Rates and Mechanisms of Substitution Reactions of Square-planar Dithiocarbamate and Dithiophosphate Complexes of the Nickel Triad in Methanol

By **Michael J. Hynes** * and **Patricia F. Brannick**, Chemistry Department, University College, Galway, Ireland

Rate constants for the substitution reactions of square-planar dithiophosphate and dithiocarbamate complexes of Ni^{II}, Pd^{II}, and Pt^{II}, with ethylenediamine and cyanide ion as nucleophiles, have been measured in methanol at an ionic strength of 0.1 mol dm^{-3} sodium perchlorate. A general mechanism is proposed to account for the kinetic data. The order of the reactivity of the complexes is approximately Ni : Pd : Pt = $10^5 : 10^3 : 1$. The results are compared with those obtained in previous investigations and are interpreted in terms of the stabilities of the five-co-ordinate species which are formed prior to substitution.

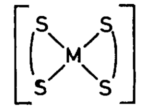
We have recently been investigating the substitution reactions of square-planar complexes of Ni^{II}, Pd^{II}, and Pt^{II} containing sulphur-donor atoms. It is possible to compare the substitution reactions of square-planar complexes of these three metals using sulphur ligands. Most of the previous investigations of such reactions of these metals have dealt with complexes of one or other of the metals but there are very few studies where the reactivities of complexes of the three metals with a given ligand are compared.[1-10] There are many difficulties involved in studying an isoligand series of complexes of the nickel triad. One of the main problems involved is finding ligands which will give square-planar complexes with Ni^{II}. This is due to the greater tendency of Ni^{II} towards octahedral rather than square-planar geometry.[11] Platinum(II) complexes of ligands which give square-planar complexes with all three metals tend to be very unreactive. It is frequently impossible to obtain nucleophiles which will displace the ligands, but the cyanide ion and 1,2-dithiolenes have been used successfully.[10] Finally, with cyanide ion as nucleophile, the order of the reactions could vary for the different metals, thus prohibiting a valid comparison of the kinetic data. Only reactions of the same order may be meaningfully compared. We now report the kinetics and mechanisms of the substitution reactions of dithiophosphate and dithiocarbamate complexes of Ni^{II}, Pd^{II}, and Pt^{II} with ethylenediamine and cyanide ion as nucleophiles. All the reactions were carried out in methanol.

EXPERIMENTAL

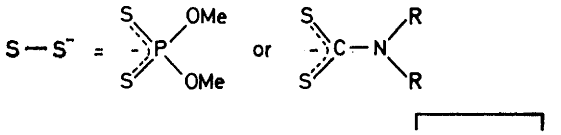
The ligands and complexes used were all prepared as described in the literature.[12-15] Reagent-grade methanol was purified by refluxing with magnesium and iodine prior to use. The sodium cyanide solutions were standardized by titration with silver(I) nitrate. Ethylenediamine was purified by distillation. The rate constants were measured using either an Applied Photophysics stopped-flow device or a Beckman DB-GT u.v.–visible spectrophotometer equipped with a chart recorder. The stopped-flow data were recorded using a Tektronix model 5100 storage oscilloscope and a polaroid camera. The reactions were all run under pseudo-first-order conditions with the nucleophile present in excess. The temperature was maintained at 25.0 ± 0.1 °C. Sodium perchlorate was used as an inert electrolyte to maintain a constant ionic strength of 0.1 mol dm^{-3}. Generally, the pseudo-first-order rate constants were obtained from plots of $\ln(A - A_\infty)$ against time. In the case of successive reactions the rate constant of the faster step was determined at an isosbestic point of the slower step. In the absence of such an isosbestic point, the Guggenheim method was used to calculate the rate constant for the fast step. Standard errors were calculated as described in the literature.[16]

RESULTS AND DISCUSSION

The structures of the complexes and ligands used in this study are shown below. The pseudo-first-order and second-order rate constants for the reactions studied in methanol are shown in Tables 1 and 2. Two reaction steps were observed when methanol solutions of the dithiophosphate and dithiocarbamate complexes were treated with cyanide ion. As in previous investigations,[5,7,8,10] the two steps were assigned as in



M = Ni^{II}, Pd^{II}, or Pt^{II}



NR_2 = NEt_2 or $NCH_2CH_2CH_2CH_2CH_2$

---

[1] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, 1962, **4**, 381.

[2] C. H. Langford and H. B. Gray, ' Ligand Substitution Processes,' Benjamin, New York, 1965, ch. 2.

[3] U. Belluco, R. Etorre, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1966, **5**, 591.

[4] A. Peloso, *Co-ordination Chem. Rev.*, 1973, **10**, 123.

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

[6] M. J. Hynes and A. Moran, *J.C.S. Dalton*, 1973, 2280.

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

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

[9] M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1969, **8**, 795.

[10] M. J. Hynes and P. F. Brannick, *Proc. Roy. Irish Acad.*, 1977, in the press.

[11] H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260.

[12] S. E. Livingstone and A. E. Mihkelson, *Inorg. Chem.*, 1970, **9**, 2545.

[13] C. J. Jørgenson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571.

[14] J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.

[15] J. McCormack and R. I. Kaplan, *Canad. J. Chem.*, 1970, **48**, 1876.

[16] E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971.

(1) and (2) where $[S{-}S]^-$ represents the bidentate sulphur ligand and $M = Ni^{II}$, Pd^{II}, or Pt^{II}. It was only

$$[M(S{-}S)_2] + 2[CN]^- \longrightarrow [M(S{-}S)(CN)_2]^- + [S{-}S]^- \quad (1)$$

$$[M(S{-}S)(CN)_2]^- + 2[CN]^- \longrightarrow [M(CN)_4]^{2-} + [S{-}S]^- \quad (2)$$

possible to measure the rate constants for the substitution reactions of the nickel(II) complexes when ethylenediamine (en) was the nucleophile; the complexes of Pd^{II} and Pt^{II} were inert to substitution with this nucleophile. For the nickel(II) complexes the reaction sequence is as in (3) and (4). The complexes $[M(S_2CNC_4H_8)_2]$ ($M = Pd^{II}$ or Pt^{II}) were extremely

$$[Ni(S{-}S)_2] + en \xrightarrow{slow} [Ni(S{-}S)(en)]^+ + [S{-}S]^- \quad (3)$$

$$[Ni(S{-}S)(N{-}N)]^+ + 2\ en \xrightarrow{fast} [Ni(en)_3]^{3+} + [S{-}S]^- \quad (4)$$

insoluble in methanol and could not be investigated kinetically.

TABLE 1

Pseudo-first-order rate constants for substitution reactions of square-planar complexes of Ni^{II}, Pd^{II}, and Pt^{II} with cyanide ion and ethylenediamine in methanol

Substrate	$10^2[CN^-]$/ mol dm^{-3}	$10^2k_{obs.}$/s^{-1}
$[Ni(S_2CNEt_2)_2]$	0.49	258
	0.98	850
	1.97	3 225
	2.95	6 800
	3.94	11 250
$[Ni(S_2CNEt_2)(CN)_2]^-$	0.143	0.19
	0.161	0.22
	0.189	0.41
	0.234	0.73
	0.964	12.35
$[Pd(S_2CNEt_2)_2]$	2.95	206
	3.44	218
	3.94	246
	4.43	260
	4.92	300
$[Pd(S_2CNEt_2)(CN)_2]^-$	0.65	0.21
	0.96	0.43
	1.31	1.73
	1.97	1.63
	2.62	2.70
$[Pt(S_2CNEt_2)_2]$	0.65	0.047
	1.31	0.095
	1.97	0.145
	2.62	0.212
	3.28	0.260
$[Pt(S_2CNEt_2)(CN)_2]^-$	1.97	0.026 5
	2.62	0.031 1
	3.28	0.036 1
	3.94	0.044 4
	$10^2[en]$/ mol dm^{-3}	
$[Ni(S_2CNEt_2)_2]$	0.5	1 219
	1.0	2 750
	1.5	4 700
	2.0	6 800
	2.5	8 100
$[Ni(S_2CNC_4H_8)_2]$	0.05	2 100
	0.10	4 730
	0.15	70 000
	0.20	103 000
	0.25	119 000
	$10^2[CN^-]$/ mol dm^{-3}	
$Ni(S_2CNC_4H_8)_2]$	0.049	216
	0.296	2 700
	0.395	3 867
	0.494	5 133
	1.480	12 400
$[Ni(S_2CNC_4H_8)(CN)_2]^-$	0.296	80
	0.346	90
	0.395	108
	0.445	151
	0.494	226
$[Ni\{S_2P(OMe)_2\}_2]$	0.039 4	3 200
	0.044 3	4 833
	0.049 3	5 500
	0.100 0	10 357
	0.148 0	12 400
$[Ni\{S_2P(OMe)_2\}(CN)_2]^-$	0.044 3	400
	0.049 3	416
	0.098 6	1 117
	0.148 0	1 625
	0.197 0	2 350
$[Pd\{S_2P(OMe)_2\}_2]$	0.48	510
	0.96	1 400
	1.92	2 800
	2.88	4 350
	3.84	5 500
$[Pd\{S_2P(OMe)_2\}_2(CN)_2]^-$	0.49	42
	0.99	85
	1.97	160
	2.96	238
	3.94	302
$[Pt\{S_2P(OMe)_2\}_2]$	0.82	1.20
	1.14	1.87
	1.64	3.20
	1.97	3.85
	2.30	4.80
$[Pt\{S_2P(OMe)_2\}(CN)_2]^-$	1.97	0.163
	2.30	0.197
	2.63	0.214
	3.00	0.260
	3.29	0.284

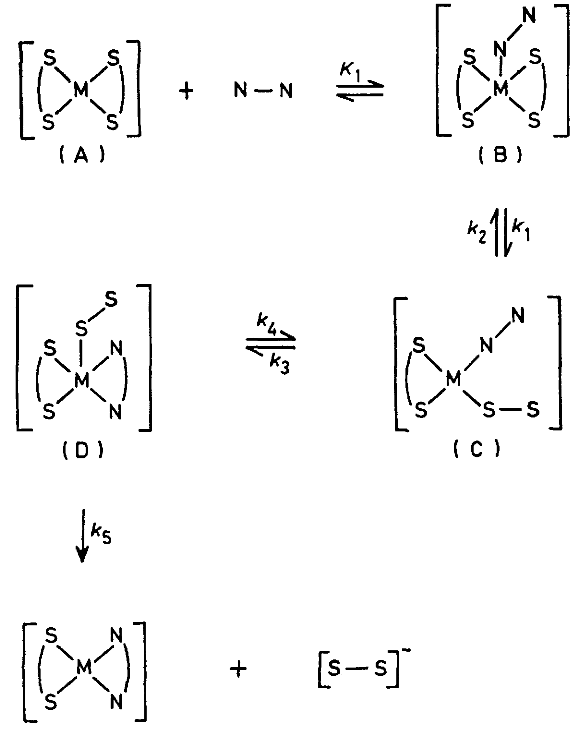
TABLE 2

Second-order rate constants for substitution reactions of complexes of Ni^{II}, Pd^{II}, and Pt^{II}

Substrate	Nucleophile	k/s^{-1}
$[Ni(S_2CNEt_2)_2]$	$[CN]^-$	$(7.2 \pm 0.18) \times 10^4[CN^-]^2$
$[Ni(S_2CNEt_2)(CN)_2]^-$	$[CN]^-$	$(13.33 \pm 0.01) \times 10^2[CN^-]^2$
$[Pd(S_2CNEt_3)_2]$	$[CN]^-$	$0.67 + (47 \pm 0.05)[CN^-]$
$[Pd(S_2CNEt_2)(CN)_2]^-$	$[CN]^-$	$55.25[CN^-]^2/(1 + 2.8[CN^-])$
$[Pt(S_2CNEt_2)_2]$	$[CN]^-$	$(8.0 \pm 0.29) \times 10^{-2}[CN^-]$
$[Pt(S_2CNEt_2)(CN)_2]^-$	$[CN]^-$	$8.0 \times 10^{-5} + (8.82 \pm 0.92) \times 10^{-3}[CN^-]$
$[Ni(S_2CNEt_2)_2]$	en	$(3.5 \pm 0.14) \times 10^3[en]$
$[Ni(S_2CNC_4H_8)_2]$	en	$(4.8 \pm 0.2) \times 10^4[en]$
$[Ni(S_2CNC_4H_8)_2]$	$[CN]^-$	$(1.0 \pm 0.05) \times 10^4[CN^-]$
$[Ni(S_2CNC_4H_8)(CN)_2]^-$	$[CN]^-$	$(8.75 \pm 0.75) \times 10^4[CN^-]^2$
$[Ni\{S_2P(OMe)_2\}_2]$	$[CN]^-$	$(9.0 \pm 1.1) \times 10^4[CN^-]$
$[Ni\{S_2P(OMe)_2\}(CN)_2]^-$	$[CN]^-$	$(1.17 \pm 0.04) \times 10^4[CN^-]$
$[Pd\{S_2P(OMe)_2\}_2]$	$[CN]^-$	$(1.4 \pm 0.05) \times 10^3[CN^-]$
$[Pd\{S_2P(OMe)_2\}(CN)_2]^-$	$[CN]^-$	$0.1 + (7.5 \pm 0.1) \times 10^1[CN^-]$
$[Pt\{S_2P(OMe)_2\}_2]$	$[CN]^-$	$(2.00 \pm 0.06)[CN^-]$
$[Pt\{S_2P(OMe)_2\}(CN)_2]^-$	$[CN]^-$	$(8.46 \pm 0.56) \times 10^{-2}[CN^-]$
$[Ni(cimd)_2]^{2-}$ [a]	en	$9.04 \times 10^2[en]$ [b]
$[Ni(nped)_2]^{2-}$ [c]	en	$9.14 \times 10^2[en]$ [b]
$[Pd(nped)_2]^{2-}$	$[CN]^-$	$2.47(CN^-]$ [b]
$[Pd(cimd)_2]^{2-}$	$[CN]^-$	$3.2 \times 10^{-3} + (10.5 \times 10^{-2}) \times [CN^-]$ [b]
$[Ni(cimd)_2]^{2-}$	$[CN]^-$	$2.0 \times 10^4[CN^-]^2$ [b]
$[Pt(cimd)_2]^{2-}$	$[CN]^-$	$13.7 \times 10^{-3}[CN^-]$ [b]

[a] cimd = *N*-Cyanoiminomethanedithiolate. [b] Ref. 10.
[c] nped = 1-Nitro-1-phenylethylenedithiolate.

The mechanism for the substitution reactions with ethylenediamine as nucleophile is shown in Scheme 1.



Scheme 1

The subsequent steps are rapid and will not affect the rate law. Assuming the steady-state approximation for (C) and (D), for excess of ethylenediamine one obtains (5) where $k' = k_1k_3k_5/[k_2(k_4 + k_5) + k_3k_5]$. If

$$k_{\text{obs.}} = \frac{k'K[\text{N-N}]}{1 + K[\text{N-N}]} \qquad (5)$$

$K[\text{N-N}] \leqslant 1$, then we obtain equation (6). A plot of $k_{\text{obs.}}$ against [N-N] yields a straight line of gradient k^1K.

$$k_{\text{obs.}} = k'K[\text{N-N}] \qquad (6)$$

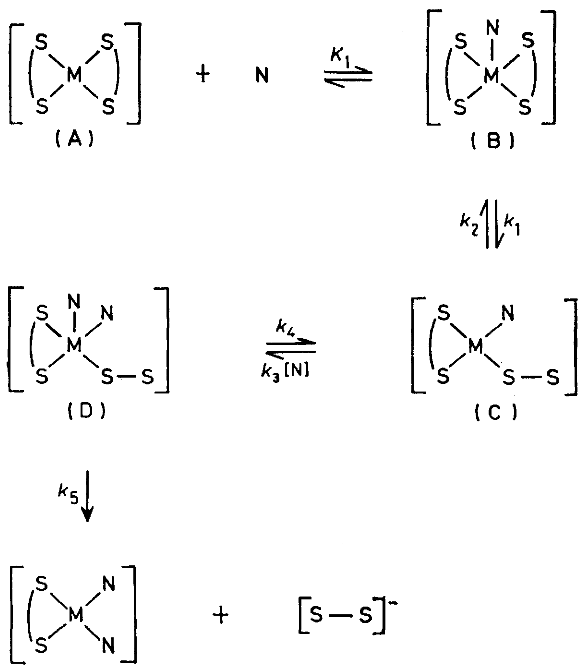
Scheme 2 is the proposed mechanism for the substitution reactions with cyanide ion as the nucleophile. Assuming the steady-state approximation for (C) and (D), for excess of cyanide ion, relation (7) is obtained. Assuming

$$k_{\text{obs.}} = \frac{k_1k_5K_1K_2[\text{N}]^2}{(1 + K_1[\text{N}])(k_2 + K_2k_5[\text{N}])} \qquad (7)$$

$k_2 \geqslant k_5K_2[\text{N}]$, equation (8) follows where $k'' = k_1k_5K_2/k_2$.

$$k_{\text{obs.}} = \frac{k''K_1[\text{N}]^2}{1 + K_1[\text{N}]} \qquad (8)$$

It is apparent from equation (8) that, depending on the relative magnitudes of the various rate and equilibrium constants, $k_{\text{obs.}}$ may show a first ($K_1[\text{N}] \geqslant 1$), intermediate first–second, or second-order ($K_1[\text{N}] \leqslant 1$) dependence on cyanide concentration. The differences in the $k_{\text{obs.}}$ dependence on nucleophile concentration for bi- and uni-dentate nucleophiles is fortunate because it provides means of testing the proposed mechanisms. The reactions involving ethylenediamine as the nucleophile are all first order in concentration of the entering group. This is in agreement with equation (6). The order of the reactions when cyanide is used as the nucleophile varied from first to second as demanded by equation (8). A nucleophile-independent path was detected (Table 2) for the reactions of $[\text{Pd}(\text{S}_2\text{CNEt}_2)_2]$, $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{CN})_2]^-$, and $[\text{Pd}\{\text{S}_2\text{P}(\text{OMe})_2\}(\text{CN})_2]^-$ with cyanide ion as entering group. This is attributed to a solvent path. It is significant that this path is absent for all the reactions of the nickel(II) complexes. It would be expected for Ni^{II} that $k_{\text{L}}[\text{N}] \geqslant k_{\text{S}}$ where k_{L} and k_{S} represent the nucleophile- and solvent-dependent steps respectively.



Scheme 2

The reactions of $[\text{Ni}(\text{S}_2\text{CNEt}_2)(\text{CN})_2]^-$ and $[\text{Ni}(\text{S}_2\text{CNC}_4\text{H}_8)(\text{CN})_2]^-$ with cyanide ion as nucleophile are both second order in $[\text{CN}^-]$. Therefore it is possible to compare the rate constants for the two reactions. The ratio obtained is $\text{S}_2\text{CNC}_4\text{H}_8 : \text{S}_2\text{CNEt}_2 = 65 : 1$. For the reactions of $[\text{Ni}(\text{S}_2\text{CNC}_4\text{H}_8)_2]$ and $[\text{Ni}(\text{S}_2\text{CNEt}_2)_2]$ with ethylenediamine the ratio of the rate constants is equal to 14 : 1. A previous study [17] has shown that the stability constants for $[\text{Ni}(\text{S}_2\text{CNEt}_2)_2]$ and $[\text{Ni}(\text{S}_2\text{CNC}_4\text{H}_8)_2]$ are very similar. Therefore it is reasonable to assume that $[\text{Ni}(\text{S}_2\text{CNC}_4\text{H}_8)(\text{CN})_2]^-$ and $[\text{Ni}(\text{S}_2\text{CNEt}_2)(\text{CN})_2]^-$ also have similar stabilities. When Ni^{II} is displaced from $[\text{Ni}(\text{S}_2\text{CNC}_4\text{H}_8)_2]$ and $[\text{Ni}(\text{S}_2\text{CNEt}_2)_2]$ by Cu^{2+} the ratio $\text{S}_2\text{CNC}_4\text{H}_8 : \text{S}_2\text{CNEt}_2$ is at least 10 : 1.[18] The mechanism proposed was attack of the Cu^{2+} at either the

---

[17] R. R. Scharfe, V. S. Sastri, and C. L. Chakrabarti, *Analyt. Chem.*, 1973, **45**, 413.

[18] R. R. Scharfe, V. S. Sastri, and C. L. Chakrabarti, *Canad. J. Chem.*, 1972, **50**, 3384.

nitrogen or sulphur atom of the dithiocarbamate, and the results were interpreted in terms of steric factors. Obviously, such an attack does not take place in the present study and it is unlikely that the substituent groups are large enough to hinder attack on the central metal atom by the incoming nucleophile. Furthermore, *it was shown that* Ni^{2+} was displaced more rapidly from $[Ni(S_2CNEt_2)_2]$ than from $[Ni(S_2CNMe_2)_2]$ in methanol. It is therefore unlikely that steric factors alone are responsible for the differences in the observed rate constants.

Table **3** gives the ratios of the rate constants for the reactions of *OO′*-dimethyl dithiophosphate and diethyldithiocarbamate complexes of Ni^{II}, Pd^{II}, and Pt^{II} with cyanide ion as nucleophile and summarizes the values obtained by previous workers. The mechanism proposed for substitution (Schemes 1 and 2) involves the formation of five-co-ordinate species when both cyanide ion and ethylenediamine are the nucleophiles. The equilibrium constant for this step appears in the numerator of the rate equations [(6) and (8)] and thus the larger the value of this constant the greater the observed rate constant. The ability of square-planar nickel(II)–sulphur complexes to form five-co-ordinate adducts has been previously investigated.[19] The order of decreasing ability for adduct formation with nitrogenous bases has been shown to be dithiocarbonates, dithio-acids, > dithiocarbamates > dithiocarbimates, trithiocarbonates, ethylene-1,1-dithiolates. The lability of square-planar nickel(II) complexes with a given nucleophile should follow the above order. Table 4 shows that the order holds for both cyanide ion and ethylenediamine as nucleophiles.

TABLE 3

Summary of the ratios of the rate constants for the reactions of planar complexes of Ni^{II}, Pd^{II}, and Pt^{II} with a variety of nucleophiles

Substrate	Nucleophile	Product	Ni : Pd : Pt	Ref.
$[M\{S_2P(OMe)_2\}_2]$	$[CN]^-$	$[M\{S_2P(OMe)_2\}(CN)_2]^-$	$10^5 : 10^3 : 2$	
$[M\{S_2P(OMe)_2\}_2(CN)_2]^-$	$[CN]^-$	$[M(CN)_4]^{2-}$	$10^5 : 10^3 : 1$	
$[M(S_2CNEt_2)_2]$	$[CN]^-$	$[M(S_2CNEt_2)(CN)_2]^-$	*a* : $10^3 : 2$	
$[M(S_2CNEt_2)(CN)_2]^-$	$[CN]^-$	$[M(CN)_4]^{2-}$	*a* : $10^3 : 1$	
$[M(nped)_2]^{2-}$	en	[M(nped)(en)]	$3 \times 10^6 : 1 : 1$	10
$[M(nped)_2]^{2-}$	$[CN]^-$ [b]	$[M(nped)(CN)_2]^{2-}$	*a* : 1 : 2	10
$[M(nped)(CN)_2]^{2-}$	$[CN]^-$ [b]	$[M(CN)_4]^{2-}$	*a* : 5 : 1	10
$[M(cimd)_2]^{2-}$	en [b]	[M(cimd)(en)]	$2 \times 10^6 : 1$	10
$[M(nped)_2]^{2-}$	en [c]	[M(nped)(en)]	$2 \times 10^5 : 1 : 1$	10
$[M(cimd)(CN)_2]^{2-}$	$[CN]^-$ [c]	$[M(CN)_4]^{2-}$	$1 \times 10^5 : 1$	10
$[M(PEt_3)_2(C_6H_4Me\text{-}o)Cl]$	py [d]		$10^7 : 10^5 : 1$	*e*
$[MCl_4]^{2-}$	phen [f]		$10^3 : 1$	*g*
$[MCl_4]^{2-}$	NH_3 [b]		$10^6 : 1$	*h*

[a] The reaction for Ni^{II} is second order. [b] In water. [c] In methanol. [d] In ethanol; py = pyridine. [e] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207. [f] phen = 1,10-Phenanthroline. [g] J. V. Rund, *Inorg. Chem.*, 1970, **9**, 1211; J. H. Cawley and J. V. Rund, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1406. [h] D. S. Martin, jun., *Inorg. Chim. Acta Rev.*, 1967, **1**, 87; R. A. Reinhart and W. W. Monk, *Inorg. Chem.*, 1970, **9**, 2026.

It is interesting to compare the results for the ratios of the rate constants of Ni^{II}, Pd^{II}, and Pt^{II} shown in Table 3 with those previously reported. Obviously, it is only valid to compare reactions having similar rate laws. It is significant that the ratio $k_{Ni} : k_{Pt}$ remains relatively constant for all the reactions reported. From the data presented it can be seen that palladium(II) complexes can show widely differing behaviour. The reactivity of Pd^{II} can vary from approximately an order of magnitude less than that of Ni^{II} to a reactivity comparable to that of Pt^{II}. The limited data available appear to indicate that the latter reactivity is 'typical' of palladium(II) complexes when the metal is not involved in a delocalized π-electron ligand system.[4,20,21] The adduct-forming ability of nickel(II) square-planar complexes has been interpreted in terms of the availability of the $4p_z$ orbital to form a σ bond to a fifth group.[8,11,22,23] When this orbital is involved in a delocalized π-electron system its availability for σ-bond formation is reduced and consequently the four-co-ordinate geometry is stabilized.[24,25] The adduct-forming abilities of square-planar complexes of Pd^{II} and Pt^{II} have not been investigated to the same extent as those of Ni^{II}. However, it would be reasonable to interpret them in the same manner. The experimental data indicate that the availability of the Pd $5p_z$ orbital for σ-bond formation

TABLE 4

Summary of the lability series of square-planar complexes of Ni^{II}, Pd^{II}, and Pt^{II} with cyanide ion and ethylenediamine as nucleophiles

(*a*) Ni^{II}: nucleophile = $[CN]^-$

$[Ni\{S_2P(OMe)_2\}_2] > [Ni(S_2CNC_4H_8)_2] > [Ni(cimd)_2]^{2-}$

nucleophile = en

$[Ni(S_2CNC_4H_8)_2] > [Ni(S_2CNEt_2)_2] > [Ni(cimd)_2]^{2-} \simeq [Ni(nped)_2]^{2-}$

(*b*) Pd^{II}: nucleophile = $[CN^-]$

$[Pd\{S_2P(OMe)_2\}_2] > [Pd(S_2CNEt_2)_2] > [Pd(nped)_2]^{2-} > [Pd(cimd)_2]^{2-}$

(*c*) Pt^{II}: nucleophile = $[CN]^-$

$[Pt\{S_2P(OMe)_2\}_2] > [Pt(S_2CNEt_2)_2] > [Pt(cimd)_2]^{2-}$

---

[19] D. Coucouvanis and J. P. Fackler, jun., *Inorg. Chem.*, 1967, **6**, 2047.

[20] F. Basolo, *Adv. Chem. Ser.*, 1965, **49**, 81.

[21] R. Reinhardt and R. Sparkes, *Inorg. Chem.*, 1967, **6**, 2190.

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

[23] S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**, 6669.

[24] S. I. Shupack, *J. Amer. Chem. Soc.*, 1964, **86**, 4594.

[25] H. B. Gray, *Inorg. Chem.*, 1964, **3**, 663.

with incoming nucleophiles is sensitive to the ligand environment. Despite the apparent widely varying ability of square-planar palladium(II)–sulphur complexes to form five-co-ordinate species, the overall order of lability as reflected in the rate constants is the same as for Ni^{II} (Table 4). The platinum(II) complexes also follow the same lability order (Table 4).

Conclusion.—The results presented indicate the comparative insensitivity of the rate constants of substitution reactions of square-planar complexes of Ni^{II} and Pt^{II} to the ligand environment. However, they do highlight the sensitivity of the reactivity of the palladium(II) complexes to the nature of the surrounding ligands. This study illustrates the kinetic consequences of the adduct-forming ability of square-planar palladium(II)–sulphur complexes. In general, the results are in agreement with those obtained for similar nickel(II) systems using physical and preparative methods.

One of us (P. F. B.) thanks the Department of Education for support.

[7/808 *Received, 9th May,* 1977]