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1,4,7-Triazacycloalkane Complexes of Palladium(II) with a Many Membered Chelate Ring Bridging *trans*-Positions

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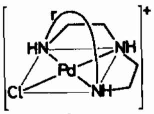
Palladium(II) complexes of 1,4,7-triazacycloalkanes (L), $\overline{NH(CH_2)_2NH(CH_2)_2NH(CH_2)_r}$ (r = 2, 5, 6, 7, 8, and 10), were prepared and characterized. In the complexes [$PdCl_2(LH)$]$ClO_4 \cdot H_2O$ obtained for the ligands with a small ring size (r = 2 and 5) the cyclic triamines were bidentate and one amino group protonated, while in the complexes [PdClL]ClO_4 of the ligands with a large ring size (r = 6, 7, 8, and 10) the triamines were terdentate and the longest polymethylene chains, $(CH_2)_r$, bridge the trans *positions of a square plane.*

Introduction

Cyclic triamines such as 1,4,7-triazacyclononane have recently commanded much attention as ligands and their transition metal complexes have been studied [1–4]. In the complexes the cyclic triamines act as terdentate ligands occupying facial sites of coordination polyhedra [3, 5, 6]. It is very interesting to study the mode of coordination of these ligands coordinated to palladium(II) and platinum(II) which prefer inherently a square-planar geometry. It is expected that, if one of the three polymethylene chains of cyclic triamines, $\overline{NH(CH_2)_pNH(CH_2)_qNH(CH_2)_r}$ (abbreviated as pqr-cy and in this paper p = q = 2 and r is a variable), is sufficiently long, the longest chain, $(CH_2)_r$, can span *trans* positions of a square plane (Structure I). The palladium(II) complexes of the cyclic triamines were prepared to see the features of pqr-cy towards central metal ions with an inherently square-planar geometry. Platinum(II) complexes of these cyclic triamines are being investigated in anticipation of anti-cancer effects [7] and will be reported elsewhere.



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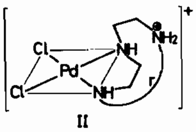

II

Experimental

Preparation

The ligands were synthesized by the methods reported [8].

The complexes were prepared as described below, and the yields and analytical data are summarized in Table I. One mmol of palladium(II) chloride and 1 mmol of pqr-cy·3HCl in 30 ml of water were stirred

TABLE I. Yields and Analytical Data for the Complexes.

Complex	Yield %	Analysis, found (calcd. %)		
		C	H	N
[$PdCl_2$(222-cyH)]$ClO_4 \cdot H_2O$	48	17.11(16.96)	4.01(4.03)	10.11(9.89)
[$PdCl_2$(225-cyH)]$ClO_4 \cdot H_2O$	66	22.86(23.14)	5.08(5.18)	9.17(9.00)
[$PdBr_2$(225-cyH)]$ClO_4 \cdot H_2O$	69	19.58(19.44)	4.28(4.35)	7.65(7.56)
[PdCl(226-cy)]ClO_4	47	27.92(28.15)	5.35(5.43)	9.28(9.84)
[PdBr(226-cy)]ClO_4	67	25.44(25.50)	4.75(4.92)	9.03(8.92)
[PdCl(227-cy)]ClO_4	51	29.67(29.98)	6.05(5.72)	9.65(9.54)
[PdCl(228-cy)]ClO_4	62	31.49(31.70)	6.18(5.98)	8.77(9.24)
[PdCl(2210-cy)]ClO_4	81	34.36(34.83)	6.54(6.47)	8.60(8.70)

TABLE II. Infrared and Electronic Spectra of the Complexes (Nujol Mulls).

Complex	Infrared (cm^{-1})				Electronic ($\times 10^3$ cm^{-1})
	ν(OH)	ν(NH)	δ(HOH)	ν(Pd–X)	
$[PdCl_2(222\text{-cyH})]ClO_4 \cdot H_2O$	3495	3130	1585	317	26.4
	3520sh[a]	3220sh	1603	336	
		3240			
$[PdCl_2(225\text{-cyH})]ClO_4 \cdot H_2O$	3460	3150	1585	290	26.2
	3520	3170	1615	330	
		3228			
$[PdBr_2(225\text{-cyH})]ClO_4 \cdot H_2O$	3465	3140	1582	204	25.2
	3527	3165	1609	228	30.8sh
		3220			
$[PdCl(226\text{-cy})]ClO_4$		3238		293	27.9
		3281			
$[PdBr(226\text{-cy})]ClO_4$		3230		209	27.1
		3258			
$[PdCl(227\text{-cy})]ClO_4$		3210		326	28.2
		3245			
$[PdCl(228\text{-cy})]ClO_4$		3118		322	29.3
		3229			
		3242sh			
$[PdCl(2210\text{-cy})]ClO_4$		3116		298	29.7
		3215			

[a] sh = shoulder.

on a steam bath until a clear solution had been obtained. The solution was neutralized with an aqueous solution of lithium hydroxide and the pH was adjusted to 4.5. Lithium perchlorate (2 mmol) was added and the mixture was concentrated to a small volume. The product was washed with water and dried in air.

The bromo complexes were prepared by metathesis of the chloro complexes with excess lithium bromide in water.

Measurements

All the measurements were carried out by the methods reported previously [9]. The absorption spectra and electric conductances were measured within one hour of dissolution.

Results and Discussion

The complexes of the type (A), $[PdCl_2(LH)]ClO_4 \cdot H_2O$, are obtained for the ligands 222-cy and 225-cy, while those of the type (B) $[PdClL]ClO_4$, for 226-cy, 227-cy, 228-cy and 2210-cy (Table II). The infrared spectra of all the complexes (Table II) reveal that ClO_4 is not coordinated and show ν(NH), ν(OH), and δ(HOH) in the normal regions. Other bands are difficult to assign except for ν(Pd–Cl).

The electronic spectra measured on nujol mulls of (A) are very similar to that of $[PdCl_2(R\text{-pn})]$ (R-pn = R-1,2-diaminopropane) (Table III) [10], suggesting that the donor atoms are N_2Cl_2. In these complexes one of the three amino groups is not coordinated but protonated (Structure II), that is, 222-cy and 225-cy are N,N-bidentate ligands with a positive charge. The length of the pentamethylene chain of 225-cy is not sufficient to span the *trans* positions of a square plane. The two complexes dissolved in water (10^{-3} *M*) undergo hydrolysis as the electronic spectra differ from those of the solid state (Table III). The hydrolysis is also suggested by the electric conductances [11]. When these complexes are dissolved in 0.2 *N* aqueous sodium chloride solution, the hydrolysis is, however, suppressed (Table III).

The two complexes $[PdClL]ClO_4$ (L = 228-cy and 2210-cy) give nujol mull electronic spectra (Table II) very similar to that of $[PdCl(dien)]^+$ (dien = diethylenetriamine) with a chromophore $[PdN_3Cl]$ (Table III) [12]. The two cyclic triamines, therefore, act as N,N,N-terdentate ligands (Structure I). The absorption maximum of the nujol mull spectra of $[PdClL]ClO_4$ (L = 226-cy and 227-cy) lies at slightly lower frequencies than that of $[PdCl(dien)]^+$ and this may be caused by distortion produced by a hexa- and

TABLE III. Electric Conductances and Absorption Spectra of 10^{-3} *M* Solutions of the Complexes.

Complex	Conductance Mho, cm^2/mol	Absorption maxima, × 10^3 cm^{-1} (logϵ)	
		Aqueous solution	0.2 *M* NaCl solution
$[PdCl_2(222\text{-}cyH)]ClO_4 \cdot H_2O$	233	27.1(2.53) 37.0sh 46.2(4.25)	26.2(2.59) 46.1(4.35)
$[PdCl_2(225\text{-}cyH)]ClO_4 \cdot H_2O$	249	28.1(2.67) 36.4sh 48.4(4.19)	26.6(2.58) 36.9sh 44.8(4.31)
$[PdBr_2(225\text{-}cyH)]ClO_4 \cdot H_2O$	192	26.0sh 30.8(2.94) 41.9(4.28)	
$[PdCl(226\text{-}cy)]ClO_4$	311	33.8(3.16) 44.8(4.00)	28.7(2.89) 46.3(4.14)
$[PdBr(226\text{-}cy)]ClO_4$	277	27.8sh 33.9(3.10) 44.7(4.10)	
$[PdCl(227\text{-}cy)]ClO_4$	138	29.7(2.89) 46.4(4.09)	29.0(2.90) 46.6(4.16)
$[PdCl(228\text{-}cy)]ClO_4$	122	29.8(2.86) 46.4(4.12)	29.2(2.89) 46.8(4.20)
$[PdCl(2210\text{-}cy)]ClO_4$	115	29.9(2.84) 46.6(4.17)	29.4(2.85) 46.9(4.24)
$[PdCl_2(R\text{-}pn)]$		26.2(2.37)[a]	
$[PdCl(dien)]^+$		29.8(2.70)[b] 29.6(2.70)[c]	

[a] R-pn = R-1,2-diaminopropane. H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, *40*, 2584 (1967). [b] H.-H. Schmidtke and C. K. Jørgensen, *Chem. Phys. Lett.*, *5*, 202 (1970). dien = diethylenetriamine. [c] W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting, and A. J. Poë, *Inorg. Chem.*, *2*, 921 (1963).

hepta-methylene chain bridging donor nitrogen atoms at *trans* positions.

The absorption spectra of $[PdClL]ClO_4$ (L = 228-cy and 2210-cy) dissolved in water (10^{-3} *M*) are almost identical with those of the solid state and the electric conductances of the solutions are typical for 1:1 electrolytes (Table III). The absorption spectra of $[PdCl(227\text{-}cy)]ClO_4$ in water and 0.2 *N* NaCl solution are different from the solid state but resemble that of $[PdCl(dien)]^+$. The electric conductance is slightly higher than that of a typical 1:1 electrolyte. In solution the complex $[PdCl(227\text{-}cy)]ClO_4$ is rather similar to $[PdClL]ClO_4$ (L = 228-cy and 2210-cy) and the distortion caused by a hepta-methylene chain is considerably removed.

The absorption spectrum of $[PdCl(226\text{-}cy)]ClO_4$ in water is markedly different from that of the solid state and from those of the above three complexes. The absorption maximum lies at a very high wave-number, near that of $[Pd(NH_3)_4]^{2+}$ (ν_{max} = 33.9 × 10^3 cm^{-1} and logϵ = 2.30). The conductance of the solution is unexpectedly high and close to a 1:3 electrolyte. Aquation, hydrolysis, and/or complete decomposition may occur but this point requires a study of solution chemistry and this is not the purpose of the present paper. The hexamethylene chain is too short and cannot relieve the complex from distortion and/or strain even in aqueous solution. In the presence of excess sodium chloride the spectrum is in good agreement with those of the series $[PdClL]ClO_4$. The spectrum changes gradually.

Metathesis of the chloro complexes with excess lithium bromide gave the corresponding bromo complexes and the two $[PdBr_2(225\text{-}cyH)]ClO_4 \cdot H_2O$ and $[PdBr(226\text{-}cy)]ClO_4$ were characterized. In the infrared spectra ν(Pd–Cl) is replaced with ν(Pd–Br) (Table II) and the electronic spectra show redshift as expected. There is no unusual difference between the chloro and bromo complexes.

A hexamethylene chain seems to be the shortest polymethylene chain required to bridge the two donor atoms coordinated to mutually *trans* positions of a square plane. The hexamethylene chain without remnant in length brings about appreciable strain and/or distortion, so that properties of [PdCl(226-cy)]ClO_4 differ from those of [PdClL]ClO_4 (L = 227-cy, 228-cy, and 2210-cy) which contain a hepta-, octa-, and deca-methylene chain, respectively. In the complex *trans*-$[Pt(NH_3)_2(dienH)]^{3+}$ where the secondary amino group of dien is protonated and only the terminal amino groups are coordinated to the mutually *trans* positions, an eight member chelate ring is formed [13]. The bridging group corresponds to a pentamethylene chain. This is contrary to our results and may be due to the difference in central metal ions and in the nature of the ligands, that is, one is an open chain triamine and the other cyclic triamines. The two cyclic ligands 235-cy and 335-cy with extra methylene groups gave [$PdCl_2$(235-cyH)]·$PF_6 \cdot H_2O$ and [$PdCl_2$(335-cyH)PF_6, respectively, under similar conditions [14]. The two ligands behave like 225-cy and a pentamethylene chain seems too short to bridge two *trans* donor atoms in square-planar palladium(II) complexes.

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14 Calcd. for [$PdCl_2$(235-cyH)]$PF_6 \cdot H_2O$: C, 22.81; H, 4.98; N, 7.98. Found: C, 22.57; H, 5.04; N, 7.62%. Calcd. for [$PdCl_2$(335-cyH)]PF_6: C, 25.28; H, 5.01; N, 8.04. Found: C, 25.27; H, 4.96; N, 7.72%.