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Raman and Infrared Spectra of the Square Planar Tetraammine Palladium(II) Chloride and its Deuterate

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Numerous works have reported the infrared spectra of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ [1–11], $[Pd(NH_3)_4]Br_2$ [6, 7, 9], $[Pd(NH_3)_4][PdCl_4]$ [6, 10], $[Pd(NH_3)_4][PtCl_4]$ [12] and recently of $[^{104}Pd/^{110}Pd(NH_3)_4]Cl_2 \cdot H_2O$ [13]. Regarding the Raman spectrum, there is almost a complete lack of data as only Hendra [8] reported three Raman lines (skeletal vibrations) in the solid state spectrum of the tetraammine palladium(II) chloride recorded in the range 0–600 cm^{-1}. Some preliminary discussions about the assignments of the vibrations of the complex $[Pd(NH_3)_4]^{2+}$ may be found in the review of Schmidt and Müller [14] and in our recent work [15] where a tentative determination of a general valence force field was also given.

In this communication we give:

(i) the infrared spectra of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ and of its deuterate $[Pd(ND_3)_4]Cl_2 \cdot D_2O$ recorded for the first time,

(ii) the Raman spectra of the above cited compounds in the solid state, over the range 0–4000 cm^{-1}, which give for the first time all the vibrations of the whole complexes (framework, ligand and ligand–framework couplings),

(iii) the Raman spectra of the compounds in aqueous solution (H_2O/D_2O) with the polarizations.

All these newly obtained data permit us first of all to confirm more precisely the earlier IR bands assignments, to complete the insufficient set of Raman results on the mother molecule (as no wide-range spectrum has been reported previously) and finally to use the polarizations as well as the isotopic frequency shifts upon deuteration to solve definitively the assignment problem.

Experimental

The compound tetraammine palladium(II) chloride (monohydrate) was purchased from Alfa Division, U.S.A. The deuterate substituted complex was prepared by dissolving $[Pd(NH_3)_4Cl_2 \cdot H_2O$ in D_2O and evaporating to dryness; the procedure being carried out three times.

Infrared spectra of nujol mulls and pressed KBr discs were recorded, at room temperature, by using a Perkin Elmer 521 spectrometer (for the range 4000–250 cm^{-1}, calibrated with polystyrene lines) and a Grubb Parsons IRS interferometer for the far infrared.

Raman spectra of compounds, solid and solution (2.10^{-1} *M*), were scanned both with the technical spinning cell on a Coderg triple monochromator spectrometer T800, using an ionized argon laser from Coherent Radiation (excitation line 4880 Å; calibration with argon plasma lines). Spectral slit widths down to 4 cm^{-1} were used. Infrared and Raman frequencies are considered accurate to ± 1 cm^{-1} and ± 4 cm^{-1} for broad lines.

The intensity of the Raman bands was measured by their peak heights and corrected. The polarization of the lines was determined by taking spectra with the incident polarization both parallel and perpendicular to the scattering light wave vector.

Results and Discussion

Table I lists infrared and Raman frequencies for $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ and its deuterate. The normal modes for the whole complex [15] $[Pd(NH_3)_4]^{2+}$ are distributed among the C_{4h} symmetry group according to

$$\Gamma(C_{4h}) = 6A_g(R) + 7B_g(R) + 4E_g(R) + 5A_u(IR) + 5B_u(-) + 7E_u(IR).$$

$[Pd(NH_3)_4]Cl_2 \cdot H_2O$ crystallizes in the space group D^5_{4h}($z = 2$). The site symmetry of $[Pd(NH_3)_4]^{2+}$ in the crystal is C_{4h} and in this case the degeneracy of the E_g and E_u modes are not removed. As seen from Table I, the frequencies corresponding to the degenerate modes are not split.

Skeletal Region

The skeletal vibrations are distributed among the local D_{4h} species as follows: $\Gamma = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u$.

The PdN symmetric stretching mode (a_{1g}) is observed at 507 cm^{-1} in the Raman solid spectrum and at 504 cm^{-1} (pol.) in the aqueous solution. The corresponding line in the deuterates shifts by 34 cm^{-1} and 36 cm^{-1} respectively. The PdN asymmetric stretching mode (b_{1g}) is seen at 471 cm^{-1} (solid) and 468 cm^{-1} dep. (aq. sol.) for the H-compound and decreases by 38 cm^{-1} (solid) and 37 cm^{-1} (aq. sol.) on deuteration.

TABLE I. Raman and Infrared Frequencies of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ Solid and Its Deuterate; Raman Frequencies of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ in Aqueous Solution and Its Deuterate.

$[Pd(NH_3)_4]Cl_2 \cdot H_2O$		$[Pd(NH_3)_4]^{2+}$ in H_2O		$[Pd(ND_3)_4]Cl_2 \cdot D_2O$		$[Pd(ND_3)_4]^{2+}$ in D_2O
Raman	IR	Raman	Assignments[b]	Raman	IR	Raman
79	82		Lattice mode	69		
	116					
	160[c]	166 sh, l, dp[c]	torsion (A_u, E_g)		123	
	242 w		$\gamma(NPdN)A_u$		212 w	
284 sh	292 w		$\delta(NPdN)E_u$	256 sh	256 w	
305(17), l		264 sh, dp[c]	$\delta(NPdN)B_g$	277(35)		236 sh, dp[c]
				318?		319?
471(12)		468(12), dp	$\nu(PdN)B_g$	433(13)		431(11), dp
	491 m		$\nu_{as}(PdN)E_u$		453 m	
	503 sh				465 sh	
507(100)		504(100), p	$\nu_s(PdN)A_g$	473(100)		468(100), p
729		811 l, dp[c]	$\rho_r(NH_3)A_g$, B_g, E_g	546[c]		626 l, dp[c]
	802 s		$\rho_r(NH_3)A_u$, E_u		616 s	
	845 s				647 s	
1263 (17)		1289(10), dp	B_g	974(20)		995(15), dp
	1297 s		E_u		1008 s	
1300			$\delta_s(HNH)$			
1339(6)		1334(8), p	A_g	1016(14)		1016(17), p
				1073		
1490 sh						
1546		1586	$\delta_{as}(HNH)$	1128		
	1592 s, l		(A_g, B_g, E_g, A_u, E_u)		1160 s, l	
1624 l						
	3145 s, l		$\nu_s(NH)E_u$		2295 s, l	
3146 ep						
3203(12), l			$\nu_s(NH)A_g$, B_g	2328(19), l		
				2359 sh		
	3260 s, l		$\nu_{as}(NH)A_u$, E_u		2432 s, l	
3296 sh, l			$\nu_{as}(NH)A_g$, B_g, E_g	2426 l		
3461	3542		H_2O, D_2O	2463		

[a] Relative intensity (%) ref: $\nu_s(PdN)$; sh, shoulder; l, large; s, strong; m, medium; w, weak; dp, depolarized; p, polarized. [b] Gives species designation according to the C_{4h} overall structure. [c] Very roughly estimated.

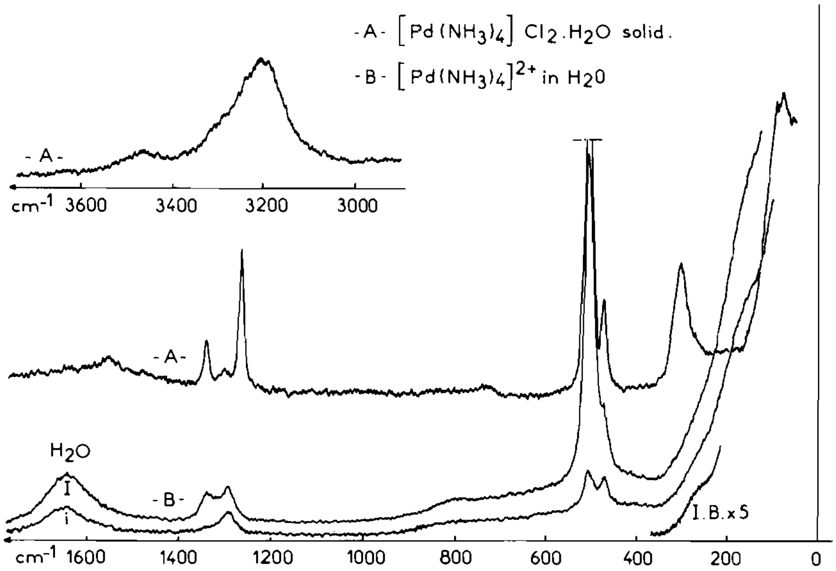

Fig. 1. Raman spectra of tetraammine palladium(II) chloride: (A), solid; (B), H_2O solution with polarizations I and i. Exciting wave-length: 4880 Å; slit width: (A) 4 cm^{-1}, (b) 6 cm^{-1}. Rate of scan: 25 cm^{-1}/min.

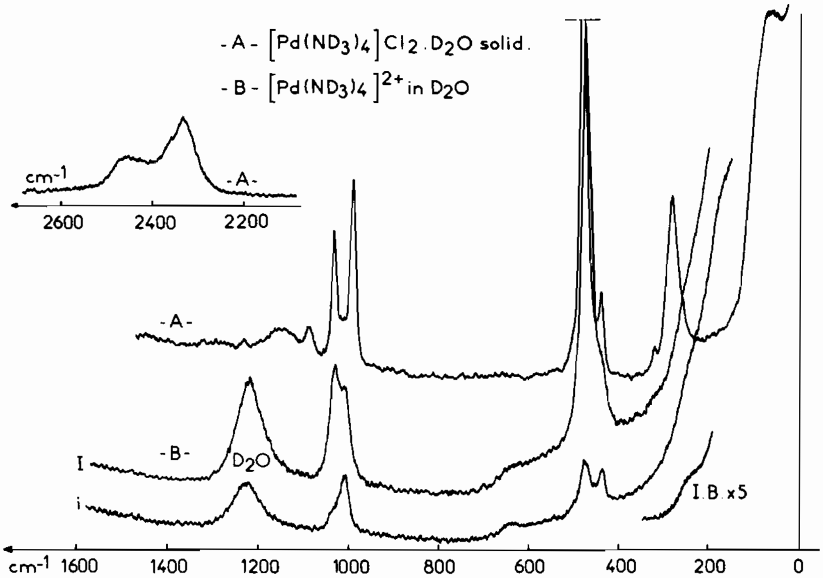

Fig. 2. Raman spectra of deuterated tetraammine palladium(II)chloride: (A), solid; (B) D_2O solution with polarizations I and i.

The Raman line at 305 cm^{-1}, corresponding to the b_{2g} PdN deformation mode is observed at 264 cm^{-1} (dep.) in the complex in aqueous solution. This frequency shift (41 cm^{-1}) is due to new hydrogen bonds (N–H•••O) [16]. The corresponding frequencies are 277 cm^{-1} and 236 cm^{-1} in the spectra of the deuterate.

As there were no unexpected features in the IR-bands assignments, for the sake of brevity the discussion is not reported here.

Ligand Modes

The assignment of the NH_3 modes is straightforward (see also [17–19]). Bands occurring in the range 3145–3296 cm^{-1} are assigned to N–H stretching; these shift to 2295–2426 cm^{-1} on deuteration.

The NH-deformation modes range in frequency from 1263 to 1339 cm^{-1} (symmetric type) and from 1490 to 1624 cm^{-1} (antisymmetric type). The corresponding modes for ND_3 have frequencies of 974–1073 cm^{-1} (sym.) and 1128–1160 (antisym.). All the isotopic frequency shifts correspond to $\nu_H/\nu_D \simeq 1.3_0$ thus confirming this assignment.

Framework–Ligand Couplings

The intense infrared active rocking modes (A_u, E_u) at 802 and 845 cm^{-1} shift to 616 and 647 cm^{-1} on deuteration. The very weak corresponding Raman line was observed at 729 cm^{-1} (solid) increasing to 811 cm^{-1} (aq. sol.) in the H-compound and at 546 cm^{-1} (solid) increasing to 626 cm^{-1} (aq. sol.) in the D-compound. The frequency shifts observed in the solid and solution spectra are interpreted as deriving from new hydrogen bonds of the type N–H•••O (see [16]).

Perry *et al.* [9] have assigned a band at 160 cm^{-1} to the out-of-plane deformation vibration, in the I.R. spectrum of $[Pd(NH_3)_4]Cl_2$. It seems that we can recognize that band which appears very weak and very broad, but we assign it to NH_3 torsional mode (A_u). The corresponding I.R.-frequency in the deuterate lies at 123 cm^{-1}. In an earlier paper [17] we have shown evidence of a weak band corresponding to the torsional motion in the Raman spectra of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and its deuterate (see also the work of Hall and Hirons [19] on the Magnus' Green Salt). According to the present work, a similar band is observed at 166 cm^{-1} in the Raman spectrum of the complex in solution. This line is assigned to the E_g-torsional mode of vibration. Howard and Waddington [20] have obtained the inelastic neutron scattering spectra of some transition metal ammines. A band corresponding to the NH_3 torsional modes was clearly observed at 176 cm^{-1} in the beryllium filter detector spectra of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ recorded at 77 K, which confirms our assignment.

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