

Nucleophilic Substitution Reactions at Planar Four-co-ordinate Monoanionic Platinum(II) Complexes

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The kinetics of displacement of chloride from complex anions of the type $[\text{Pt}(4\text{R-pydc})\text{Cl}]^-$ (pydca = pyridine-2,6-dicarboxylate; R = H, Cl or OMe) by a number of anionic and neutral nucleophiles have been studied in aqueous solution, at 25.0 °C, $I = 0.50 \text{ mol dm}^{-3}$ (LiClO_4). Apart from the reactions with OH^- , the reactivities of the substrates are not greatly sensitive to the nature of the substituent in the 4 position. Anionic nucleophiles can be as much as two orders of magnitude less reactive than neutral nucleophiles with similar n_{Pt}^0 values. The rate law for the reaction with OH^- takes the form $-\text{dln}[\text{substrate}]/\text{dt} = k_s + k_3[\text{OH}^-]^2$, where k_s is the first-order rate constant for the solvolytic pathway observed in all the substitution reactions, and where k_3 is sensitive to the basicity of the nitrogen in the terdentate ligand.

The quantitative nucleophilicity sequence towards four-co-ordinate planar d^8 platinum(II) in terms of the n_{Pt} and/or n_{Pt}^0 scale^{1,2} was originally intended to be applied to all substrates, irrespective of charge. However, it soon became apparent that the position of certain nucleophiles in this reactivity sequence was sensitive to the nature of the substrate and it was necessary to invoke the concept of *biphilicity*³ whereby certain nucleophiles were able to utilise π back donation from the metal to stabilise the transition state. The extent of this contribution depended upon the π basicity of the platinum in the particular substrate. In recent years, systematic studies have shown that it is possible to assign specific nucleophilicity scales to substrates of a particular charge type.⁴⁻⁸

The study of the displacement of the chloride *trans* to L, from a series of monoanionic platinum complexes of the type $[\text{Pt}(\text{L})\text{Cl}_3]^-$ containing moderate to high *trans*-effect ligands (L = Me_2SO , Et_2S , PMe_3 , PEt_3 , PPh_3 , or AsEt_3), showed that, compared to the rate constants for the entry of neutral nucleophiles, those for the entry of anionic nucleophiles were much smaller than expected on the basis of the n_{Pt}^0 scale⁹ and were often too small to offer a measurable pathway for substitution. In these cases substitution required a rate-determining solvolysis. The same relatively low reactivity has been observed for the displacement of chloride from the anionic complex $[\text{Pt}(\text{pydca})\text{Cl}]^-$ (pydca = pyridine-2,6-dicarboxylate) by anionic nucleophiles, when compared to its displacement by water.¹⁰

In order to add to our knowledge of this type of charge effect, we have studied a number of substitution reactions of three substrates of the type $[\text{Pt}(\text{L})\text{Cl}]^-$ [L = pydca, 4-chloropyridine-2,6-dicarboxylate (cpydca) or 4-methoxypyridine-2,6-dicarboxylate (mopydca)]. The results are discussed in this paper.

Experimental

Preparations.—The complex $\text{K}[\text{Pt}(\text{pydca})\text{Cl}]$ was prepared by the method of Cattalini *et al.*¹⁰

4-Methoxypyridine-2,6-dicarboxylic acid was prepared according to the method of Markees.¹¹ Yield 61%, m.p. 223 °C (Found: C, 48.0; H, 3.30; N, 6.75. $\text{C}_8\text{H}_7\text{NO}_5$ requires C, 48.7; H, 3.60; N, 7.10%).

4-Chloropyridine-2,6-dicarboxylic acid monohydrate was prepared by the method of Robinson.¹² Phenylphosphonic

dichloride (17.016 cm^3 , 0.12 mol) was added to pyridine-2,6-dicarboxylic acid (5.493 g, 0.03 mol), and the reaction mixture was heated at 130 °C for 2 h. Water (150 cm^3) was added and the acid neutralised by base. The residual impurities were filtered off and the solution was acidified with HCl until the pale pink product was completely precipitated. This was filtered off, dried in an oven under vacuum and recrystallised from glacial acetic acid. Yield 2.412 g (36.6%), m.p. 210 °C (Found: C, 38.8; H, 2.90; Cl, 16.45; N, 6.50. $\text{C}_7\text{H}_6\text{ClNO}_5$ requires C, 38.3; H, 2.75; Cl, 16.15; N, 6.40%).

Potassium chloro(4-chloropyridine-2,6-dicarboxylato)platinate(II) dihydrate. A solution of 4-chloropyridine-2,6-dicarboxylic acid (0.219 g, 1 mmol) in water (5 cm^3), neutralised to pH 5 with KOH (1 mol dm^{-3}), was slowly added at 70 °C under stirring to a solution of $\text{K}_2[\text{PtCl}_4]$ (0.415 g, 1 mmol) in water (20 cm^3). The pH decreased to 2.5 and a dark yellow precipitate was formed. On increasing the pH to 5 by adding aqueous KOH solution (1 mol dm^{-3}) the precipitate dissolved giving a mustard-yellow solution. After 1 h at 70 °C the crystalline product separated on cooling and was filtered off, washed with cold water (5 cm^3) and dried in vacuum. Yield 0.354 g (70%), m.p. > 220 °C (Found: C, 16.85; H, 1.05; Cl, 13.90; N, 2.70. $\text{C}_7\text{H}_6\text{Cl}_2\text{KNO}_6\text{Pt}$ requires C, 16.65; H, 1.20; Cl, 14.05; N, 2.75%). Relevant infrared bands (in KBr and polyethylene) at 1670s(br) [$\nu(\text{COO})$] and 340m cm^{-1} [$\nu(\text{Pt}-\text{Cl})$].

Potassium bromo(4-chloropyridine-2,6-dicarboxylato)platinate(II) hydrate. Potassium bromide (0.059 g, 0.5 mmol) dissolved in water (2 cm^3) was added under stirring to a hot solution of $\text{K}[\text{Pt}(\text{cpydca})\text{Cl}]$ dissolved in water (2 cm^3). At 80 °C the colour changed from orange to yellow within 30 min. On cooling slowly, the product separated as yellow needle crystals, which were filtered off, washed with cold water (1 cm^3) and dried in vacuum. Yield 0.175 g (68%), m.p. > 220 °C (Found: C, 15.60; H, 0.80; N, 2.60. $\text{C}_7\text{H}_4\text{BrClKNO}_5\text{Pt}$ requires C, 15.80; H, 0.75; N, 2.65%). Relevant infrared bands (in KBr and polyethylene) at 1670s(br) [$\nu(\text{C}-\text{O})$] and 282m cm^{-1} [$\nu(\text{Pt}-\text{Br})$].

Potassium (4-chloropyridine-2,6-dicarboxylato)iodoplatinate(II) monohydrate. Potassium iodide (0.083 g, 0.5 mmol) was dissolved in water (1 cm^3) and added dropwise, under stirring, to a solution of $\text{K}[\text{Pt}(\text{cpydca})\text{Cl}]$ dissolved in water (3 cm^3). After stirring for 15 min at 70 °C the solution was cooled to 0 °C. Addition of ethanol (15 cm^3) precipitated white crystals

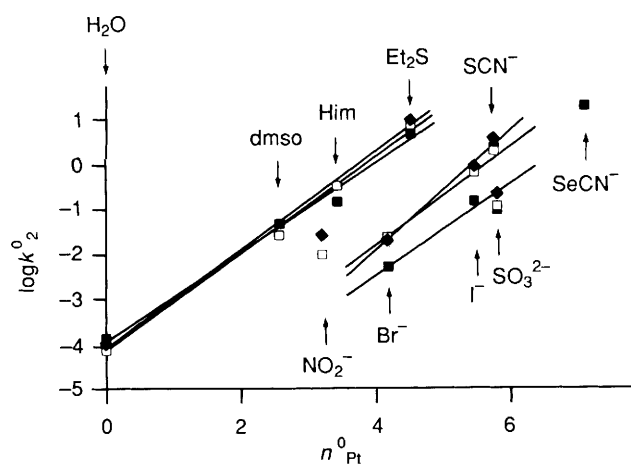


Fig. 1 Plots of $\log k_2^0$ vs. n_{Pt}^0 for the displacement of Cl^- from $[\text{Pt}(\text{L})\text{Cl}]^-$. L = pydca (\square), cpydca (\blacklozenge) or mopydca (\blacksquare)

(KCl), which were filtered off. The solution was kept at 0°C and the product precipitated as ochre-yellow crystals within 15 h and was filtered off and dried in vacuum. Yield 0.224 g (80%), m.p. $>220^\circ\text{C}$ (Found: C, 14.30; H, 0.70; N, 2.35. $\text{C}_7\text{H}_4\text{ClIKNO}_5\text{Pt}$ requires C, 14.5; H, 0.70; N, 2.40%). Relevant infrared bands (in KBr and polyethylene) at 1670s(br) $[\nu(\text{C}-\text{O})]$ and 172m cm^{-1} $[\nu(\text{Pt}-\text{I})]$.

Potassium (4-chloropyridine-2,6-dicarboxylato)nitroplatinate(II). A solution of KNO_2 (0.043 g, 0.5 mmol) in water (1 cm^3) was added dropwise to a solution of $\text{K}[\text{Pt}(\text{cpydca})\text{Cl}]$ (0.252 g, 0.5 mmol) in water (3 cm^3) and the reaction mixture kept at 70°C for 10 min. Silver nitrate (0.085 g, 0.5 mmol) was then added. In 30 min, AgCl precipitated and was filtered off. On cooling the product separated as red crystals, which were filtered off and dried in vacuum. Yield 0.138 g (58%), m.p. $>220^\circ\text{C}$ (Found: C, 16.95; H, 0.40; Cl, 7.70; N, 5.20. $\text{C}_7\text{H}_2\text{ClIKN}_2\text{O}_6\text{Pt}$ requires C, 17.5; H, 0.40; Cl, 7.40; N, 5.85%). Relevant infrared bands (in KBr and polyethylene) at 1670s(br) $[\nu(\text{C}-\text{O})]$, 1390s(br) $[\nu_{\text{asym}}(\text{NO}_2)]$, 1338s(br) $[\nu_{\text{sym}}(\text{NO}_2)]$, and 362m cm^{-1} $[\nu(\text{Pt}-\text{NO}_2)]$.

Potassium chloro(4-methoxy-pyridine-2,6-dicarboxylato)platinate(II) hydrate. 4-Methoxy-pyridine-2,6-dicarboxylic acid (0.197 g, 1 mmol) was dissolved in water (5 cm^3) and added, under stirring, to a solution of $\text{K}_2[\text{PtCl}_4]$ (0.415 g, 1 mmol) in water (20 cm^3) at 70°C . On keeping the temperature at 70°C for 1 h the pH decreased to 0.8 and a white precipitate separated from the red solution. On adding KOH to increase the pH of the solution to 4, the precipitate dissolved and the colour changed from red to dark orange. The product separated on cooling as ochre-yellow crystals which were filtered off, washed with cold water (2 cm^3) and dried in vacuum. Yield 0.205 g (50%), m.p. $>220^\circ\text{C}$ (Found: C, 19.80; H, 1.20; Cl, 7.15; N, 2.85. $\text{C}_8\text{H}_7\text{ClIKNO}_6\text{Pt}$ requires C, 19.9; H, 1.45; Cl, 7.35; N, 2.90%). Relevant infrared bands (in KBr and polyethylene) at 1670s(br) $[\nu(\text{C}-\text{O})]$ and 334m cm^{-1} $[\nu(\text{Pt}-\text{Cl})]$.

Potassium (4-methoxy-pyridine-2,6-dicarboxylato)nitroplatinate(II) hydrate. 4-Methoxy-pyridine-2,6-dicarboxylic acid (0.197 g, 1 mmol) and $\text{K}_2[\text{PtCl}_4]$ (0.415 g) were dissolved in water (20 cm^3) and allowed to react under stirring, at 70°C . The pH initially decreased to 1 and a white solid separated from the red solution. This was redissolved by increasing the pH to 4.5 by adding KOH (1 mol dm^{-3}). Sodium nitrate (0.069 g, 1 mmol) was added and the mixture heated for 30 min at 70°C . Silver nitrate (0.615 g, 4 mmol) was added and the precipitated AgCl was filtered off. On cooling a red powder separated and was filtered off, washed with cold water (5 cm^3) and dried in vacuum. Yield 0.185 g (30%), m.p. $>220^\circ\text{C}$. (Found: C, 19.45; H, 1.05; N, 5.70. $\text{C}_8\text{H}_7\text{KN}_2\text{O}_8\text{Pt}$ requires C, 19.45; H, 1.40; N, 5.70%). Relevant infrared bands (in KBr and polyethylene) at 1670s(br) $[\nu(\text{COO})]$, 1390s(br) $[\nu(\text{NO}_2)]$ and 362m cm^{-1} $[\nu(\text{Pt}-\text{NO}_2)]$.

All other chemicals were reagent grade (Aldrich or Fluka) unless otherwise specified.

Kinetics.—Reactions were initiated by mixing equal volumes of solutions of the substrate and nucleophile in the thermostatted cell of a Perkin-Elmer Lambda-5 spectrophotometer at 25.0°C and the absorbance, A_t , at an appropriate wavelength was measured as a function of time, t . The pseudo-first-order rate constants, k_{obs} , were calculated using a non-linear regression analysis of the function $A_t = A_\infty - (A_\infty - A_0)[\exp(-k_{\text{obs}}t)]$ based on the Gauss-Newton algorithm, with three optimised parameters, the initial absorbance A_0 , the final absorbance A_∞ , and k_{obs} . All the kinetic runs were carried out in the presence of excess of nucleophile, to provide pseudo-first-order conditions, in water at 25.0°C and at constant ionic strength (0.50 mol dm^{-3} , LiClO_4). The values of k_{obs} are summarised in Table 1.

Results and Discussion

Careful examination of the spectral changes that occur after the reagents are mixed and the close similarity of the spectra at the end of the reaction with those of authentic samples of the expected reaction product demonstrate that all the reactions that have been studied kinetically involve the displacement of co-ordinated chloride by the nucleophile Y^{n-} . When there are subsequent changes, it is the spectrum at the end of the first stage that is identical to that of the expected reaction product. The number of stages observed, the spectral characteristics of the changes and the conditions of measurement are all summarised in Table 1.

The first reaction with OH^- , clearly identified as the displacement of Cl^- by OH^- , is followed by slower subsequent changes. The ^1H NMR spectra show that the second change involves opening of the $\text{Pt}, \text{N}, \text{O}$ ring at oxygen and the ligand becomes bidentate. Eventually there is disproportionation to give the bis(chelate, N, O) complex which separates out and has been identified by elemental analysis. These observations are only mentioned briefly here and will be reported in detail elsewhere when they are complete.

The changes, studied in the presence of a sufficient excess of Y^{n-} over substrate, are all first order and, apart from the reactions with hydroxide ion which will be discussed below, all the pseudo-first-order rate constants, k_{obs} , obey the general relationship $k_{\text{obs}} = k_1 + k_2[\text{Y}^{n-}]$, which is normal for nucleophilic substitution at planar four-co-ordinate d^8 metal complexes. The values of the measured rate constants k_1 and k_2 are summarised in Table 2, together with the corresponding values of the second-order rate constant at zero ionic strength, k_2^0 , calculated using the relationship (1) where $z_a = -1$, $z_b =$

$$\log k_2^0 = \log k_2 - 2z_a z_b I^{1/2} / (1 + I^{1/2}) \quad (1)$$

$-n$ and $\alpha = 0.51$. The experimental error in the determination of k_1 is large.

The plots of $\log k_2^0$ vs. n_{Pt}^0 for the three substrates examined are shown in Fig. 1. The first obvious observation is that there is little variation in k_1 or k_2 on changing from cpydca to pydca to mopydca even though the basicity of the nitrogen probably changes considerably. (The pK_a values of the corresponding protonated pyridines in water are 3.84, 5.17 and 6.47 respectively.) This agrees with observations made in earlier studies using monodentate substituted pyridines *trans* to the leaving group. Reactivity in such systems depends on the basicity of the pyridine *cis* to the leaving group and is barely affected by changes in the *trans* position.¹³

It is also clear that, while the n_{Pt}^0 scale cannot be applied to all nucleophiles irrespective of their charge when they react with the three anionic substrates, there are some residual relationships. For example, the points for neutral nucleophiles lie close to a line of slope 1.06 ± 0.05 while those for the anionic species lie

Table 1 Pseudo-first-order rate constants for the reactions of substrates of the type $[\text{Pt}(\text{R-pydca})\text{Cl}]^-$ with nucleophiles in water, at 25 °C, $I = 0.50$ mol dm⁻³ (LiClO₄)

Nucleophile	Wavelength/nm			$10^3[\text{Y}^{n-}]/$ mol cm ⁻³	$10^3k_{\text{obs}}/s^{-1}$	Nucleophile	Wavelength/nm			$10^3[\text{Y}^{n-}]/$ mol dm ⁻³	$10^3k_{\text{obs}}/s^{-1}$				
	Range	Isosbestic points	Used for calculation				Range	Isosbestic points	Used for calculation						
R-pydca = Pyridine-2,6-dicarboxylate															
OH ⁻	240–360	256	270	5	3.65 ± 0.12	dmso	235–350	290	340	50	3.34 ± 0.03				
		294		10	3.87 ± 0.06			263		100	5.04 ± 0.03				
		258*		20	4.28 ± 0.07			238		150	6.55 ± 0.04				
		276*		30	5.13 ± 0.04					200	7.54 ± 0.1				
		352*		40	6.10 ± 0.07					250	8.92 ± 0.09				
				50	7.20 ± 0.03										
				60	8.74 ± 0.05			Et ₂ S		240–350	—	282	1.0	7.35 ± 0.1	
				70	10.56 ± 0.08								1.2	9.57 ± 0.02	
				80	12.04 ± 0.09								1.4	10.45 ± 0.04	
				100	17.9 ± 0.4								1.6	11.2 ± 0.08	
Him	240–340	305	272	5	6.71 ± 0.58					2.0	14.5 ± 0.1				
		(273)*		10	8.18 ± 0.43										
				15	10.55 ± 0.3										
				20	11.7 ± 0.3										
R-pydca = 4-Chloropyridine-2,6-dicarboxylate															
OH ⁻	240–330	254	264	1	5.85 ± 0.05	SCN ⁻	250–360	—	284	1.0	8.45 ± 0.2				
		286		10	6.43 ± 0.03					1.5	12.5 ± 0.3				
				20	8.74 ± 0.05					2.0	18.1 ± 0.3				
				30	12.3 ± 0.1					2.5	25.5 ± 0.2				
				35	14.7 ± 0.1					3.0	27.5 ± 0.6				
				40	17.3 ± 0.1					3.5	32.1 ± 0.7				
				45	19.8 ± 0.1					4.0	35.2 ± 1				
				50	22.7 ± 0.1										
				60	29.5 ± 0.2					SO ₃ ²⁻	250–340	—	270	1	3.78 ± 0.05
				65	33.1 ± 0.3									3	6.94 ± 0.08
	70	36.6 ± 0.4	5	10.0 ± 0.2											
	100	64.6 ± 1.5	9	16 ± 0.5											
NO ₂ ⁻	250–360	301	259	10	2.73 ± 0.05	Him	250–340	—	277	5	13.3 ± 0.04				
		(249,259)*		30	204.00 ± 0.02					15	17.3 ± 0.08				
				40	4.26 ± 0.03					20	19.0 ± 0.01				
				60	5.03 ± 0.08										
				60	6.27 ± 0.07										
Br ⁻	250–380	—	372	50	6.26 ± 0.1	dmso	250–350	—	240	25	2.51 ± 0.02				
				150	10.8 ± 0.25					50	3.92 ± 0.03				
				200	15.5 ± 0.2					75	4.91 ± 0.02				
				250	18.2 ± 0.3					100	6.0 ± 0.03				
				350	22.4 ± 0.8					125	7.15 ± 0.1				
I ⁻	250–380	311	360	1.0	5.69 ± 0.06	Et ₂ S	240–350	—	350	1	7.56 ± 0.03				
		275		2.0	8.35 ± 0.11					1.4	12.1 ± 0.03				
				3.0	11.6 ± 0.1					1.6	13.7 ± 0.1				
				4.0	16.1 ± 0.3					1.8	15.9 ± 0.1				
				5.5	17.5 ± 0.4					2	16.5 ± 0.1				
				6.0	18.0 ± 0.7										
				6.5	21.8 ± 0.8										
R-pydca = 4-Methoxypyridine-2,6-dicarboxylate															
OH ⁻	250–360	283	320	5	6.67 ± 0.1	Br ⁻	250–340	—	340	50	2.51 ± 0.05				
				10	6.93 ± 0.05					150	3.56 ± 0.09				
				15	7.19 ± 0.04					200	4.75 ± 0.1				
				20	7.63 ± 0.04					250	5.23 ± 0.1				
				25	8.38 ± 0.07					350	6.79 ± 0.08				
				30	8.63 ± 0.1					450	8.1 ± 0.2				
				40	11.2 ± 0.1					500	8.75 ± 0.3				
				60	12.1 ± 0.2										
				70	14.2 ± 0.2					I ⁻	250–380	306	360	2	2.58 ± 0.05
				80	16.0 ± 0.1									4	3.13 ± 0.04
				90	17.8 ± 0.2									6	4.21 ± 0.03
				100	20.6 ± 0.1									8	4.94 ± 0.05
				120	26.5 ± 0.2									10	6.2 ± 0.1
				140	37.3 ± 0.3									12	6.45 ± 0.1
				160	47.4 ± 0.4										

Table 1 (continued)

Wavelength/nm						Wavelength/nm					
Nucleophile	Range	Isosbestic points	Used for calculation	$10^3[Y^{n-}]/\text{mol cm}^{-3}$	$10^3k_{\text{obs}}/\text{s}^{-1}$	Nucleophile	Range	Isosbestic points	Used for calculation	$10^3[Y^{n-}]/\text{mol dm}^{-3}$	$10^3k_{\text{obs}}/\text{s}^{-1}$
R-pydc = 4-Methoxypyridine-2,6-dicarboxylate (continued)											
SO_3^{2-}	250-340	—	340	3	4.15 ± 0.08	Him	250-340	285	294	5	6.0 ± 0.7
				7	7.0 ± 0.2					10	6.6 ± 0.2
				11	9.6 ± 0.1					15	7.5 ± 0.7
				15	11.9 ± 0.3					20	8.2 ± 0.5
				19	15.32 ± 0.2						
SCN^-	250-340	287	340	1	4.20 ± 0.09	dmso	240-350	—	258	50	2.32 ± 0.03
				2	9.24 ± 0.06					100	4.72 ± 0.07
				3	15.5 ± 0.3					150	6.62 ± 0.08
				4	22.6 ± 0.6					200	9.45 ± 0.2
				5	27.7 ± 0.4					250	11.8 ± 0.2
				6	34.0 ± 0.6						
SeCN^-	270-340	—	330	0.2	13.0 ± 0.06	Et_2S	240-350	—	260	0.75	4.6 ± 0.2
				0.4	14.4 ± 0.01					0.875	5.4 ± 0.1
				0.6	32.3 ± 0.2					1	5.47 ± 0.01
				0.8	44.6 ± 0.1					1.2	5.99 ± 0.02
				1	55.5 ± 0.2					1.4	8.02 ± 0.01
				1.2	65.3 ± 0.2					1.5	8.57 ± 0.05
		1.6	9.95 ± 0.1								
				2	10.4 ± 0.1						

* Isosbestic points during following stages.

Table 2 First- and second-order rate constants for the reactions of nucleophiles displacing chloride from substrates of the type $[\text{Pt}(\text{R-pydc})\text{Cl}]^-$, in water at 25 °C, $I = 0.50 \text{ mol dm}^{-3}$ (LiClO_4)

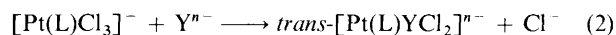
Nucleophile	$10^3 k_1/\text{s}^{-1}$	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k^0/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
R-pydc = Pyridine-2,6-dicarboxylate			
NO_2^- ^a	3.53 ± 0.08	0.025 ± 0.001	0.0096
Br^- ^a	3.2 ± 0.9	0.065 ± 0.003	0.024
SO_3^{2-} ^a	2.00 ± 0.03	0.81 ± 0.01	0.12
I^- ^a	2.6 ± 0.1	1.74 ± 0.02	0.67
SCN^- ^a	0.4 ± 0.2	4.81 ± 0.09	1.82
SeCN^- ^a	4.0 ± 0.7	49.9 ± 0.9	18.9
dmso ^b	2.2 ± 0.2	0.027 ± 0.001	0.027
Him ^c	4.9 ± 0.3	0.36 ± 0.02	0.36
Et_2S	0.8 ± 0.7	6.8 ± 0.4	6.8
R-pydc = 4-Chloropyridine-2,6-dicarboxylate			
NO_2^-	2.14 ± 0.009	0.0701 ± 0.0003	0.027
Br^-	3 ± 1	0.056 ± 0.004	0.021
SO_3^{2-}	2.4 ± 0.4	1.50 ± 0.06	0.21
I^-	3.2 ± 0.7	2.6 ± 0.2	1.0
SCN^-	-0.5 ± 1	9.31 ± 0.4	3.5
dmso	1.5 ± 0.1	0.045 ± 0.002	0.045
Him	11.3 ± 0.2	0.39 ± 0.01	0.39
Et_2S	-1.2 ± 1	9.2 ± 0.8	9.2
R-pydc = 4-methoxypyridine-2,6-dicarboxylate			
Br^-	1.7 ± 0.1	0.0141 ± 0.0004	0.0053
SO_3^{2-}	2.1 ± 0.3	0.68 ± 0.02	0.098
I^-	1.7 ± 0.2	0.42 ± 0.03	0.16
SCN^-	-2.3 ± 0.5	6.0 ± 0.1	2.3
SeCN^-	2.5 ± 0.9	52 ± 1	20
dmso	-0.1 ± 0.2	0.047 ± 0.0002	0.047
Him	5.26 ± 0.09	0.144 ± 0.006	0.14
Et_2S	0.6 ± 0.8	5.2 ± 0.6	5.2

^a From ref. 10. ^b dmso = Dimethyl sulphoxide. ^c Him = imidazole.

well below this line. The 'normal' anionic nucleophiles are some two orders of magnitude less reactive than neutral nucleophiles with comparable n_{Pt}^0 values. The points for the 'biphilic' nucleophiles, NO_2^- , SCN^- and SeCN^- , general lie between these limits. This is a further example of the great importance of charge in determining relative nucleophilicities in d⁸ systems. It

is of interest to observe that the points for the dianionic nucleophile SO_3^{2-} lie near the line for the 'normal' anionic reagents and do not reflect any further decrease in reactivity arising from the higher charge.

The concept of a separate nucleophilicity scale for mono-anionic substrates involving a series of n_{Pt}^- values has already been used to correlate the data for reaction (2) using data for the



reactions of the standard substrate, $\text{L} = \text{AsEt}_3$, to establish an n_{Pt}^- scale.⁹ However, the reactions of this substrate were studied in 95% methanol + 5% water at $I = 0.50 \text{ mol dm}^{-3}$ (LiClO_4). Because of the uncertainties involved in calculating k^0 from data determined at $I = 0.50 \text{ mol dm}^{-3}$ in methanol, no attempt was made to calculate the rate constants at zero ionic strength and so, in any comparison of anionic nucleophiles (rate constants diminish in magnitude as the salt effects decrease) and neutral nucleophiles (rate constants insensitive to ionic strength), the anionic nucleophiles appear to be relatively more reactive than they would be at zero ionic strength. Since the displacement of Cl^- from $[\text{Pt}(\text{R-pydc})\text{Cl}]^-$ was studied in aqueous solution, extrapolation to zero ionic strength is feasible and we propose to use the $\log k^0$ values for the displacement of Cl^- from $[\text{Pt}(\text{pydc})\text{Cl}]^-$ as a measure of nucleophilicity. In Fig. 2 the values of $\log k^0$ for the substrates with $\text{L} = \text{cpydc}$ or mopydc have been plotted against the corresponding $\log k^0$ values when $\text{L} = \text{pydc}$. As in the case of the data for the $[\text{Pt}(\text{L})\text{Cl}_3]^-$ complexes, the plots are much less scattered than those using the n_{Pt}^0 values.

However, even within the limited range of comparison, the sequences of reactivity derived from the two groups of anionic substrates appear to be rather different. In this work the sequence {as expressed by the relative values of $\log [k^0_2/k^0_2]$ (for Br^-)} for the displacement of chloride from $[\text{Pt}(\text{pydc})\text{Cl}]^-$ is $\text{Br}^- (0.0) < \text{dmso} (0.1) < \text{I}^- (1.5) < \text{SCN}^- (1.9) < \text{Et}_2\text{S} (2.5)$, whereas in the previous work studied in 95% methanol + 5% water, $I = 0.50 \text{ mol dm}^{-3}$, the sequence of values for $\log [k_2/k_2]$ (for Br^-) for the displacement of Cl^- from $[\text{Pt}(\text{Et}_3\text{As})\text{Cl}_3]^-$ is $\text{Br}^- (0.0) < \text{SCN}^- (0.6) < \text{I}^- (0.7) < \text{dmso} (1.2) < \text{Et}_2\text{S} (2.3)$. Apart from the inversion of the reactivities of iodide and thiocyanate, which in all cases are reasonably close together, the

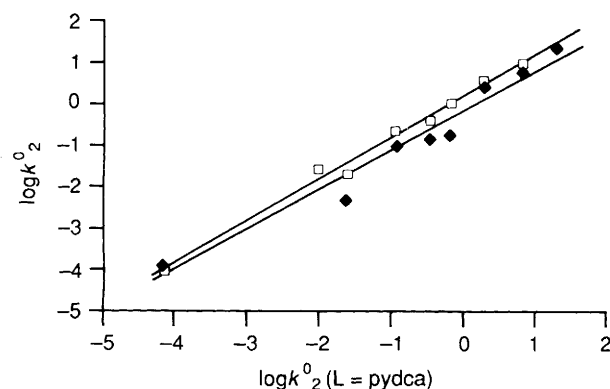


Fig. 2 Plots of $\log k_0^2$ for the complexes with $L = \text{cpydca}$ (\square) or mopydca (\blacklozenge) against $\log k_0^2$ for the complex with $L = \text{pydca}$

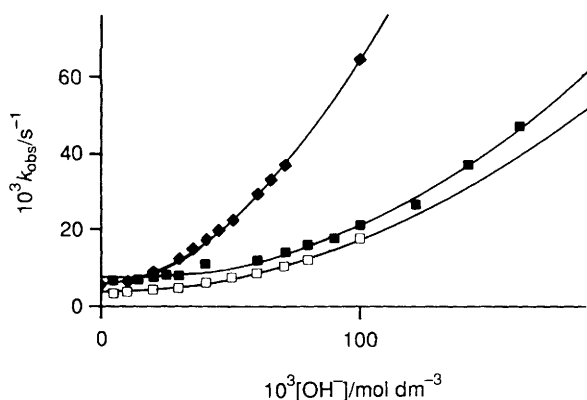


Fig. 3 Plots of k_{obs} vs. $[\text{OH}^-]$ for the reaction $[\text{Pt}(\text{L})\text{Cl}]^- + \text{OH}^- \rightarrow [\text{Pt}(\text{L})(\text{OH})]^- + \text{Cl}^-$ with symbols as in Fig. 1. Curves calculated as best fit to the polynomial $k_{\text{obs}} = k_a + k_b[\text{OH}^-] + k_c[\text{OH}^-]^2$. Values collected in Table 4.

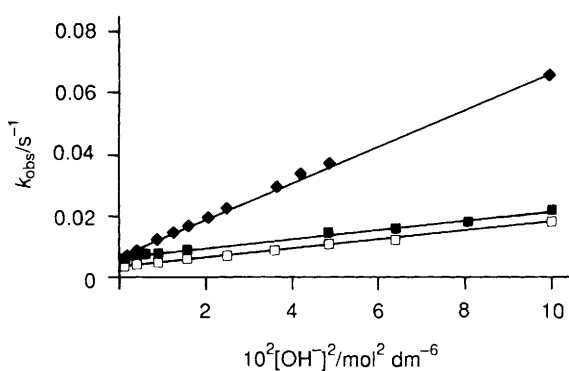


Fig. 4 Plots of k_{obs} vs. $[\text{OH}^-]^2$ for the reaction $[\text{Pt}(\text{L})\text{Cl}]^- + \text{OH}^- \rightarrow [\text{Pt}(\text{L})(\text{OH})]^- + \text{Cl}^-$ with symbols as in Fig. 1

most significant difference is the lower nucleophilic discrimination in the Et_3As complex, which is typical for a substrate with a moderate to strong *trans*-effect ligand. The relative positions of the neutral and anionic ligands cannot be compared because the data in methanol are not extrapolated to $I = 0$. Even when the different ionic strength conditions are taken into account, dmsO is relatively much less reactive in the sequence for the $[\text{Pt}(\text{pydca})\text{Cl}]^-$ anion, where the *trans* effect is weak, than it is in that of the $[\text{Pt}(\text{AsEt}_3)\text{Cl}_3]^-$ anion where the *trans* effect is strong. This is typical of the behaviour of dimethyl sulphoxide (dmsO) whose reactivity both as an entering group and as a leaving group is very sensitive to the nature of the substrate.¹³

The reactions with hydroxide are of considerable interest. The plots of k_{obs} vs. $[\text{OH}^-]$ are non-linear, Fig. 3, but the intercepts are comparable in magnitude to the intercepts of the linear plots of k_{obs} versus $[\text{nu}]$ for the other nucleophiles

Table 3 Pseudo-first-order rate constants for the reaction of $[\text{Pt}(\text{pydca})\text{Cl}]^-$ with OH^- in the presence of other ions in water, at 25 °C

$10^3[\text{OH}^-]/\text{mol dm}^{-3}$	$10^3[\text{X}^-]/\text{mol dm}^{-3}$ $\text{X} = \text{Br}^-^a$	$10^3 k_{\text{obs}}/\text{s}^{-1}$
70	0	10.56 ± 0.08
70	50	8.98 ± 0.05
70	150	8.7 ± 0.1
70	300	9.8 ± 0.1
70	400	10.3 ± 0.2
10	0	3.87 ± 0.06
10	50	3.1 ± 0.5
10	400	3.2 ± 0.5
$\text{X} = \text{F}^-$		
5	495	5.08 ± 0.06
15	485	5.8 ± 0.1
30	470	6.85 ± 0.1
40	460	6.6 ± 0.3
50	450	9.75 ± 0.1
70	430	12.0 ± 0.1
80	420	12.9 ± 0.1
90	410	16.4 ± 0.2
100	400	18.4 ± 0.3
20 ^a	—	4.28 ± 0.07
20 ^b	—	3.95 ± 0.1

^a $I = 0.50 \text{ mol dm}^{-3}$ (LiClO_4). ^b $I = 0.50 \text{ mol dm}^{-3}$ (NaClO_4).

Table 4 Analysis of the non-linear dependence of k_{obs} on $[\text{OH}^-]$ for the reaction $[\text{Pt}(\text{R-pydca})\text{Cl}]^- + \text{OH}^- \rightarrow [\text{Pt}(\text{R-pydca})(\text{OH})]^- + \text{Cl}^-$

R	$k_{\text{obs}} = k_a + k_b[\text{OH}^-] + k_c[\text{OH}^-]^2$		$k_{\text{obs}} = k_s + k_3[\text{OH}^-]^2$	
	$10^3 k_c/\text{s}^{-1}$	$k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_s/\text{s}^{-1}$	$k_3 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
4-Cl	4.4	0.133	4.7	7.4
H	3.8	-0.003	1.4	3.7
4-OMe	7.5	-0.040	1.8	6.5

(nu) and probably represent the solvolytic rate constants, k_s . Analysis by a polynomial expression of the sort, $k_{\text{obs}}/\text{s}^{-1} = k_a + k_b[\text{OH}^-] + k_c[\text{OH}^-]^2$, gives values for k_b that are small and negative in the cases of the two less basic terdentate ligands. A simpler plot of k_{obs} versus $[\text{OH}^-]^2$ is reasonably linear in all three cases, Fig. 4, although deviations at the lower hydroxide concentrations in the reaction of the 4-chloropyridine-2,6-dicarboxylate complex are consistent with the appearance of the first-order $[\text{OH}^-]$ term. It would be rash to give significance to this observation without more detailed studies and care must be taken to avoid overparameterising the analysis. Values of the derived rate constants are collected in Table 4.

Although hydroxide is reputed to exert no independent nucleophilicity and enters the complex by way of rate-determining solvolysis by water and subsequent rapid deprotonation, a dependence of rate on $[\text{OH}^-]^2$ (albeit together with a significant first-order contribution) is no longer uncommon. It was originally observed in the reactions of the dicationic complex *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{Me}_2\text{S})_2]^{2+}$,¹⁴ and has been reported in a number of other cases involving reactions of dicationic complexes¹⁵⁻¹⁷ and also in the displacement of RCO_2^- from the monocationic $[\text{Pt}(\text{dien})(\text{RCO}_2)]^+$ ¹⁸ and even, marginally, for $[\text{Pt}(\text{dien})\text{Br}]^+$ ($\text{dien} = \text{diethylenetriamine}$).¹⁹ A common feature in all of these reactions is that, if the rate constants are measured in the presence of fluoride ions instead of perchlorate ions (to control ionic strength), the rate law reduces to a simple zero- and first-order dependence on $[\text{OH}^-]$. This is actually due to the addition of an extra cross-

term in the rate equation which takes the form $k_{\text{obs}} = a + b[\text{OH}^-] + c[\text{OH}^-]^2 + d[\text{OH}^-][\text{F}^-]$ with $c \approx d$ {using NaF to maintain constant ionic strength requires that $([\text{OH}^-] + [\text{F}^-])$ remains constant}. The presence of fluoride ions, however, has no effect upon the rate of the reaction of these anionic complexes with hydroxide, Table 3. The measured rate constants are also independent of the nature of the cation, as proved by experiments carried out by controlling the ionic strength with NaClO_4 instead of LiClO_4 . In the presence of excess of Br^- and OH^- the final product is the hydroxo complex, and the spectrophotometric changes are consistent with a combination of direct replacement of chloride by OH^- and replacement of Cl^- by Br^- followed by the replacement of Br^- by OH^- . The rate constants for the individual processes are the same as those found for the reactions when studied separately. There is therefore no cross-term involving $[\text{Br}^-][\text{OH}^-]$. Such cross-terms are not observed in reactions between the cationic substrates and anions other than F^- .

In the case of cationic substrates the interpretation of the first- and second-order dependence on $[\text{OH}^-]$ and the cross-term, $[\text{OH}^-][\text{F}^-]$, as consequences of ion association and a facilitated interchange is not unreasonable (OH^- and F^- having similar charge and size have almost the same abilities to associate with the substrate, but F^- is unable to enter the strong bonding co-ordination shell of the Pt^{II}). The suggestion that there can be an association of two anions with an anionic substrate seems to be unlikely. There is no longer any indication of catalysis by fluoride but the dependence of the second-order rate constant upon inductive effects within the co-ordination shell (the second-order rate constant is most prominent for the least basic pyridinedicarboxylate, when charge transfer towards the metal is least) parallels the observations made with the cationic complexes.

Alternative explanations involving reversible ring opening have been considered but there is no obvious reason why OH^- should displace the carboxylate chloride under conditions where much stronger nucleophiles exert no effect and, in any case, the ring-opening reaction can be observed independently as a much slower second stage.

These observations serve as a further reminder that the anomalous behaviour of hydroxide and similar oxygen donors (MeO^- and possibly RCO_2^-), which are usually poor nucleo-

philes but which form exceptionally stable complexes with square-planar d^8 metal-ion complexes, is far from being understood and still requires extensive study.

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References

- 1 U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *J. Am. Chem. Soc.*, 1965, **87**, 241.
- 2 R. G. Pearson, H. Sobel and J. Songstad, *J. Am. Chem. Soc.*, 1968, **90**, 319.
- 3 L. Cattalini, A. Orio and M. Nicolini, *J. Am. Chem. Soc.*, 1966, **88**, 5734.
- 4 M. Bonivento, L. Cattalini, G. Marangoni, G. Michelon, A. P. Schwab and M. L. Tobe, *Inorg. Chem.*, 1980, **19**, 1743.
- 5 M. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *Inorg. Chem.*, 1981, **20**, 3728.
- 6 R. Romeo and M. Cusumano, *Inorg. Chim. Acta*, 1981, **49**, 167.
- 7 G. Annibale, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *Inorg. Chem.*, 1984, **23**, 2705.
- 8 G. Annibale, L. Cattalini, G. Chessa, G. Marangoni, B. Pitteri and M. L. Tobe, *Gazz. Chim. Ital.*, 1985, **115**, 279.
- 9 M. L. Tobe, A. T. Treadgold and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1988, 2347.
- 10 L. Cattalini, G. Chessa, G. Marangoni, B. Pitteri and E. Celon, *Inorg. Chem.*, 1989, **28**, 1944.
- 11 D. G. Markees, *J. Org. Chem.*, 1958, **23**, 1030.
- 12 M. H. Robinson, *J. Am. Chem. Soc.*, 1958, **80**, 5481.
- 13 R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 1991.
- 14 G. Annibale, M. Bonivento, L. Cattalini, G. Michelon and M. L. Tobe, *Inorg. Chem.*, 1984, **23**, 2829.
- 15 C. A. Blakeley, L. Cattalini and M. L. Tobe, unpublished work.
- 16 L. Canovese, L. Cattalini, P. Uguagliati and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1990, 867.
- 17 L. Canovese, L. Cattalini, P. Uguagliati and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1990, 3271.
- 18 L. Canovese, unpublished work.
- 19 L. Canovese, L. Cattalini, L. Gemelli and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1988, 1049.

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