

III. OPTICAL AND INFRARED SPECTROSCOPY*

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A. FAR INFRARED SPECTRA OF TETRAHALO, TETRAAMMINE, AND DIHALODIAMMINE COMPLEXES OF PALLADIUM

1. Introduction

Recently, a number of far infrared studies of platinum halide complexes have been reported.¹⁻⁵ The majority of the compounds studied were alkali salts of the halide complexes of platinum (II). Thus far, the infrared investigation of the corresponding palladium complexes has covered only the spectral range 4000-250 cm^{-1} .⁶⁻⁸ In this region the only skeletal vibrations observed are the Pd-N and Pd-Cl antisymmetric and symmetric stretching vibrations.

2. Discussion

The infrared spectra of a number of square planar palladium (II) complexes of the type M_2PdX_4 , PdL_4X_2 , and trans and cis isomers of PdL_2X_2 (where $\text{M} = \text{NH}_4^+$, K^+ , Rb^+ or Cs^+ ; $\text{L} = \text{NH}_3$; $\text{X} = \text{Cl}^-$, Br^- or I^-) have been recorded from 4000 to 40 cm^{-1} with the use of instrumentation described previously.⁹ The compounds were examined both at room temperature and at liquid-nitrogen temperature.

The investigation of four tetrachloropalladium (II) complexes gave Pd-Cl stretching vibrations in the range 327-336 cm^{-1} , Pd-Cl in-plane bending vibrations in the range 183-205 cm^{-1} , and Pd-Cl out-of-plane bending vibrations from 160 to 175 cm^{-1} . Four similar bromo complexes gave the corresponding Pd-Br vibrations in the ranges 249-260 cm^{-1} , 130-169 cm^{-1} , and 114-140 cm^{-1} , respectively. The Pd-N in- and out-of-phase bending vibrations of the tetraammine complexes were found in the ranges 245-273 cm^{-1} and 160-190 cm^{-1} , respectively. In the M_2PdCl_4 and M_2PdBr_4 compounds, the two bands of lowest frequency correspond to the lattice vibrations, and these assignments are confirmed by the decrease in these frequencies for the compounds in the order $\text{NH}_4^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ which is expected as the atomic (or molecular) weight of the cation increases.

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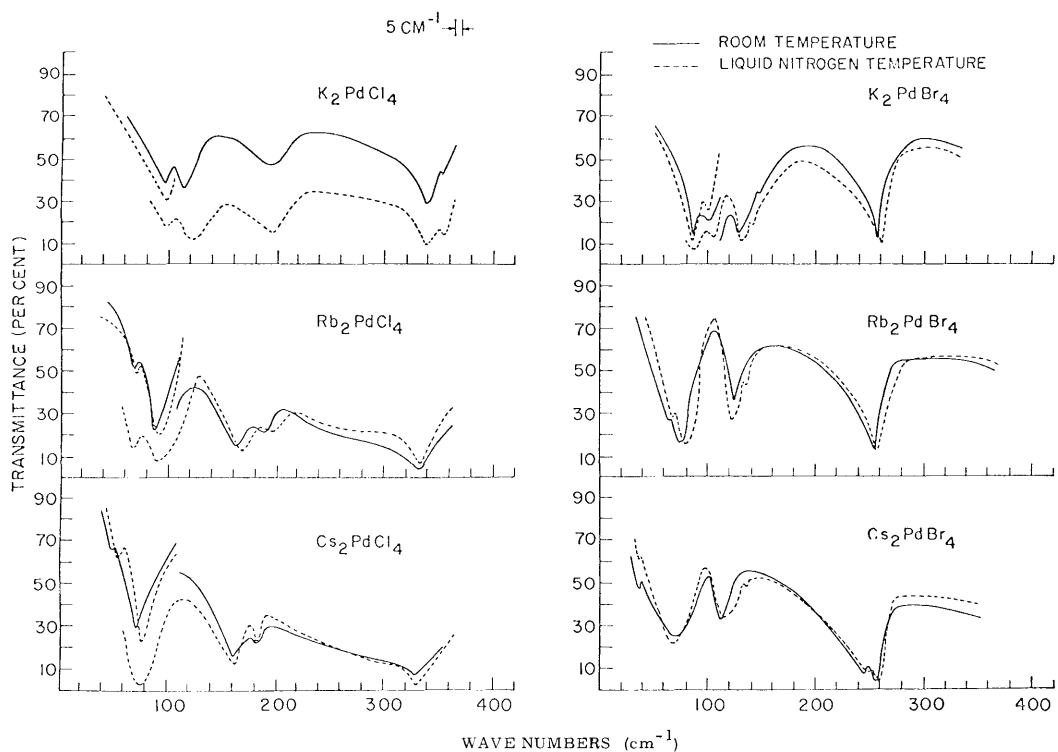


Fig. III-1. Far infrared spectra of some Tetrahalopalladium (II) Salts.

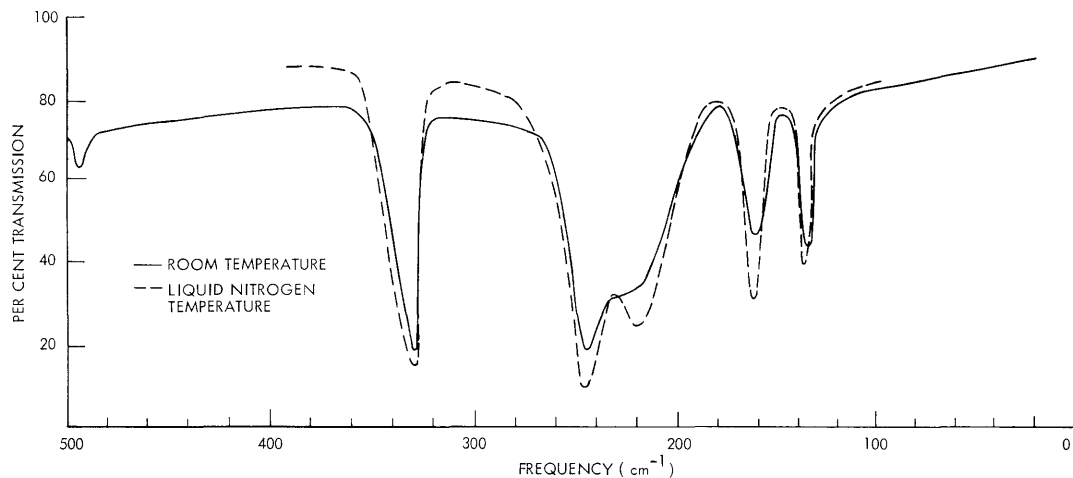


Fig. III-2. Far infrared spectrum of Trans $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. Solid line: room temperature; dotted line, liquid-nitrogen temperature.

Table III-1. Internal and lattice vibrations of M_2PdX_4 complexes.

$(NH_4)_2PdCl_4$	K_2PdCl_4	Rb_2PdCl_4	Cs_2PdCl_4	$(NH_4)_2PdBr_4$	K_2PdBr_4	Rb_2PdBr_4	Cs_2PdBr_4	Assignment
3182s				3170s				NH_4^+ stretching
3038s				3020s				NH_4^+ stretching
2812w				2796w				$2 \times 1398 = 2796$
1649m				1624m				NH_4^+ antisymmetric deformation
1398s				1398s				NH_4^+ symmetric deformation
340sh	356sh			363m				combination
							255sh	
327s	336s	331s	328s	254s	260s	258s	249s	ν_6 Pd-X stretching
205sbroad	193m	188m	183m	169sbroad	140sh	135sh	130sh	ν_7 in-plane bending
175s	n. o.	166m	160m	140sh	130s	125m	114m	ν_2 out-of-plane bending
120s	110s	88s	75s	n. o.	100s	76s	67m	A_{2u} lattice mode
n. o.	95s	70sh	50sh	97s	85s	65sh	38sh	E_u lattice mode

Abbreviations: m = medium, s = strong, w = weak, sh = shoulder, n. o. = not observed.

Table III-2. Infrared frequencies of $\text{Pd}(\text{NH}_3)_4\text{X}_2$ complexes.

$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$	$\text{Pd}(\text{NH}_3)_4\text{Br}_2$	Assignment
3230s	3240s	NH_3 stretching
3140s	3147s	NH_3 stretching
2618w		$2 \times 1301 = 2602?$
2365w	2373w	?
2130w	2130w	$1301 + 830 = 2131$
2065w	2064w	?
1608s	1618s	NH_3 antisymmetric deformation
1320sh	1319sh	NH_3 rocking + Pd-N stretching
1301s	1301s	NH_3 symmetric deformation
1285sh	1284sh	?
1278sh	1277sh	?
830s	825s	NH_3 rocking
	515	?
505sh	501sh	?
500sh	495sh	?
494m	490m	Pd-N stretching
476w	471w	$2 \times 245 = 490$
330vw		?
245m	273m	in-plane bending
160w	190w	out-of-plane bending
115m	n. o.	lattice modes

Abbreviations: m = medium, s = strong, w = weak, sh = shoulder, n. o. = not observed.

Table III-3. Infrared frequencies of trans and cis isomers of $\text{Pd}(\text{NH}_3)_2\text{X}_2$.

<u>trans</u> $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	<u>trans</u> $\text{Pd}(\text{ND}_3)_2\text{Cl}_2$	<u>cis</u> $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	<u>trans</u> $\text{Pd}(\text{NH}_3)_2\text{Br}_2$	<u>cis</u> $\text{Pd}(\text{NH}_3)_2\text{Br}_2$	<u>trans</u> $\text{Pd}(\text{NH}_3)_2\text{I}_2$	Assignments
3320s	2479s	3314s	3307s	3307s	3296m	NH_3 stretching
3240m	2352m	3237s	3233m	3234s	3223m	NH_3 stretching
3181sh	2328m	3177sh	3171sh	3169sh	3152sh	NH_3 stretching
1605m	1183m	1610m	1598m	1601m	1594m	NH_3 antisymmetric deformation
	1148sh					$2 \times 579 = 1158$
	1116sh					?
1255sh	1051m	1269sh	1251sh	1263m	1256sh	NH_3 rocking + Pd-N anti-symmetric stretching
1247s	974s	1248s	1245s	1245m	1242s	NH_3 symmetric deformation
				774sh		?
753m	579m	752s	753m	741m	n. o.	NH_3 rocking
496w	461w	495w	490w	480w	480w	Pd-N antisymmetric stretching
		476w		460w		Pd-N symmetric stretching
333s	329s	327s	n. o.	258w	191s	Pd-X antisymmetric stretching
		306s		n. o.		Pd-X symmetric stretching
245s	218vs	245s	220s	225s	263w	Pd-N bending
222s	194vs	218s	220s	225s	218s	Pd-N bending
				190m		?
				177m		?
162m	161m	160m	122m	120m	109m	Pd-X bending
137m	134m	135m	101m	100w	n. o.	Pd-X bending
	109vw	109w				lattice mode

Abbreviations used: m = medium, s = strong, w = weak, v = very, sh = shoulder, n. o. = not observed.

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Weak shoulders are observed in some of the compounds and have been assigned as combinations of infrared and Raman active modes in the corresponding platinum complexes.¹ These bands in the palladium complexes cannot be uniquely assigned, however, as the Raman spectra have not been obtained, owing to their intense colors.

By using the assignments for the tetrahalo and tetraammine complexes, as well as the isotopic shift data, assignments for the fundamental modes for a series of cis and trans dihalodiammine complexes of palladium (II) are given. The results are summarized in Tables III-1, III-2, and III-3, and the far infrared spectra of some tetrahalopalladium (II) salts are shown in Fig. III-1. Figure III-2 shows the far infrared spectrum of trans Pd(NH₃)₂Cl₂. The interpretation of the data and discussion of the results in more detail are contained in a paper submitted to Spectrochimica Acta as Part III in a series on palladium complexes.^{6, 10}

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References

1. J. H. Fertel and C. H. Perry, *J. Phys. Chem. Solids* 26, 1773 (1965).
2. D. M. Adams and H. A. Gebbie, *Spectrochim. Acta* 19, 925 (1963).
3. H. Poulet, P. Delorme, and J. P. Mathieu, *Spectrochim. Acta* 20, 1855 (1964).
4. A. Sabatini, L. Sacconi, and V. Scheltino, *Inorg. Chem.* 3, 1775 (1964).
5. R. A. Walton, *Spectrochim. Acta* 21, 1795 (1965).
6. J. R. Durig, R. Layton, D. W. Sink, and B. R. Mitchell, *Spectrochim. Acta* 21, 1367 (1965).
7. S. Mizushima, I. Nakagawa, M. J. Schmely, C. Cuirraw, and J. V. Quagliano, *Spectrochim. Acta* 13, 31 (1958).
8. D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, p. 734, 1964.
9. C. H. Perry, Quarterly Progress Report No. 70, Research Laboratory of Electronics, M. I. T., July 15, 1963, pp. 19-31; R. Geick, C. H. Perry, E. C. Reifenstein III, H. D. Wactlar, and E. F. Young, Quarterly Progress Report No. 76, January 15, 1965, pp. 27-38.
10. J. R. Durig, B. R. Mitchell, D. W. Sink, and A. S. Wilson (to appear in *Spectrochim. Acta*, Vol. 22, 1966).

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B. FAR INFRARED SPECTRA OF METAL CLUSTER COMPOUNDS

Recent crystallographic studies have revealed the existence of a surprisingly large number of inorganic compounds containing discrete, well-defined metal-metal bonds, and these compounds have recently been reviewed.¹ Great interest has been expressed by inorganic and theoretical chemists in the properties of these metal-metal bonds, but there is very little experimental data available. Since most of these compounds are intensely colored, Raman data will be scarce for some time, and any vibrational data must be obtained by far infrared spectroscopy.

The octahedral metal-atom cluster compounds were chosen for study mainly due to

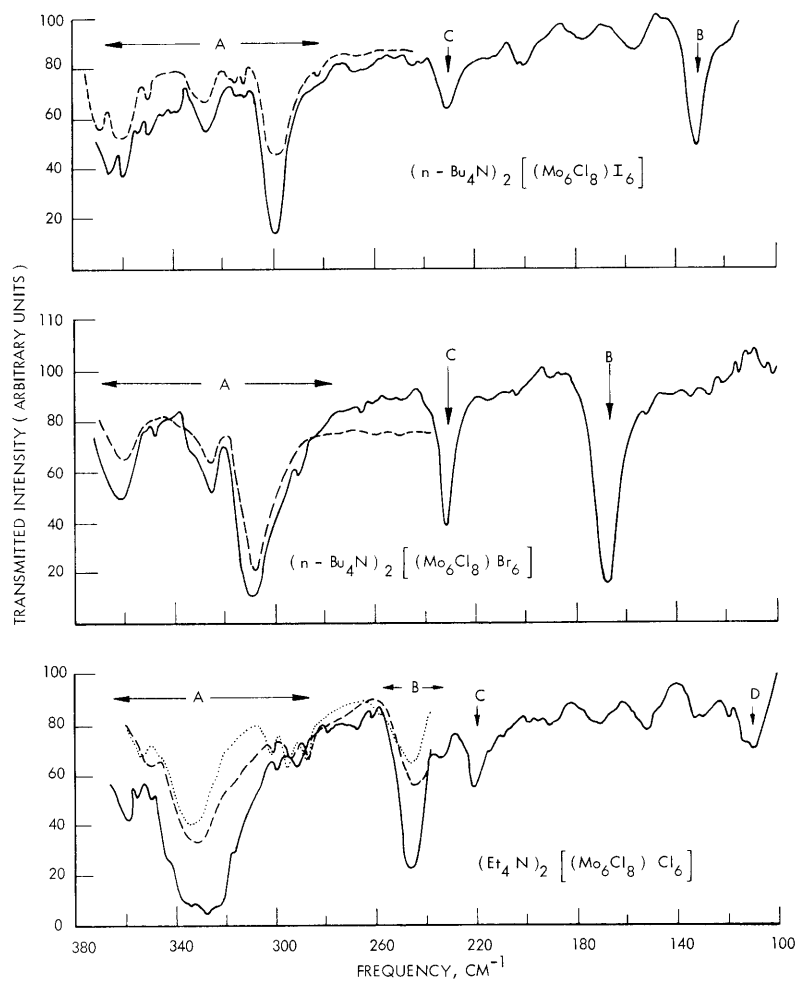


Fig. III-3. Far infrared spectra of $[(\text{Mo}_6\text{X}_8)\text{Y}_6]^{2-}$ compounds. Solid curves: spectra obtained on the interferometer; dashed curves, same sample run on the Perkin-Elmer 521; dotted curve, a nujol mull run on the Perkin-Elmer 521.

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the completion of a molecular orbital calculation for these structures.² Spectra have been obtained over the region 350 to 100 cm^{-1} for the compounds $[\text{Mo}_6\text{Cl}_8(\text{X})_6]^{2-}$ (X = Cl, Br, I), $[\text{W}_6\text{Cl}_8\text{Cl}_6]^{2-}$, and $[\text{Nb}_6\text{Cl}_{12}(\text{X})_2]^{2-}$ (X = Cl, Br). The only satisfactory results thus far, however, are for the $[\text{Mo}_6\text{Cl}_8(\text{X})_6]^{2-}$ compounds, and these spectra are shown in Fig. III-3. To make an assignment of the observed bands with assurance, we must wait for the spectra of the compounds $[\text{Mo}_6\text{X}_8(\text{Y})_6]^{2-}$ (X = Br, I) (Y = Cl, Br, I) which have been prepared and will be run soon. Several considerations, however, have led to the present tentative assignment of the bands as follows: Bands A, 2 degenerate vibrations of the triply-bridging Cl's; Band B, stretching of the terminal X_6 groups; Band C, stretching vibration of the metal-metal bonds in the M_6 octahedral frame.

All samples used were pressed polyethylene discs of the compound, and the spectra were run on the interferometer kindly made available by the Optical and Infrared Spectroscopy Group of the Research Laboratory of Electronics.

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References

1. F. A. Cotton (paper to be published in Quart. Rev.)
2. F. A. Cotton and T. E. Haas, Inorg, Chem. 3, 10 (1964).