

COMPLEXES OF PALLADIUM(II) AND PLATINUM(II) WITH 2-AMINOMETHYLPYRIDINE (2-PICOLYLAMINE)*

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The reactivity of the chelating ligand 2-picolylamine (2-aminomethylpyridine) towards nickel(II) (Sutton 1960), together with the observation of Hartkamp (1958) that palladium(II) reacted with this ligand, prompted the following investigation. For comparison, both palladium(II) and platinum(II) are readily coordinated by the ligands ethylenediamine, 1,10-phenanthroline, and 2,2'-bipyridyl with the formation of complexes such as $[\text{PdphenX}_2]$ and $[\text{PdbipyX}_2]$, in which X represents univalent addenda such as Cl, Br, I, SCN, NO_2 (Livingstone 1952, 1953). Furthermore, it was thought that a study of physical measurements might be facilitated by the use of the ligand 2-picolylamine, since complexes of heterocyclic bases are usually sufficiently soluble in polar solvents for such measurements to be made.

Results and Discussion

When 2-picolylamine is warmed with aqueous potassium tetrachloropalladate(II) in the presence of excess of the appropriate anion, pale orange to yellow complexes of the type $[\text{PdpicX}_2]$ settle out as microcrystalline precipitates ($\text{X}=\text{Cl}, \text{Br}, \text{NO}_2$). Similarly, by allowing the ligand to react with the corresponding platinum salt (potassium tetrachloroplatinate(II)) under similar conditions, the highly coloured complexes $[\text{PtpicX}_2]$ as well as $[\text{Ptpic}(\text{SCN})_2]$ may be formed. Flashes of green during these preparations may have been due to the formation of the electrolytes $[\text{Pdpic}_2][\text{PdX}_4]$ and $[\text{Ptpic}_2][\text{PtX}_4]$ as intermediates, although these salts were not isolated. Conductance measurements in nitrobenzene and nitromethane showed that the complexes are non-electrolytes, very slight conductances having been due to some ionization or impurities (Table 1). This is in agreement with their structures as the monomers $[\text{PdpicX}_2]$ and $[\text{PtpicX}_2]$; although a less likely polymeric structure by halogen bridging is also possible. However, this would give rise to an increase in the coordination number of the central atoms with a probable lowering of solubility in polar solvents and darkening of colour. Unfortunately, molecular weight determinations were not possible due to limits of solubility in suitable solvents. By doubling the proportion of ligand to metal in the appropriate salts, the bis-(2-picolylamine)palladium and platinum complexes were formed and were precipitated as perchlorates. The latter complexes behaved as bi-univalent electrolytes in nitromethane and nitrobenzene (Table 1). In all of the complexes

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studied, measurements of magnetic susceptibility have shown that they are diamagnetic. A study was made of the absorption spectra in the near ultraviolet region between 220 and 350 $m\mu$ and the logarithms of the molecular extinction coefficients (ϵ) plotted against wavelengths ($m\mu$) (Table 2). Both the bis-(2-picolyamine) complexes $[\text{Pdpic}_2]^{2+}$ and $[\text{Ptpic}_2]^{2+}$ give two absorption peaks

TABLE 1
MOLECULAR CONDUCTANCES IN NITROBENZENE AND NITROMETHANE AT 25 °C AT 10^{-3}M

Substance	Molecular Conductances		Substance	Molecular Conductances	
	Nitro-benzene (Ω^{-1})	Nitro-methane (Ω^{-1})		Nitro-benzene (Ω^{-1})	Nitro-methane (Ω^{-1})
$[\text{PdpicCl}_2]$..	0.17	1.4	$[\text{PtpicBr}_2]$..	0.41	3.5
$[\text{PdpicBr}_2]$..	0.24	2.7	$[\text{Ptpic}(\text{SCN})_2]$..	0.37	3.0
$[\text{Pdpic}(\text{NO}_2)_2]$..	0.75	4.7	$[\text{Ptpic}(\text{NO}_2)_2]$..	0.49	4.6
$[\text{Pdpic}_2][\text{ClO}_4]_2$..	42.4	149.9	$[\text{Ptpic}_2][\text{ClO}_4]_2$	41.5	144.0
$[\text{PtpicCl}_2]$..	0.33	2.81			

within the range studied, whilst the monopicolyamine complexes $[\text{PdpicX}_2]$ and $[\text{PtpicX}_2]$ ($\text{X}=\text{Cl}, \text{Br}$) have only one absorption peak with a general absorption in the far ultraviolet region of the spectrum (below 220 $m\mu$). From the results obtained there is a shift of absorption towards longer wavelength in the order $[\text{PtpicX}_2] > [\text{PdpicX}_2]$, $[\text{Ptpic}_2]^{2+} > [\text{Pdpic}_2]^{2+}$, and $\text{Cl} > \text{Br}$ in both cases.

TABLE 2
ABSORPTION SPECTRA OF COMPLEXES IN 95% ETHANOL

Substance	Maxima		Minima	
	Wavelength ($m\mu$)	Extinction Coefficient ($\log \epsilon$)	Wavelength ($m\mu$)	Extinction Coefficient ($\log \epsilon$)
$[\text{PdpicCl}_2]$..	260	2.93		
$[\text{PdpicBr}_2]$..	256	2.98		
$[\text{Pdpic}_2][\text{ClO}_4]_2$..	234, 265	3.67, 3.56	249	3.18
$[\text{PtpicCl}_2]$..	279	3.07		
$[\text{PtpicBr}_2]$..	265	3.25		
$[\text{Ptpic}_2][\text{ClO}_4]_2$..	263, 280	3.29, 3.16	273	3.14

Since a shift of absorption towards longer wavelength is usually associated with a release of constraint on the bonding electrons in a complex, this could also indicate that the order of stability follows the above pattern. Since the iodo complexes were not readily obtained in the pure state, the order of stability of both Pd and Pt complexes of 2-picolyamine is $\text{Cl} > \text{Br}$. As a basis for com-

parison in the following conductances (Table 1), the conductances of bi-univalent electrolytes in nitrobenzene and nitromethane are usually in the vicinity of 50 and $130 \Omega^{-1}$ respectively.

Experimental

The conductance measurements were made with a Philoscope model GM4249/01 and cell GM4221. The nitromethane was purified by drying over anhyd. CaSO_4 and retaining the distillate, boiling at $101-101.5^\circ\text{C}$. A.R. nitrobenzene was allowed to freeze, the unfrozen portion was decanted, and the solid allowed to liquefy. The latter was treated with anhyd. MgSO_4 and distilled. Magnetic measurements were made by the Gouy method on the powdered substance and the measurements of absorption spectra were determined with a Beckmann quartz spectrophotometer, model DU.

(a) *Dichloromono(2-picolyamine)palladium(II)*.—Potassium tetrachloropalladate(II) (0.33 g; 1 mm) in water (10 ml) was treated with 2-picolyamine (0.11 g; 1 mm) in water (5 ml) and the mixture heated to boiling point. The yellow microcrystalline precipitate which formed was washed with water and then with a small volume of acetone (1 ml) and dried at 105°C (yield 0.24 g). The yellow microcubes were found to be slightly soluble in acetone and decomposed above 250°C (Found: C, 24.9; H, 2.7; Pd, 37.0%. Calc. for $\text{C}_6\text{H}_8\text{N}_2\text{Cl}_2\text{Pd}$: C, 25.2; H, 2.8; Pd, 37.3%).

(b) *Dibromomono(2-picolyamine)palladium(II)*.—Procedure (a) was repeated with the addition of NaBr (1 g) prior to the treatment with the ligand. The orange microcubes which resulted were found to be stable to above 250°C (yield 0.34 g) (Found: C, 19.5; H, 2.2; Pd, 28.4%. Calc. for $\text{C}_6\text{H}_8\text{N}_2\text{Br}_2\text{Pd}$: C, 19.3; H, 2.2; Pd, 28.5%).

(c) *Dinitromono(2-picolyamine)palladium(II)*.—Procedure (a) was repeated adding NaNO_2 (1 g) prior to the addition of the ligand. The pale yellow microcrystals which resulted were found to decompose at 208°C (yield 0.24 g) (Found: C, 23.0; H, 2.5; Pd, 34.4%. Calc. for $\text{C}_6\text{H}_8\text{N}_4\text{O}_4\text{Pd}$: C, 23.5; H, 2.6; Pd, 34.7%).

(d) *Bis(2-picolyamine)palladium(II) Perchlorate*.—Procedure (a) was repeated taking 2-picolyamine (0.22 g; 2 mm) and NaClO_4 (2 g). The pale yellow microcrystals which resulted were not decomposed below 250°C (yield 0.41 g) (Found: C, 27.4; H, 3.1; Pd, 20.3%. Calc. for $\text{C}_{12}\text{H}_{16}\text{N}_4\text{Cl}_2\text{O}_8\text{Pd}$: C, 27.6; H, 3.1; Pd, 20.4%).

(e) *Dichloromono(2-picolyamine)platinum(II)*.—Potassium tetrachloroplatinate(II) (0.42 g; 1 mm) was dissolved in water (10 ml) and heated to boiling point with a solution of 2-picolyamine (0.11 g; 1 mm) with stirring. The pale orange acicular crystals which formed and settled rapidly were removed by centrifugation, washed with water and acetone, and dried at 105°C (yield 0.34 g). The complex was found to be stable to above 300°C (Found: C, 19.5; H, 2.2; Pt, 49.6%. Calc. for $\text{C}_6\text{H}_8\text{N}_2\text{Cl}_2\text{Pt}$: C, 19.3; H, 2.2; Pt, 52.1%).

(f) *Dibromomono(2-picolyamine)platinum(II)*.—Procedure (e) was repeated with the addition of NaBr (1 g). The orange-yellow acicular crystals which resulted were found to be stable to above 300°C (yield 0.45 g) (Found: C, 15.7; H, 1.4; Pt, 42.0%. Calc. for $\text{C}_6\text{H}_8\text{N}_2\text{Br}_2\text{Pt}$: C, 15.6; H, 1.7; Pt, 42.2%).

(g) *Dinitromono(2-picolyamine)platinum(II)*.—Procedure (e) was repeated with the addition of NaNO_2 (1 g). The pale yellow acicular crystals which resulted were found to decompose at 238°C (yield 0.34 g) (Found: C, 17.9; H, 2.1; Pt, 49.5%. Calc. for $\text{C}_6\text{H}_8\text{N}_4\text{O}_4\text{Pt}$: C, 18.2; H, 2.0; Pt, 49.5%).

(h) *Dithiocyanatomono(2-picolyamine)platinum(II)*.—Procedure (e) was repeated with the addition of NaCNS (1 g). The bright yellow acicular crystals which resulted were found to decompose at 218°C (yield 0.30 g) (Found: C, 22.4; H, 1.9; Pt, 46.3%. Calc. for $\text{C}_6\text{H}_8\text{N}_4\text{S}_2\text{Pt}$: C, 22.9; H, 1.9; Pt, 46.5%).

(i) *Bis(2-picolyamine)platinum(II) Perchlorate Monohydrate*.—Procedure (e) was repeated using 2-picolyamine (0.22 g; 2 mm) and NaClO_4 (2 g), when pink microrhombic crystals resulted. The substance lost water without change of colour at about 110°C , and the anhyd. salt was found to be stable to above 300°C (yield 0.59 g) (Found: C, 22.9; H, 3.3; Pt, 31.4%. Calc. for $\text{C}_{12}\text{H}_{16}\text{N}_4\text{Cl}_2\text{O}_9\text{Pt}$: C, 22.9; H, 2.9; Pt, 31.1%).

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