Inorganica Chimica Acta, 50 (1981) 147–152
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Raman and Infrared Studies of the Square Planar Tetraammine Gold(III) Nitrate and its Deuterate

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Received December 4, 1980

The Raman spectra of the gold(III) complex $[Au(NH_3)_4](NO_3)_3$ *and* $[Au(ND_3)_4](NO_3)_3$ *in the solid state and in aqueous solution* (H_2O/D_2O) *and the infrared spectra of the above complexes in the solid state have been obtained and discussed in detail. All the ligand vibrations in the deformation and rocking regions have been studied. The polarization data and the high quality spectra obtained in this study allow a complete assignment of the vibrational modes of the complex. Additionally, comparisons are given with compounds of similar structure,* ($[X(NH_3)_4]^{2+}$, *X = Cu, Pd, Pt).*

Introduction

The compound tetraammine gold(III) nitrate was discovered by Weitz [1] in 1915. Since that time, the square planar $[Au(NH_3)_4]^{3+}$ was subject of very few studies. The crystal structure was obtained by Weishaupt and Strähle [2] in 1976. These authors also gave at that time [2] a preliminary study of the Raman and infrared spectra of the complex in solid state, showing evidence of only three lines assigned to the metal–ligand stretching mode, and just recently [3] have published the infrared spectrum of the ammine trichloro gold(III): $Au(NH_3)Cl_3$.

Regarding the fact that there is almost a complete lack of data *i.e.*,

. no Raman studies of aqueous solutions,

. neither Raman nor infrared studies of the isotopic derivatives ($^{14}N/^{15}N$, H/D)

our aim was to make a complete vibrational study of this complex as well as of its deuterate in order to perform a normal coordinate analysis of the whole complex [4]. (in solid state: symmetry D_{2h}; ion in aqueous solution: symmetry C_{4h}).

In the present work we give,

i) the Raman spectra of $[Au(NH_3)_4](NO_3)_3$ and of its deuterate $[Au(ND_3)_4](NO_3)_3$ in the solid state, over the range 0–4000 cm^{-1}, which give for the first time all the vibrations of the whole complexes (skeleton, ligand and framework ligand couplings),

ii) the Raman data of the compounds (H, D) in aqueous solution (H_2O, D_2O) with the polarizations,

iii) the infrared spectra of the above cited compounds.

All these newly obtained data permit us to give all the assignments of the different lines (in particular to discuss some incorrect attributions proposed elsewhere [2]), and finally to make further comparisons with earlier studies (experimental and/or theoretical) on similar compounds where the central atom is Cu(II) [5, 6], Pd(II) [7, 8] and Pt(II) [9, 10]. (For other complementary details, the reader may refer to reviewal materials (see [11–13]) and/or conference reports (see [14, 15]).

Experimental

Materials

The compound tetraammine gold(III) nitrate was prepared according to Skibstedt and Bjerrum [16]. Aqueous ammonia (approximately 3 mol/dm^3) was slowly added to a cold solution of $HAuCl_4 \cdot 3H_2O$ (1.5 g for 50 cm^3 of solution) saturated with NH_4NO_3. The addition of ammonia was performed over a day with an automatic device keeping the pH under 4.8. Then the white precipitate was filtered and washed with water and dried under vacuum. Elemental analysis for a freshly prepared sample gave 2.68 H, 21.73 N and 43.66% Au. Theory requires 2.80 H, 21.63 N and 42.97% Au.

The deuterate substituted complex was prepared by dissolving $[Au(NH_3)_4](NO_3)_3$ in D_2O. The solution was filtered and evaporated to dryness at room temperature in a vacuum, the procedure being carried out three times. Elemental analysis gave 5.32 D, 21.26 N and 43.33% Au where the theory requires 5.22 D, 21.17 N and 42.53% Au. It was pointed out that compound turns slowly greyish over several weeks.

Instrumentation

Raman spectra of compounds, solid and solution (4.10^{-2} *M*), were scanned both with the technical spinning cell on a Coderg triple monochromator spectrometer T 800 equipped with an ionized argon laser from Coherent Radiation using 500–800 mW of power from the 488.0 nm line; a small two-prism monochromator (Anaspec 300 S) was used to remove the background plasma lines. Spectral slit widths down to 4 cm^{-1} and 6 cm^{-1} were used respectively for solid and solution. The intensity of the Raman bands was measured by their peak heights and corrected. Polarization data were obtained with a polarizer and a scrambler.

Infrared spectra of pressed KBr discs were recorded, at room temperature by using a Perkin Elmer 521 spectrometer (for the range 4000–300 cm^{-1} calibrated with polystyrene lines) and a Grubb Parson IRS interferometer for the far infrared. Infrared and Raman frequencies are considered accurate to ±1 cm^{-1} and ±4 cm^{-1} for broad lines.

Results and Discussion

Figures 1 and 2 show respectively the Raman and infrared spectra of the tetraammine gold(III) nitrate and its deuterate.

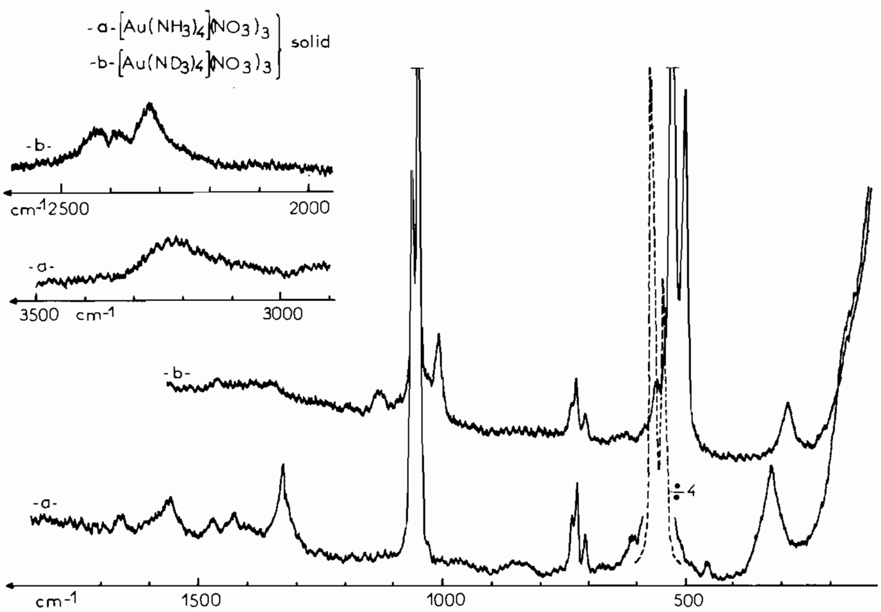


Fig. 1. Raman spectra of tetraammine gold(III) nitrate (a) and its deuterate (b) in solid state. Exciting wave-length: 488.0 nm; slit width: 4 cm^{-1}; rate of scan: 25 cm^{-1}/mn.

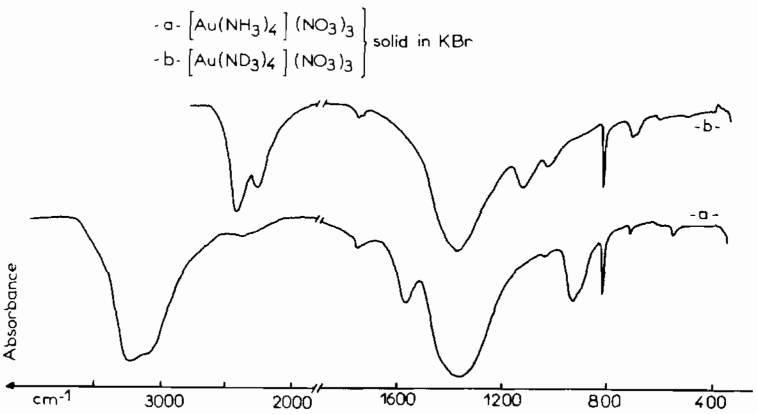


Fig. 2. Infrared spectra of tetraammine gold(III) nitrate (a) and its deuterate (b) in a KBr pellet at room temperature.

TABLE I. Raman and Infrared Frequencies of $[Au(NH_3)_4](NO_3)_3$ Solid and its Deuterate; Raman Frequencies of $[Au(NH_3)_4](NO_3)_3$ in Aqueous Solution and its Deuterate.[a]

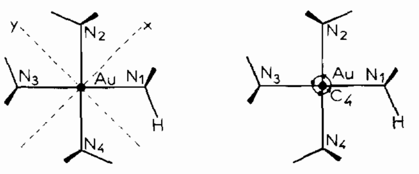
$[Au(NH_3)_4](NO_3)_3$		$[Au(ND_3)_4](NO_3)_3$		Assignments			$[Au(NH_3)_4]^{3+}$	$[Au(ND_3)_4]^{3+}$
Raman	IR	Raman	IR	D_{2h}[b]	Descriptions	C_{4h}[b]	Raman	(aqueous solution)
	84				lattice modes			
	116							
178^c	188	–	125^c	(B_{2g}, B_{3g}, B_{1u})	torsion	(E_g, A_u)		
	272 w		247 w	B_{1u}	$\gamma(AuN_2)$	A_u		
	307 w		268 w	(B_{2u}, B_{3u})	$\delta_{as}(AuN_2)$	E_u		
327 m		291 m		A_g	$\delta_s(AuN_2)$	B_g	286^c sh, dp^c	–
461 w								
544 s		501 s		B_g	$\nu(AuN)$	B_g	543 m, dp	506 m, dp
	555 w		506 w	(B_{2u}, B_{3u})	$\nu_{as}(AuN)$	E_u		
566 vs		526 vs		A_g	$\nu_s(AuN)$	A_g	569 s, p	528 s, p
611 vw		559 w						
706		*702*			NO_3^-			
723		*721*						
730		*730*						
	822		822					
846^c w, l		620^c w, l		$(A_g, B_{1g}, B_{2g}, B_{3g})$	$\rho_r(NH_3)$	(A_g, B_g, E_g)		
	914 sh		690 m, sh	(B_{1u}, B_{2u}, B_{3u})	$\rho_r(NH_3)$	(A_u, E_u)		
	936 m		711 m					
1046 s	*1044* w	*1044* s	*1040* w		NO_3^-			
1059 m		*1058* m					*1060* s, p	*1060* s, p
1321 m		1001 m		B_{1g}	$\delta_s(NH_2)$	B_g	1370 w, dp	1026 w, dp
	1331^d m		1025 m	(B_{2u}, B_{3u})	$\delta_s(NH_2)$	E_u		
	1375 vs, l		*1375* vs, l		NO_3^-			
1421 w		–		A_g	$\delta_s(NH_2)$	A_g	1415 w, p	–
1462 w								
1553 w, l			1088 sh	$(A_g, B_{1g}$ B_{2g}, B_{3g} $B_{1u}, B_{2u}, B_{3u})$	$\delta_{as}(NH_2)$	$(A_g, B_g,$ E_g $A_u, E_u)$		
1576 sh	1571 m	1121 w	1126 m				1543 w, dp	1146 w
1659 w								
	3105 s, l		2270 s, l	(B_{2u}, B_{3u})	$\nu_s(NH)$	E_u		
3199 w, l		2315 m, l		(A_g, B_{1g})	$\nu_s(NH)$	(A_g, B_g)		
	3220 s, l		2322 s, l	(B_{1u}, B_{2u}, B_{3u})	$\nu_{as}(NH)$	(A_u, E_u)		
3251 w, sh		2386 sh		$(A_g, B_{1g}, B_{2g}, B_{3g})$	$\nu_{as}(NH)$	(A_g, B_g, E_g)		
		2424 w, l						
	3490 sh							

[a] sh, shoulder; l, large; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; dp, depolarized; p, polarized. [b] Gives species designation according to the overall structures: D_{2h} in solid state, C_{4h} in aqueous solution. [c] Very roughly estimated. [d] Measured from the spectrum of $[Au(NH_3)_4](ClO_4)_3$ [17].

Table I lists the Raman and infrared frequencies of $[Au(NH_3)_4](NO_3)_3$ and of its deuterate as well as their assignments according to the symmetries of the ion $[Au(NH_3)_4]^{3+}$ and of its deuterate in solid state and in aqueous solution:

i) complex in solid state:

$[Au(NH_3)_4](NO_3)_3$ crystallizes in the orthorombic space group $C_{mmm}(D_{2h}^{19})$ (z = 2) [2]. The site symmetry of the $[Au(NH_3)_4]^{3+}$ ion in the crystal is D_{2h} so it results that in that particular case, the molecular symmetry of the whole complex is necessarily D_{2h}: *i.e.*, the ammine groups NH_3 (local symmetry C_{3v}) in *trans* position are in staggered positions (Au is the inversion center), the ligands in *cis* position are obtained by reflexion, the dihedral plans between the framework AuN_4 (square planar, local symmetry D_{4h}) being the mirrors (see Fig. 3a).



(a) D_{2h} (b) C_{4h}

Fig. 3. Molecular models for the $[Au(NH_3)_4]^{3+}$ complex: Symmetries D_{2h} (solid state), C_{4h} (aqueous solution).

ii) ion in aqueous solution:

The molecular symmetry of the ion $[Au(NH_3)_4]^{3+}$ and of its deuterate, in aqueous solution is assumed to be C_{4h}, *i.e.*, the same symmetry as the ones adopted for similar square planar tetraammine Cu [6], Pd [7, 8], Pt [9, 10]. This highest symmetry where the ligands groups are in staggered positions and such that the hydrogen atoms belonging to two groups in *cis* position occupe positions corresponding to the maximal distances between themselves is the most probable (the reorientation in aqueous solution takes then into account the repulsive forces between the H-atoms). The C_{4h} symmetry contrasts with the D_{2h} one where the positions of the ligands are forced, and where the dihedral plans are not equivalent (see Fig. 3).

The vibrational normal modes for the whole complex $[Au(NH_3)_4]^{3+}$ are distributed among the D_{2h} and C_{4h} overall symmetries according to:

$$\Gamma(D_{2h}) = 7A_g(R) + 6B_{1g}(R) + 4B_{2g}(R) + 4B_{3g}(R) + \\ + 5A_u(-) + 5B_{1u}(IR) + 7B_{2u}(IR) + 7B_{3u}(IR)$$

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

The vibrational modes (D_{2h}) may be separated in:

ligand vibrations

$$\Gamma(\text{lig}) = 4A_g(4A_g) + 4B_{1g}(4B_g) + 2B_{2g}(2E_g{}^a) + \\ + 2B_{3g}(2E_g{}^b) + 2A_u(2B_u) + 2B_{1u}(2A_u) + \\ + 4B_{2u}(4E_u{}^a) + 4B_{3u}(4E_u{}^b)$$

ligand framework couplings

$$\Gamma(\text{cpl}) = 1A_g(1A_g) + 1B_{1g}(1B_g) + 2B_{2g}(2E_g{}^a) + \\ + 2B_{3g}(2E_g{}^b) + 2A_u(2B_u) + 2B_{1u}(2A_u) + \\ + 1B_{2u}(1E_u{}^a) + 1B_{3u}(1E_u{}^b)$$

and framework vibrations

$$\Gamma(\text{fr}) = 2A_g(A_g + B_g) + 1B_{1g}(B_g) + 1A_u(B_u) + \\ + 1B_{1u}(A_u) + 2B_{2u}(2E_u{}^a) + 2B_{3u}(2E_u{}^b).$$

In these equations, the correlations with corresponding species for the C_{4h} model are included in parentheses.

Skeletal Region

The skeletal vibrations are distributed among the local D_{4h} species as follow:

$$\Gamma = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u$$

The AuN symmetric stretching mode (a_{1g}) is observed at 566 cm^{-1} in the Raman solid spectrum and at 569 cm^{-1} (pol.) in the aqueous solution. The corresponding line in the deuterates shifts by 40 cm^{-1} and 41 cm^{-1} respectively. The AuN asymmetric stretching mode (b_{1g}) is seen at 544 cm^{-1} (solid) and 543 cm^{-1} dep. (aq. sol.) for the H-compound and decreases by 43 cm^{-1} (solid) and 37 cm^{-1} (aq. sol.) on deuteration. The Raman line at 327 cm^{-1}, corresponds to the b_{2g} AuN_2 deformation mode and is observed at 291 cm^{-1} in the spectrum of the deuterate. This line is only roughly observed in the Raman spectrum of $[Au(NH_3)_4]^{3+}$ in aqueous solution at 286 cm^{-1} and seems to be depolarized. The frequency shift ν(solid state) – ν(aq. sol.) = 39 cm^{-1} is due to new hydrogen bonds N–H···O.

Regarding this line which belongs to A_g species in the solid state (D_{2h}), its depolarization permits us to assign it to the species B_g in aqueous solution, which confirms the assumed molecular symmetry of the ion in solution, *i.e.*, C_{4h}.

The degenerated AuN asymmetric stretching mode (e_u) is observed in the infrared spectra respectively at 555 cm^{-1} and 506 cm^{-1} for the complex and its deuterate. The degenerated AuN_2 asymmetric deformation mode (e_u) is seen at 307 cm^{-1} and 268 cm^{-1} for the H-compound and the D-compound respectively. The out of plane a_{2u} mode $\gamma(AuN_2)$ is

TABLE II. Skeletal Frequencies (cm^{-1}) of the Square Planar Tetraammine $[M(NH_3)_4]^{n+}$.

		Au(III)[a]	Pt(II)	Pd(II)[e]	$^{63}Cu(II)$[f]
$\nu_s(MN)$	a_g(R)	566	548[c]	507	420
$\nu_{as}(MN)$	e_u(IR)	555	510[d]	491	426
$\nu(MN)$	b_{1g}(R)	544	531[c]	471	375
$\delta(MN_2)$	b_{2g}(R)	327	303[c]	305	(300)[g]
$\delta(MN_2)$	e_u(IR)	307	297[d]	292	256
$\gamma(MN_2)$	a_{2u}(IR)	272	235[d]	242	226.5
$\gamma(MN_2)$	b_{2u}(–)	(215)[b]	(200)[b]	(200)[b]	(200)[b]
atomic mass: M		196.97	195.09	106.40	62.93

[a]This work; solid state. [b]Out of plane inactive frequency, calculated values [4, 6, 8, 10]. [c]See our work ref. [9]. [d]J. Hiraishi *et al.* ref. [18]. [e]See our work ref. [7]. [f]K. H. Schmidt *et al.* ref. [5, 6]; ligand = $^{14}NH_3$. [g]Assumed frequency [6] by comparison with results on the platinum complex.

then attributed to the 272 cm^{-1} and shifts by 35 cm^{-1} in the deuterate (one has then $\gamma(AuN_2) < \delta_{as}(AuN_2)$). The other out of plane b_{2u} deformation mode (A_u in D_{2h}, B_u in C_{4h}) is inactive.

Table II lists all the results for the skeletal frequencies of the square planar tetraammines which are related to the type of the central atom M = Au, Pt, Pd and ^{63}Cu and to its atomic mass.

Ligand Modes

The assignment of the NH_3 modes is straightforward (see also [7–10]). Bands occurring in the range 3105–3251 cm^{-1} are assigned to N–H stretching; these shift to 2270–2386 cm^{-1} on deuteration. The NH_2-deformation modes range in frequency from 1321 to 1415 cm^{-1} (symmetric type) and from 1553 to 1659 cm^{-1} (antisymmetric type). The corresponding modes for ND_3 have frequencies of 1001–1026 cm^{-1} (symm.) and 1088–1146 cm^{-1} (antisymm.). All the isotopic frequency shifts correspond to $\nu_H/\nu_D \simeq 1.3_5$; thus confirming this assignment. Weishaupt and Strähle [2] assign erroneously the infrared frequencies 920 and 935 cm^{-1} to $\delta_s(NH_3)$, by comparison with gazeous frequencies of the ammonia molecule: *i.e.*, 933 and 966 cm^{-1}. Cyvin *et al.* [6] and Alix *et al.* [4, 8, 10] have clearly shown that these gazeous frequencies increase by more than 300 cm^{-1} on complexation and may be expected in the range 1250–1350 cm^{-1} (see Table I).

Framework–Ligand Couplings

The intense infrared bands at 914 and 936 cm^{-1} which shift to 690 and 711 cm^{-1} on deuteration are assigned without ambiguity (see above discussion) to the rocking modes $\rho_r(NH_3)$. The very weak corresponding Raman line is observed at 846 cm^{-1} in the H-compound and at 620 cm^{-1} in the D-compound. Table III gives the rocking frequencies (mean value of infrared and/or Raman results) which have been used to determine the symmetry valence force constant $F(\rho_r)$ of $[M(NH_3)_4]^{n+}$. The empirical relation $F(\rho_r)/\nu^2(\rho_r)$ = ct., is satisfied for the gold complex with $\nu(\rho_r)$ = 885 cm^{-1} which confirms our assignment.

TABLE III. Frequencies and Symmetry Valence Force Constants for the Rocking Modes of $[M(NH_3)_4]^{n+}$ (Ligand-Framework Coupling).

Compound	Au(III)	Pt(II)	Pd(II)	Cu(II)	units
frequency	885[a]	842[b]	825[c]	735[d]	cm^{-1}
force constant	0.22_1	0.19_9	0.19_3	0.15_3	mdyn/Å

[a]Mean value of infrared and Raman frequencies (that work). [b]See ref. [9, 10]. [c]See ref. [7, 8]. [d]See ref. [5, 6].

In earlier papers [7, 9] Manfait *et al.* have shown evidence of a weak band corresponding to the torsional motion in

i) the Raman spectra of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and its deuterate (at 195 cm^{-1} and 155 cm^{-1} respectively)

ii) the infrared spectra of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ and its deuterates (160 cm^{-1} and 123 cm^{-1}); this line was observed at 166 cm^{-1} (dep.) in the Raman spectrum of the complex in aqueous solution.

According to the present work, a similar band is observed at 188 cm^{-1} in the infrared spectrum of the complex (at 125 cm^{-1} in the deuterate), at 178 cm^{-1} in the Raman spectrum. It is assigned to the torsional mode of vibration defined by the variation of the dihedral angle between the two planes determined by for instance the atoms N_2AuN_1 and AuN_1H (see Fig. 3).

Conclusion

In this work we have given for the first time all the vibrations of the whole complex $[Au(NH_3)_4]^{3+}$, which will be of use for the determination of its general valence force field [4]. The present experimental work concludes the series on the tetra-coordinated ammine complexes which are known to have a square-planar framework structure rather than the tetrahedral structure, *i.e.*, Cu(II), Pd(II) and Pt(II) complexes.

Acknowledgments

The authors thank Dr. Le Postelec (University of Paris VI) for recording the far infrared spectra.

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