{2-}$, rate constants for the reactions between the complexes $[Pt(S{-}S)(CN)_2]^{2-}$ and cyanide ion were obtained by measuring absorbance changes at wavelengths where there was no interference from the faster step.[10] Rate data were processed using an IBM 1800 digital computer.

RESULTS

The nucleophile dependence of the observed rate constants for substitution of square-planar platinum(II) dithiolato-complexes with cyanide ion as nucleophile are shown in Table 1. The reactions are second order overall, first order in the complex and first order in cyanide ion. Except for the reaction where $S{-}S^{2-}$ = dto, two steps were observed in all cases. The first corresponds to the substitution of one dithiolato-ligand by two cyanide ions, while the second corresponds to the replacement of the second dithiolato-ligand. The final product is $[Pt(CN)_4]^{2-}$ in all cases. When $S{-}S^{2-}$ = net the reaction was too rapid to measure with the apparatus described, while with $S{-}S^{2-}$ = ct the reaction was extremely slow. The fact that only one step was observed in the reaction between the complex $[Pt(dto)_2]^{2-}$ (dto = dithio-oxalato) and cyanide ion is apparently due to the instability of $[Pt(dto)(CN)_2]^{2-}$. Previous attempts to prepare the latter species *in situ* were unsuccessful.[11] When cyanide and $[Pt(dto)_2]^{2-}$ ions were mixed in molar ratios of 2 : 1 the product was an equimolar mixture of $[Pt(dto)_2]^{2-}$

TABLE 1

Rate constant for substitution reactions of platinum(II) dithiolato-complexes with cyanide ion as nucleophile, in aqueous solution at 25 °C and ionic strengh 0·1M (sodium perchlorate)

Reactant	Product	k_{obs}/l mol^{-1} s^{-1}
$[Pt(cimd)_2]^{2-}$	$[Pt(cimd)(CN)_2]^{2-}$	**3·05**
$[Pt(cimd)(CN)_2]^{2-}$	$[Pt(CN)_4]^{2-}$	**0·51**
$[Pt(cet)_2]^{2-}$	$[Pt(cet)(CN)_2]^{2-}$	**4·47**
$[Pt(cet)(CN)_2]^{2-}$	$[Pt(CN)_4]^{2-}$	**0·44**
$[Pt(dto)_2]^{2-}$	$[Pt(CN)_4]^{2-}$	**3·65**
$[Pt(net)_2]^{2-}$	$[Pt(CN)_4]^{2-}$	fast
$[Pt(ct)_2]^{2-}$	$[Pt(ct)(CN)_2]^{2-}$	very slow

cimd = *N*-Cyanoiminomethanedithiolato, cet = 1,1-cyanoethylenebisthiolato, dto = dithio-oxalato, net = 1-nitro-1-phenylethylenebisthiolato, and ct = 1,2-cyanoethylenebisthiolato

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[4] J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, **10**, 49.

[5] D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, **11**, 233.

[6] R. G. Pearson and D. A. Sweigart, *Inorg. Chem.*, 1970, **9**, 1167.

[7] R. G. Pearson and M. J. Hynes, *J. Co-ordination Chem.*, 1971, **1**, 245.

[8] F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, 1969, **8**, 524.

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[10] M. J. Hynes and A. J. Moran, unpublished work.

[11] S. Kida, *Bull. Chem. Soc. Japan*, 1960, **33**, 1204.

and $[Pt(CN)_4]^{2-}$. The reaction sequence is therefore as in equations (1) and (2). The reaction was strictly first order

$$[Pt(dto)_2]^{2-} + 2CN^- \xrightarrow{\text{slow}} [Pt(dto)(CN)_2]^{2-} + \text{dto} \quad (1)$$

$$[Pt(dto)(CN)_2]^{2-} + 2CN^- \xrightarrow{\text{fast}} [Pt(CN)_4]^{2-} + \text{dto} \quad (2)$$

in cyanide-ion concentration. This result is different to that obtained for the corresponding reaction with $[Pd(dto)_2]^{2-}$ where, while only one step was observed, the reaction was second order in nucleophile at low cyanide-ion concentrations.

When $S\text{–}S^{2-}$ = net the reaction with cyanide ion had a half-life of less than 10 s. This is abnormally rapid substitution of a platinum(II) complex. However, the reactions of net complexes have been anomalous in previous investigations and further investigation of such complexes will be carried out using the stopped-flow technique.

Rate constants for substitution reactions of square-planar platinum(II) dithiolato-complexes with bidentate nucleophiles are shown in Table 2. Again the reactions are second-order overall. Table 3 lists activation parameters for a number of reactions.

TABLE 2

Rate constants for substitution reactions of platinum(II) dithiolato-complexes with bidentate nucleophiles, in aqueous solution at 25 °C and ionic strength 0·1M ($NaClO_4$)

Reactant	Nucleophile	Product	k_{obs}/l mol^{-1} s^{-1}
$K_2[Pt(net)_2]$	dto	$K_2[Pt(net)(dto)]$	4·72
$K_2[Pt(net)(dto)]$	dto	$K_2[Pt(dto)_2]$	slow
$K_2[Pt(net)_2]$	cet	$K_2[Pt(net)(cet)]$	0·396
$K_2[Pt(net)(cet)]$	cet	$K_2[Pt(cet)_2]$	slow

TABLE 3

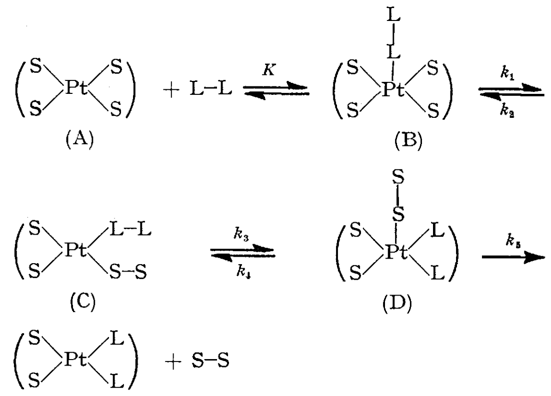
Activation parameters for substitution reactions of platinum(II) dithiolato-complexes

Reactant	Product	$\Delta G^‡$ / kJ mol^{-1}	$\Delta H^‡$ / kJ mol^{-1}	$\Delta S^‡$ / J K^{-1} mol
$[Pt(cimd)_2]^{2-}$	$[Pt(cimd)(CN)_2]^{2-}$	70·1	28·2	−141
$[Pt(cimd)(CN)_2]^{2-}$	$[Pt(CN)_4]^{2-}$	74·7	32·2	−143
$[Pt(net)_2]^{2-}$	$[Pt(net)(dto)_2]^{2-}$	69·3	13·7	−187
$[Pt(net)_2]^{2-}$	$[Pt(net)(cet)]^{2-}$	76·2	20·6	−186
Estimated uncertainty:		±6·3	±2·5	±12

DISCUSSION

In general a two-term rate law has been observed for platinum(II) substitution reactions.[1] In the present investigation no evidence was found for the nucleophile-independent term. A similar result was obtained for substitution reactions of nickel(II) and palladium(II) dithiolato-complexes.[6,7] Whether or not a solvent path appears in the rate law for a particular reaction depends on the relative magnitude of the two steps, and on whether attack by the entering nucleophile on the solvolyzed species is slower or faster than the solvolysis step. No evidence was obtained for the presence of any solvolyzed species during the present investigation.

The general mechanism proposed to account for substitution reactions of square-planar platinum(II) dithiolato-complexes with bidentate nucleophiles is shown in the Scheme. It is the same as that previously proposed for substitution reactions of nickel and palladium dithiolato-complexes.[6,7] Assuming steady-state conditions for (C) and (D), one calculates for an excess of ligand equation (3). If $K[L] \ll 1$, then $k_{obs} = K'K[L]$

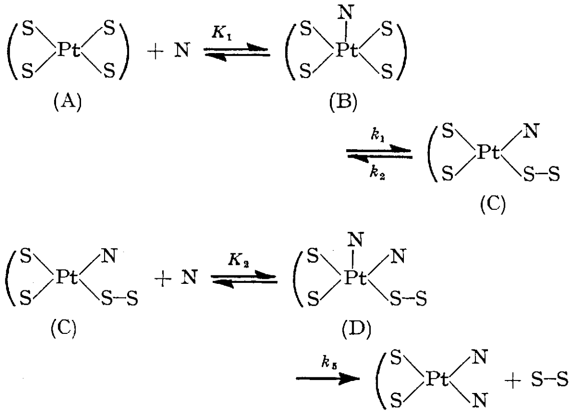


SCHEME

$$k_{obs} = \frac{k'K[L]}{1 + K[L]} \quad (3)$$

$$\text{where } k' = \frac{k_1k_3k_5}{k_2(k_4 + k_5) + k_3k_5}$$

and the reaction is first order in nucleophile, N. The proposed mechanism with cyanide ion as nucleophile is shown in equations (4) and (5). Taking [(C) + (D)] to be in a steady state, relation (6) is obtained for k_{obs} with an excess of nucleophile.



(4)

(5)

$$k_{obs} = \frac{k_1k_5K_1K_2[L]^2}{k_2 + (K_2k_5 + K_1k_2)[L] + K_1K_2k_5[L]^2} \quad (6)$$

It has generally been accepted that the rate-determining step in substitution reactions of square-planar complexes with both uni- and bi-dentate nucleophiles is formation of the necessary five-co-ordinate adduct.[1-3] While this mechanism may be modified by steric parameters,[8,9] it has also been found that formation of the five-co-ordinate intermediate is not rate determining in substitution reactions of nickel(II) dithiolato-complexes by both uni- and bi-dentate nucleophiles[6] in spite of the fact that a statistical advantage might have been expected to lead to a rapid second step with bidentate entering groups.[8,12] In this instance it was also possible to directly monitor the formation of the five-co-ordinate adducts. This is in marked contrast to square-planar substitution reactions so far reported, and in only one previous instance has formation of the five-co-ordinate adduct been directly observed.[13] In the nickel reactions, the dependence of k_{obs} on nucleophile concentration provided a further means of testing the mechanism. The reactions with cyanide ion as nucleophile were either second order or greater than first order, while those with bidentate nucleophiles displayed a first-order dependence on nucleophile concentration.

TABLE 4

Relative ratios of second-order rate constants for substitution reactions of palladium(II) and platinum(II) complexes

Reaction	$k_{Pd} : k_{Pt}$	Reference
$[M(dien)SCN]^+ + py \longrightarrow [M(dien)py]^{2+} + SCN^-$	$6\ 8 \times 10^5$	2
trans-$[M(PEt_3)_2(o\text{-tolyl})Cl]^+ + py \longrightarrow [M(PEt_3)_2(o\text{-tolyl})py]^{2+} + Cl^-$	$0{\cdot}9 \times 10^5$	2
trans-$[M(NH_3)_2Cl_2] + NH_3 \longrightarrow [M(NH_3)_3Cl]^+ + Cl^-$	$0{\cdot}9 \times 10^5$	*a*
$[M(NH_3)_3Cl]^+ + NH_3 \longrightarrow [M(NH_3)_4]^{2+} + Cl^-$	$3{\cdot}0 \times 10^5$	*a*
$[M(qas)Cl_2] + NO_2^- \longrightarrow [M(qas)(Cl)NO_2] + Cl^-$	$3{\cdot}4 \times 10^3$	2
$[M(cimd)_2]^{2-} + 2CN^- \longrightarrow [M(cimd)(CN)_2]^{2-} + cimd$	$3{\cdot}0 \times 10^2$	*b*
$[M(cimd)(CN)_2]^{2-} + 2CN^- \longrightarrow [M(CN)_4]^{2-} + cimd$	$1{\cdot}3 \times 10^2$	*b*
$[M(cet)_2]^{2-} + 2CN^- \longrightarrow [M(cet)(CN)_2]^{2-} + cet$	$1{\cdot}8 \times 10^2$	*b*
$[M(cet)(CN)_2]^{2-} + 2CN^- \longrightarrow [M(CN)_4]^{2-} + cet$	$1{\cdot}7 \times 10^2$	*b*
$[M(net)_2]^{2-} + dto \longrightarrow [M(net)(dto)]^{2-} + net$	$0{\cdot}4 \times 10^2$	*b*
$[M(net)_2]^{2-} + cet \longrightarrow [M(net)(cet)]^{2-} + net$	$3{\cdot}8 \times 10^2$	*b*

dien = Diethylenetriamine and qas = tris(*o*-dimethylarsinophenyl)arsine.

[a] D. Banerjea, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1957, **79**, 4055; R. A. Reinhardt and R. T. Sparkes, *Inorg. Chem.*, 1967, **6**, 2190. [b] Present work.

Unfortunately, no such tests were possible in the present investigation as the reactions were first order with both uni- and bi-dentate nucleophiles and the five-co-ordinate intermediate did not appear to be formed in appreciable concentrations. It therefore appears reasonable to assume that for bidentate nucleophiles $K[L] \ll 1$ so that $k_{obs} = k'K[L]$. This is in agreement with the observed kinetics. The analysis is more complex for the reactions with cyanide ion as nucleophile. Depending on the relative magnitudes of the various constants in the rate expression, the reaction may be zero, first, or second order in cyanide ion. In the case of nickel, it appears that the rate constant for ring closure, k_2, is greater than k_5, thus leading to second-order kinetics. In the present investigation it appears that $(K_2k_5 + K_1K_2)[L] \gg k_2$.

The results presented here are generally similar to those obtained for nickel. It is also obvious however that there are some significant differences in the intimate details of the reaction mechanism. These differences appear to be best interpreted in terms of relative stabilities of the five-co-ordinate intermediates. There are a number of reviews available which deal with five-co-ordinate complexes of the nickel group.[14,15] The tendency to add a fifth or sixth group is much greater for nickel than either palladium or platinum. This has been well illustrated in the case of the tetracyano-complexes of nickel and platinum.[16-19]

The general order for the ratios of the rate constants in the nickel, palladium, and platinum series is usually given[2] as Ni : Pd : Pt = $10^6 : 10^5 : 1$. This order is considerably modified in dithiolato-systems, where the order is approximately Ni : Pd : Pt = $10^5 : 10^2 : 1$. Thus, in the dithiolato-series there is an abnormally high increase on going from palladium to nickel, while the increase on going from platinum to palladium is much less than is usually found. Not many direct comparisons were possible in the case of nickel and palladium, because of experimental difficulties.[7] However, quite a number of comparisons are possible for palladium and platinum and these, together with some data from the literature, are shown in Table 4.

In the case of palladium and nickel it was thought that the abnormally high reactivity of nickel dithiolato-complexes compared to those of palladium was due to greater stability of the five-co-ordinate intermediate in the case of the former. Morgan *et al.* have also attributed the relative reactivity of palladium and platinum to their tendencies to form five-co-ordinate adducts.[20] This is in accord with the fact that in the case of substitution reactions of nickel dithiolato-complexes rates closely parallel the stability of the five-co-ordinate adduct.[6] In dithiolato-complexes, adduct formation removes the p_z orbital, which is purely π-bonding in D_{2h} or D_{4h} symmetry, from

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[12] M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.

[13] L. Cattalini, R. Ugo, and A. Orio, *J. Amer. Chem. Soc.*, 1968, **90**, 4800.

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[17] A. Terzis, K. N. Raymond, and T. G. Spiro, *Inorg. Chem.*, 1970, **9**, 2415.

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[20] T. D. B. Morgan and M. L. Tobe, *Inorg. Chim. Acta.*, 1971, **5**, 563.

the π-network as it will be involved in σ-bond formation to the entering group. If the observed order of reactivities for dithiolato-complexes of the nickel group is related to the relative electron density in the p_z orbital, it would suggest that the π-electron density in the p_z orbital is greatest in palladium as its reactions are slower than expected. However, spectroscopic evidence would appear to suggest that the reverse is in fact the case.[21] Using polarographic data, Gray [21] has shown that for a given dithiolato-ligand the stability order for the dianionic species $[\mathrm{M(S{-}S)_2}]^{2-}$ is $\mathrm{Ni} < \mathrm{Pd} > \mathrm{Pt}$. If bond breaking is important in the overall reaction, this again suggests that palladium reactions would be abnormally slow.

The results show that the entropies of activation of these reactions have high negative values. This is consistent with the associative and ionic nature of the postulated mechanism. In the reactions with cyanide ion as nucleophile the entropy of activation is the same, within experimental error, for replacement of the first and second dithiolato-ligands. The more negative entropy of activation for the reactions with bidentate nucleophiles may be at least partly due to an electrostatic factor. The change in entropy on bringing two ions from infinity to a distance of 2 Å apart in aqueous solution has been shown [22] to be $\Delta S_{\mathrm{el}} = -42Z_{\mathrm{A}}Z_{\mathrm{B}}\ \mathrm{J\ K^{-1}\ mol^{-1}}$, where Z_{A} and Z_{B} are the charges on the ions. If $\Delta S_{\mathrm{el}}^{\ddagger}$ is calculated on this basis in the present investigation it is found that a large portion of the entropy of activation is accounted for. It may be argued of course that the electrostatic factor makes only a small contribution to the total entropy of activation, because, in many of the reactions involving substitution reactions of square-planar complexes for which entropies of activation have been measured, values obtained are in the range 94—125 $\mathrm{J\ K^{-1}\ mol^{-1}}$, even where one of the reactants is uncharged.[3] Where the nucleophile is biphilic, the entropy of activation is generally more negative. This has been interpreted in terms of increased bonding in the pentagonal-bipyramidal transition state. Non-kinetic data indicate that the entropy change for a process in which the co-ordination number of a metal is increased is usually quite negative.[23,24]

In many of the reactions of square-planar complexes for which activation parameters are available, it is apparent that pure σ-donors are being replaced by purely σ-bonding or biphilic nucleophiles. In the present investigation, however, strongly π-bonding ligands are being replaced by strong π-bonding nucleophiles. Furthermore, when the dithiolato-ring is broken there is a loss of π-bonding which should result in a positive contribution to the entropy of activation. This loss may be partly or wholly compensated for by co-ordination of a fifth donor molecule. In view of this it is not unreasonable to expect that were there not a considerable electrostatic contribution to the entropy of activation, a relatively low entropy of activation would have been obtained. One other factor however contributes to the high negative entropy. In many square-planar complexes, there is evidence of weak interaction with solvent molecules in the axial positions.[25,26] This axial solvation is lost in the transition state, resulting in a positive contribution to the entropy of activation. No such interaction is present in dithiolato-complexes.[27-30]

In conclusion it may be stated that substitution reactions of square-planar platinum(II) dithiolato-complexes follow an associative path as expected. The solvent path is not important. Further work is in progress in an attempt to answer some of the problems posed by the present work.

[3/437 *Received*, 26*th February*, 1973]

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