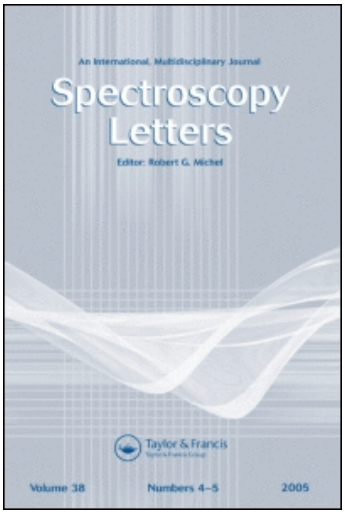

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF 1,2-*BIS*(2-FORMYLGLYCINEBENZENESULFENYL) ETHANE Pd(II) DICHLORIDE COMPLEX

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Online publication date: 31 October 2001

To cite this Article Zhang, Yu , Hang, Wei , Zhou, Shaozhen , Li, Chongde and Zhu, Longgen(2001) 'VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF 1,2-*BIS*(2-FORMYLGLYCINEBENZENESULFENYL) ETHANE Pd(II) DICHLORIDE COMPLEX', Spectroscopy Letters, 34: 5, 647 — 663
To link to this Article: DOI: 10.1081/SL-100106878
URL: http://dx.doi.org/10.1081/SL-100106878

SPECTROSCOPY LETTERS, 34(5), 647–663 (2001)

VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF 1,2-*BIS*(2-FORMYLGLYCINEBENZENESULFENYL) ETHANE Pd(II) DICHLORIDE COMPLEX

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ABSTRACT

The normal coordinate analysis of the title complex, 1,2-bis(2-formylglycinebenzenesulfenyl) ethane Pd(II) dichloride has been carried out by using the Urey-Bradley force field. According to the molecular structure determined by x-ray crystallographic analysis, 182 internal coordinates were established and 112 theoretical vibration frequencies agree well with the observed values with the average difference of 2.53 cm^{-1} and the maximum deviation of 16.0 cm^{-1}.

Key Words: IR spectra; Raman; FIR; Normal coordinate analysis; Vibrational assignment

*Corresponding author.

INTRODUCTION

Selective cleavage of peptides and proteins is one of the most common tasks in analytical biochemistry. Recent studies have shown that transition metal complexes can act as cleavage reagents since their structure and reactivity can be precisely controlled by the choice of the metals and the ligands[1–4]. One of these groups is represented by simple palladium (II) complexes[5]. Recently, more attention has been paid to sulfur containing palladium (II) complexes, some of which have highly efficient cleavage activity to amide bonds in peptides and proteins[6,7,8]. The title compound, which exhibits the ability to cleavage Met-AA (aa = amino-acid) bond, was synthesized and its structure was determined[9]. In this article, we report the vibration study for this complex. The normal coordinate analysis (NCA) was completed by using the Urey-Bradley force field; the calculations were refined on the basis of the IR, Raman and FIR spectra. The structure parameters of the title complex are given in Table 1.

Table 1. Structure Parameters of the Title Complex

Atoms	Distance(Å)	Atoms	Angles(deg.)	Atoms	Angles(deg.)
Pd1-S1	2.264	S1A-Pd1-S1	91.38	C2-C7-C6	119.93
Pd1-S1A	2.264	Cl1A-Pd1-S1	178.08	N1-C8-O1	122.48
Pd1-Cl1A	2.322	Cl1A-Pd1-S1A	86.70	C3-C8-O1	121.73
Pd1-Cl1	2.322	Cl1-Pd1-S1	86.70	C3-C8-N1	115.77
C2-S1	1.796	Cl1-Pd1-S1A	178.08	C10-C9-N1	113.70
C1-S1	1.829	Cl1-Pd1-Cl1A	95.22	O3-C10-O2	124.17
C8-O1	1.228	C1-S1-C2	103.27	C9-C10-O2	122.37
C10-O2	1.200	Pd1-S1-C2	104.40	C9-C10-O3	113.44
C8-N1	1.341	Pd1-S1-C1	102.41		
C10-O3	1.326	S1-C2-C3	118.07		
C9-N1	1.448	C9-N1-C8	119.22		
C1A-C1	1.500	S1-C1-C1A	112.74		
C7-C2	1.391	C3-C2-C7	120.12		
C3-C2	1.406	S1-C2-C7	121.61		
C4-C3	1.395	C2-C3-C4	118.70		
C8-C3	1.498	C8-C3-C4	120.92		
C5-C4	1.381	C8-C3-C2	120.37		
C6-C5	1.381	C3-C4-C5	120.81		
C7-C6	1.389	C6-C5-C4	120.18		
C9-C10	1.511	C7-C6-C5	120.23		

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EXPERIMENTAL

The synthesis and structure of the title compound was described in reference[9]. Infrared (IR) and far-infrared (FIR) spectra were obtained using a Nicolet Fourier transform IR170-SX spectrometer, with the sample at room temperature. The KBr pellet technique was used for IR in the $400 \sim 4000\,cm^{-1}$ region as shown in Fig. 1. The Nujol mull technique with polyethylene plates was used for FIR in the $100 \sim 500\,cm^{-1}$ region as shown in Fig. 2. Figure 3 shows the Raman spectroscopy in the region $0 \sim 3500\,cm^{-1}$, which was measured using a Spex Raman spectrometer model 1403. The excitation line of the Ar^{+} laser is 4880 Å with an output power of 100 mw. The sample was pressed as a disk in a stainless steel cell.

NORMAL COORDINATE ANALYSIS

The molecular structure of the title complex is shown in Fig. 4; it has C_2 point group symmetry, the Pd (II) is coordinated by two sulfur atoms and two chloride atoms nearly in a square planar. The ligand erects up the planar. In the complex, the two sulfur atoms exhibit sp^3 inequality hybridization. Due to the repulsion of the lone pair, the angles Pd1S1C1 and C1S1C2, which are less than a regular tetrahedral angle, are given to be 104.4° and 103.27°, respectively.

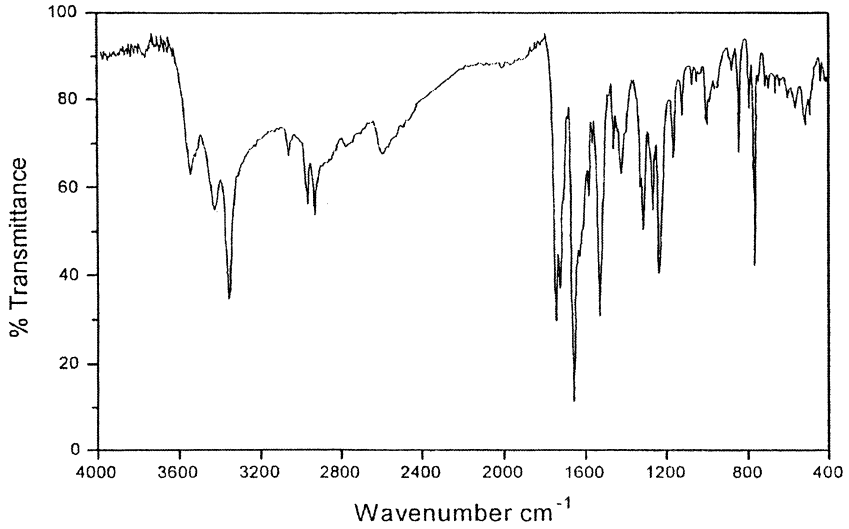

Figure 1. The IR spectrum of the title complex.

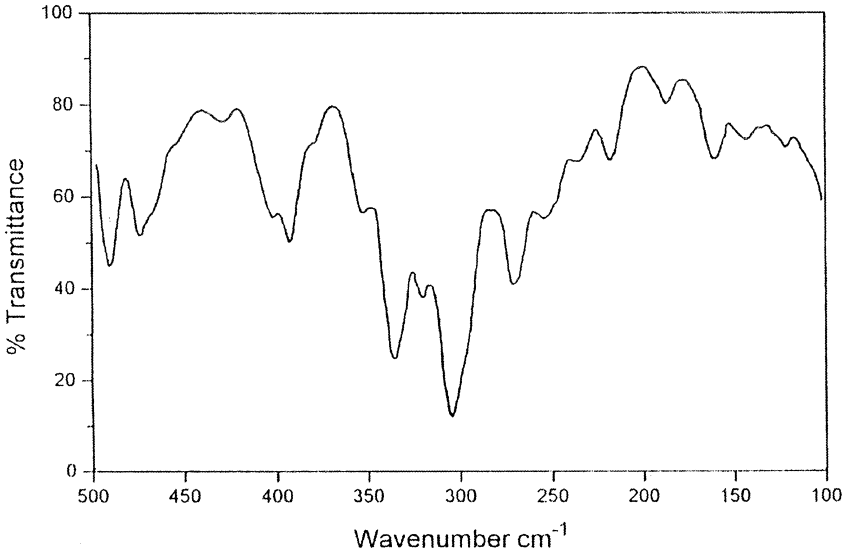

Figure 2. The far-IR spectrum of the title complex.

The calculation was performed using a Pentium-II 586 PC with CART, GMAT, and FPERT programs provided by National Research Council of Canada[10]. 182 internal coordinates were used as shown in Fig. 5, the 55 of which were attributed to stretching (ν), 92 to bending (δ), 8 to

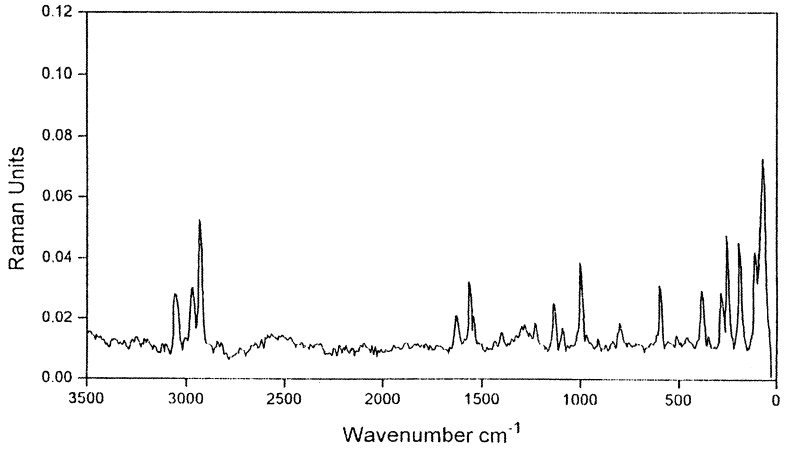

Figure 3. The Raman spectrum of the title complex.

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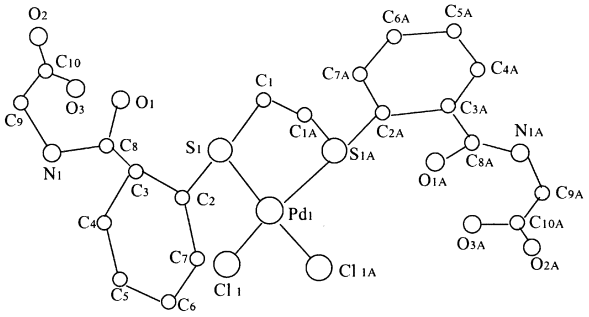

Figure 4. The molecular structure of the title complex.

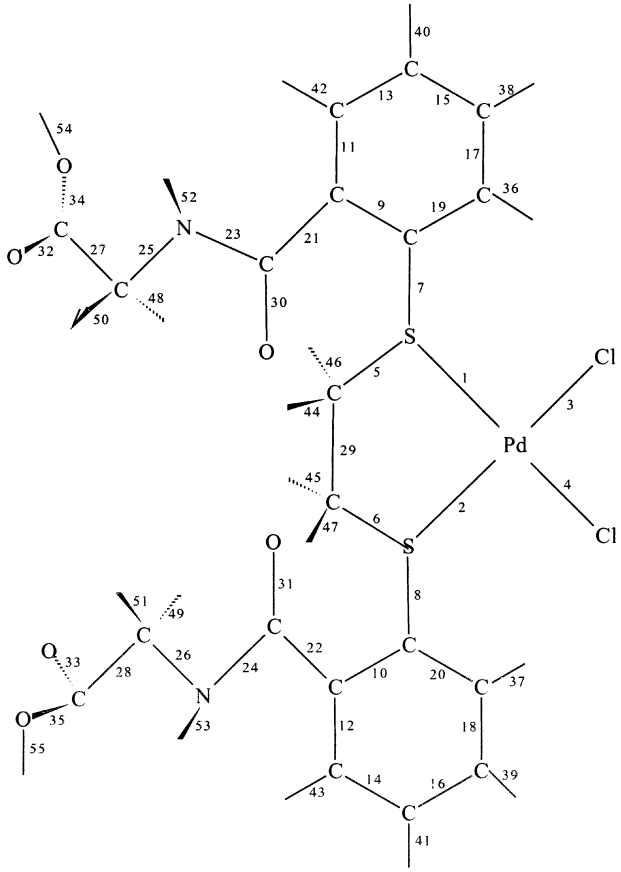

Figure 5. Numerical identification of internal coordinates of the title complex.

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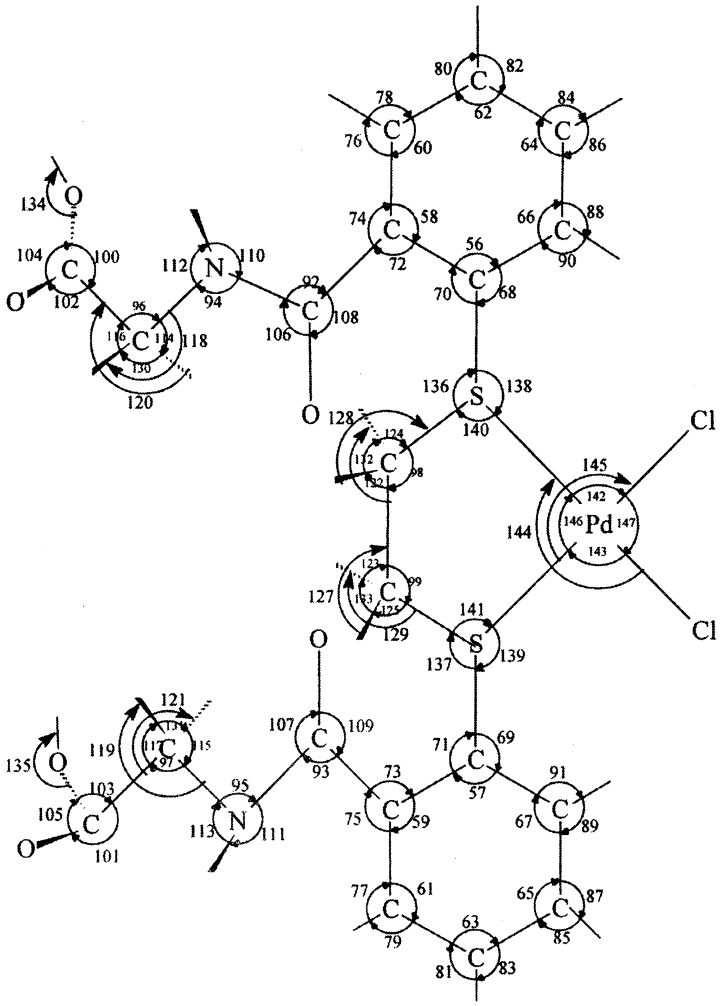

Figure 5. Continued.

wagging out-of-plane (ω) and 27 to twisting (τ). The number of internal coordinates exceeded that of normal vibrations, and redundant symmetry coordinates were eliminated during normalization by the GMAT program. A modified Urey-Bradley force field was used in the calculation.

The initial values of the force constants were collected and transferred from related molecular[11–14] and refined in accordance with the

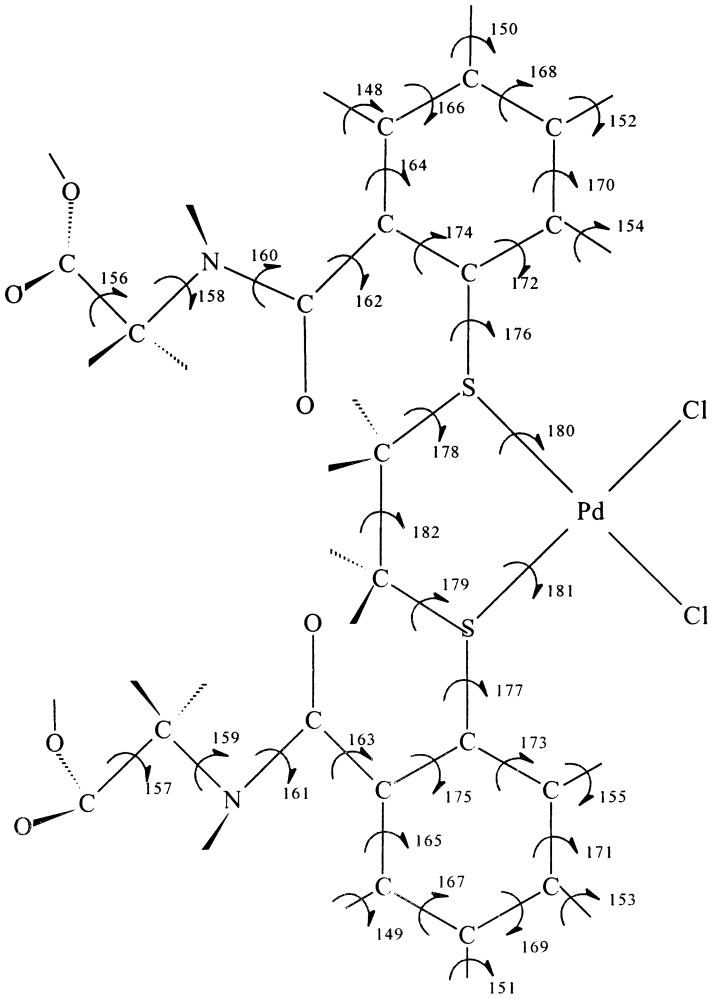

Figure 5. Continued.

position of bands in the IR, Raman and FIR spectra. The final values of the force constants are shown in Table 2. The observed and calculated frequencies, together with the percentages of potential energy distribution (PED), are presented in Table 3. The assignments of frequencies in Table 3 consider predominant contribution of the internal coordinates. The calculated fundamentals agree well with the observed ones. The average deviation of the calculated frequencies from the

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Table 2. Force Constants for the Complex

Symbol*	Coordinates Involved	Values	Symbol	Coordinates Involved	Values
K1	Pd1-S1, Pd1-S1A	1.598	H28	∠C9C10O3,	1.211
K2	Pd1-Cl1, Pd1-Cl1A	1.103		∠C9AC10AO3A	
K3	S1-C1, S1A-C1A	2.795	H29	∠O3C10O2, ∠O3AC10AO2A	1.294
K4	S1-C2, S1A-C2A	3.091	H30	∠N1C8O1, ∠N1AC8AO1A	1.677
K5	C-C(ph)	4.476	H31	∠C3C8O1, ∠C3AC8AO1A	1.602
K6	C3-C8, C3A-C8A	3.338	H32	∠C8N1H, ∠C9N1H,	0.521
K7	C8-N1, C8A-N1A	3.851		∠C8AN1AH, ∠C9AN1AH	
K8	N1-C9, N1A-C9A	4.296	H33	∠CCH(CH_2), ∠NCH(CH_2),	0.412
K9	C9-C10, C9A-C10A	3.305		∠SCH(CH_2)	
K10	C1-C1A	3.858	H34	∠HCH(CH_2)	0.328
K11	O1-C8, O1A-C8A	7.071	H35	∠C10O2H, ∠C10AO2AH	0.722
K12	C10-O3, C10A-O3A	8.146	H36	∠C1S1C2, ∠Pd1S1C2	0.435
K13	C10-O2, C10A-O2A	7.962		∠C1AS1AC2A, ∠Pd1S1AC2A	
K14	C-H(ph)	5.108	H37	∠Pd1S1C1, ∠Pd1S1AC1A	0.432
K15	C1-H, C1A-H	4.683	H38	∠S1Pd1Cl1, ∠S1APd1Cl1A	0.401
K16	C9-H, C9A-H	4.611	H39	∠S1Pd1ClA, ∠S1APd1Cl	0.402
K17	N1-H, N1A-H	6.257	H40	∠S1Pd1S1A	0.467
K18	O2-H, O2A-H	7.042	H41	∠Cl1Pd1Cl1A	0.442

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H19	∠CCC(ph)	1.043	W42	∠H-CC-C(ph)	0.333
H20	∠C7C2S1, ∠C3C2S1, ∠C7AC2AS1A, ∠C3AC2AS1A	2.119	T43	∠O2C10-C9-N1, ∠O2AC10A-C9A-N1A	0.140
H21	∠C2C3C8, ∠C4C3C8, ∠C2AC3AC8A, ∠C4AC3AC8A	1.685	T44	∠C10C9-N1-C8, ∠C10AC9A-N1A-C8A	0.102
H22	∠HCC(ph)	0.278	T45	∠C9N1-C8-C3, ∠C9AN1A-C8A-N3A	0.108
H23	∠C3C8N1, ∠C3AC8AN1A	1.062	T46	∠O1C8-C3-C4, ∠O1AC8A-C3A-C4A	0.312
H24	∠C8N1C9, ∠C8AN1AC9A	1.066	T47	∠CC-C-C(ph)	0.361
H25	∠N1C9C10 ∠N1AC9AC10A	0.345	T48	∠C3C2-S1-Pd1, ∠C3AC2A-S1A-Pd1	0.272
H26	∠S1C1C1A, ∠C1C1AS1A	0.383	T49	∠C2S1-C1-C1A, ∠C2AS1A-C1A-C1	1.109
H27	∠C9C10O2, ∠C9AC10AO2A	1.210	T50	∠C2S1-Pd1-S1A, ∠C2AS1A-Pd1-S1	0.091
			T51	∠S1C1-C1A-S1A	0.122

*Notation and dimension are as follows: K, stretching force constant(mdyne per angstrom); H, bending force constant(mdyne per angstrom); W, wagging out-of-plane force constant(mdyne per angstrom); T, twisting force constant(mdyne per angstrom).

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Table 3. Calculated and Observed Wavenumber and PED for the Complex

IR (cm^{-1}) obs.	Raman (cm^{-1}) obs.	Calculated (cm^{-1})	Potential Energy Distribution (%)	Band Assignment
3554.4		3554.7	$99.7K_{18}$	ν (OH)
		3553.2	$99.8K_{18}$	ν (OH)
3368.8		3368.2	$99.5K_{17}$	ν (NH)
		3368.2	$99.5K_{17}$	ν (NH)
3067.5		3067.7	$98.9K_{14}$	ν (CH) (ph)
		3067.6	$98.9K_{14}$	ν (CH) (ph)
		3065.7	$99.0K_{14}$	ν (CH) (ph)
		3063.6	$99.2K_{14}$	ν (CH) (ph)
	3062.3	3061.8	$99.4K_{14}$	ν (CH) (ph)
2972.7	2974.9	2972.5	$99.5K_{15}$	ν_a (CH)(CH_2) (Et)
		2968.5	$99.8K_{15}$	ν_a (CH)(CH_2) (Et)
2937.6	2938.7	2938.1	$99.5K_{16}$	ν_a (CH)(CH_2) (Me)
		2937.7	$99.5K_{16}$	ν_a (CH)(CH_2) (Me)
		2889.3	$99.3K_{15}$	ν_s (CH)(CH_2) (Et)
		2885.0	$99.7K_{15}$	ν_s (CH)(CH_2) (Et)
		2877.5	$99.4K_{16}$	ν_s (CH)(CH_2) (Me)
1746.6		1748.4	$43.3K_{12}+37.0K_{13}$	ν_a (C-O)(COOH)
1727.8		1726.1	$45.9K_{12}+37.4K_{13}$	ν_a (C-O)(COOH)
		1663.3	$22.2K_5+21.8K_{11}+12.0H_{21}$	ν (CC) (ph), ν (C=O), δ (CCC)
1659.9	1654.6	1663.2	$22.3K_5+21.7K_{11}+12.0H_{21}$	ν (CC) (ph), ν (C=O), δ (CCC)
		1588.3	$35.0K_5+8.6K_6+7.8H_7+9.7H_{21}+7.2H_{32}$	ν (CC) (ph)
1585.2	1585.6	1587.9	$35.4K_5+8.6K_6+7.7H_7+9.7H_{21}+7.0H_{32}$	ν (CC) (ph)

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		1538.7	$23.6K_5+14.5K_{11}+17.0H_{32}$	ν (CC) (ph), ν (C=O), δ (CNH)
1531.5		1537.4	$24.0K_5+15.6K_{11}+17.4H_{32}$	ν (CC) (ph), ν (C=O), δ (CNH)
		1498.7	$19.9H_5+9.1H_{11}+7.5W_{42}+7.8H_{32}$	ν (CC) (ph), ν (C=O), δ (CNH)
		1496.4	$20.1H_5+7.1H_{11}+9.3W_{42}+11.4H_{32}$	ν (CC) (ph), ν (C=O), δ (CNH)
		1495.2	$15.6K_{10}+40.8H_{33}+37.8H_{34}$	ν (CC) (Et), δ (CCH), δ_a (HCH) (Me)
		1478.0	$10.5K_9+26.5W_{42}+26.0T_{47}$	ν (CC), ω (CH) (ph), τ (CC) (ph)
		1469.5	$11.9K_5+10.6K_9+9.1K_{13}+12.5H_{32}+12.3W_{42}$	ν (CC) (ph), ω (CH) (ph), δ (CNH)
1462.3	1461.0	1464.3	$21.1K_9+10.4K_{12}+19.2K_{13}+10.3H_{29}$	ν (CC), ν_s (C-O)(COOH), δ (OCO)
		1445.8	$66.7K_5+11.9H_{22}$	ν (CC) (ph), δ (CCH) (ph)
		1445.7	$66.4K_5+11.8H_{22}$	ν (CC) (ph), δ (CCH) (ph)
1423.5	1426.0	1424.2	$42.2H_{33}+56.9H_{34}$	δ (CCH), δ (NCH), δ (SCH), δ (HCH)
		1364.9	$71.5H_{33}+21.1H_{34}$	δ (CCH), δ (NCH), δ (SCH), δ (HCH)
		1354.5	$49.1H_{33}+34.4H_{34}$	δ (CCH), δ (NCH), δ (SCH), δ (HCH)
		1352.1	$33.1K_5+42.3H_{22}$	ν (CC) (ph), δ (CCH) (ph)
		1352.0	$32.1K_5+41.0H_{22}$	ν (CC) (ph), δ (CCH) (ph)

(*continued*)

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Table 3. Continued

IR (cm^{-1}) obs.	Raman (cm^{-1}) obs.	Calculated (cm^{-1})	Potential Energy Distribution (%)	Band Assignment
1329.3		1328.9	$35.3K_5+37.0H_{22}$	ν (CC) (ph), δ (CCH) (ph)
		1328.8	$35.2K_5+37.0H_{22}$	ν (CC) (ph), δ (CCH) (ph)
1315.2	1312.4	1313.6	$11.0K_8+38.4H_{33}+28.5H_{34}$	ν (CN), δ (CCH), δ (NCH), δ (SCH), δ (HCH)
		1311.2	$10.3K_8+35.7H_{33}+33.7H_{34}$	ν (CN), δ (CCH), δ (NCH), δ (SCH), δ (HCH)
		1279.3	$30.0H_{33}+40.4H_{34}$	δ (CCH), δ (NCH), δ (SCH), δ (HCH)
		1277.7	$30.2H_{33}+34.0H_{34}$	δ (CCH), δ (NCH), δ (SCH), δ (HCH)
		1268.1	$9.8K_5+10.3K_6+9.5H_{19}+9.5H_{22}+15.1H_{32}$	δ (CNH), ν (CC), ν (CC)(ph), δ (CCC) (ph)
1265.0	1259.6	1268.0	$9.4K_5+9.9K_6+9.2H_{19}+9.1H_{22}+13.6H_{32}$	δ (CNH), ν (CC) (ph), δ (CCC) (ph)
		1180.5	$73.4H_{22}$	δ (CCH) (ph)
		1180.3	$77.6H_{22}$	δ (CCH) (ph)
		1176.5	$89.7H_{33}$	δ (CCH), δ (NCH), δ (SCH)
		1174.8	$17.0K_{12}+79.5H_{35}$	ν (C-O) (COOH), δ (CSC)
1164.8	1167.2	1163.5	$76.4W_{42}+18.1T_{47}$	ω (CH) (ph), τ (CC) (ph)
	1126.0	1125.8	$88.3H_{33}$	δ (CCH), δ (NCH), δ (SCH)
1120.3		1118.7	$28.3H_{19}+14.2H_{22}$	δ (CCC) (ph), δ (CCH) (ph)
		1117.9	$25.9H_{19}+12.2H_{22}+16.4H_{33}$	δ (CCC) (ph), δ (CCH) (ph), δ (CCH) δ (NCH), δ (SCH)
		1103.1	$93.0H_{33}$	δ (CCH), δ (NCH), δ (SCH)
		1102.3	$92.8H_{33}$	δ (CCH), δ (NCH), δ (SCH)

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1046.8	1033.9	1053.4	$63.8W_{42}$	ω (CH) (ph)
		1015.9	$17.0K_5+70.2H_{22}$	δ (CCH) (ph), ν (CC) (ph)
985.4		978.7	$24.8K_5+15.0K_8+28.0H_{22}$	ν (CC) (ph), ν (CN), δ (CCH) (ph)
		963.2	$27.6K_5+60.0H_{22}$	δ (CCH) (ph), ν (CC) (ph)
		931.1	$13.9K_5+25.0K_8+15.0H_{33}$	ν (CC) (ph), ν (CN), δ (CCH) (ph)
		909.2	$60.4K_{10}+30.8H_{33}$	ν (CC) (Et), δ (CCH)
		887.3	$98.4W_{42}$	ω (CH) (ph)
		842.4	$53.0K_5+13.3H_{22}$	δ (CCH) (ph), ν (CC) (ph)
838.6	836.3	836.2	$12.7K_7+11.2H_{24}+29.4H_{33}$	ν (CN), δ (CNC), δ (NCH)
		826.7	$15.1K_7+11.4H_{24}+27.4H_{33}+11.8W_{42}$	ν (CN), δ (CNC), δ (CCH), δ (NCH), δ (SCH), ω (CH) (ph)
		816.4	$81.6H_{33}$	δ (CCH), δ (NCH), δ (SCH)
		814.4	$11.4K_5+41.7W_{42}+18.5T_{47}$	ν (CC) (ph), ω (CH) (ph), τ(CC) (ph)
		802.3	$22.7K_9+19.5K_{12}+26.2K_{13}+11.3H_{29}$	ν (CC), ν (C-O)(COOH), ν (C-OH), δ (OCO)
787.8		787.7	$27.1K_3+61.8H_{33}$	ν (CS), δ (CCH), δ (NCH), δ (SCH)
762.0		758.0	$34.3K_9+20.3K_{12}+14.6K_{13}$	ν (CC), ν (C-O)(COOH), ν (C-OH)
703.6		702.1	$9.5K_4+18.0K_5+44.1H_{19}$	ν (ph-S), ν (CC) (ph), δ (CCC) (ph)
684.6		683.3	$10.4K_7+47.6H_{33}$	ν (CN), δ (CCH), δ (NCH), δ (SCH)

(*continued*)

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Table 3. Continued

IR (cm^{-1}) obs.	Raman (cm^{-1}) obs.	Calculated (cm^{-1})	Potential Energy Distribution (%)	Band Assignment
652.5		659.2	$45.4K_3 + 39.5H_{33}$	ν (CS), δ (CCH), δ (NCH), δ (SCH)
		642.0	$63.8K_3$	ν (CS)
632.5	636.1	630.7	$26.0K_5 + 43.3H_{19}$	ν (CC) (ph), δ (CCC) (ph)
592.4		595.8	$27.8K_9 + 13.0H_{27} + 18.0H_{29} + 16.2H_{35}$	ν (CC), δ (CCO)(COOH), δ (OCO), δ (COH)
		561.0	$16.5K_9 + 22.7H_{28} + 35.3H_{29}$	ν (CC), δ (CCO)(COOH), δ (OCO)
556.8	548.0	554.6	$26.9K_5 + 14.4H_{21} + 10.1T_{47}$	ν (CC) (ph), δ (CC(ph)C), τ (CC) (ph)
		536.2	$24.1W_{42} + 57.5T_{47}$	ω (CH) (ph), τ (CC) (ph)
506.9	502.0	523.2	$9.6K_5 + 8.9W_{42} + 27.7T_{47}$	ν (CC) (ph), ω (CH), τ (CC) (ph)
480.7		485.4	$25.9H_{28} + 11.8H_{35} + 19.3T_{47}$	δ (CCO)(COOH), δ (COH), τ (CC) (ph)
476.0		475.9	$27.2H_{27} + 12.8H_{28} + 21.2T_{47}$	δ (CCO)(COOH), τ (CC) (ph)
		456.5	$12.5H_{27} + 60.1H_{35}$	δ (CCO)(COOH), δ (COH)
		438.4	$18.4K_1 + 14.9K_5 + 14.9H_{20} + 11.0H_{21}$	ν (Pd-S), ν (CC) (ph), δ (CCC)
432.2	426.4	432.1	$15.7K_1 + 17.6K_5 + 17.8H_{20} + 9.3H_{21}$	ν (Pd-S), ν (CC) (ph), δ (CCH)
403.3		404.3	$14.9K_1 + 24.1K_4 + 15.8K_5 + 11.1H_{19}$	ν (Pd-S), ν (CC) (ph), ν (CC)
		401.6	$18.8K_1 + 24.3K_4 + 14.1K_5 + 10.9H_{19}$	ν (Pd-S), ν (CC) (ph), ν (CC)

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394.2		388.1	$16.6H_{31} + 10.6T_{47}$	δ (CCO), τ (CC) (ph)
336.2	331.7	331.3	$14.5H_{26} + 10.9T_{44} + 9.9T_{43}$	δ (CCS), τ (CN), τ (CC)
321.1		318.9	$78.9H_{24} + 10.4T_{43} + 9.0T_{46}$	δ (CNC), τ (CC) (ph), τ (ph-C)
		312.7	$11.0K_1 + 10.7H_{25} + 9.0T_{44} + 18.6T_{46}$	ν (Pd-S), δ (CCC), τ (CC) (ph)
		306.7	$20.1H_{24} + 9.1H_{26}$	δ (CNC), δ (CCS)
304.9	301.0	302.8	$15.2K_1 + 14.8K_2 + 20.0H_{26} + 9.4H_{24}$	ν (Pd-S), ν (Pd-Cl), δ (CCS)
		280.0	$40.0K_2 + 6.7T_{43}$	ν (Pd-Cl)
272.1		272.7	$34.1K_2 + 11.8T_{43}$	ν (Pd-Cl), τ (CC)
		259.3	$11.8H_{26} + 17.8H_{36} + 19.6T_{49} + 20.2T_{51}$	δ (CCS), δ (CSC), τ (CS), τ (CC) (Et)
255.1		255.8	$23.6K_2 + 14.9K_6$	ν (Pd-Cl), ν (ph-C)
		252.6	$13.8K_2 + 18.3K_6 + 11.8H_{23} + 11.5H_{30}$	ν(Pd-Cl), ν (ph-C), δ (CCN), δ(NCO)
220.0		216.4	$42.1T_{43}$	τ (CC)
		207.7	$16.7H_{24} + 10.3H_{32} + 45.3T_{43}$	δ (CNC), δ (CNH), τ (CC)
		199.9	$19.1K_1 + 20.8K_2$	ν (Pd-S), ν (Pd-Cl)
		196.3	$12.2K_1 + 11.4H_{20}$	ν (Pd-S), δ (CCS)
		183.0	$31.7H_{36} + 8.6T_{47}$	δ (CSC), τ (CC) (ph)
		175.7	$14.4H_{37} + 8.3T_{45}$	δ (CSPd), τ (CN)
146.2	155.1	143.3	$14.0H_{39} + 18.1H_{41} + 16.4T_{47} + 17.2T_{48}$	δ (SPdCl), δ (ClPdCl), τ (CC) (ph), τ (CS)
123.1		123.9	$25.5H_{36} + 18.4H_{38} + 20.2H_{39} + 15.6T_{50}$	δ (CSC), δ (SPdCl), τ (SPd)
		121.2	$26.0H_{38} + 30.6H_{41} + 9.6T_{48}$	δ (SPdCl), δ (ClPdCl), τ (SC(ph))
		115.4	$18.8H_{38} + 18.0H_{39} + 10.6T_{47} + 27.8T_{48}$	δ (SPdCl), τ (CC) (ph),τ (CS)

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observed ones is about 2.53 cm^{-1}, and the maximum deviation is 16.00 cm^{-1}.

DISCUSSION

The observed and calculated frequencies with their assignments are shown in Table 3. The frequencies above 2900 cm^{-1} are dominated by a single vibration mode (its contribution to PED is higher than 99%), while some frequencies below 1800 cm^{-1} are attributed to coupling of several vibration modes.

The complex shows a broad band at 3554 cm^{-1} that is attributed to the stretching vibration mode of O-H.

The aromatic C-H bonds stretching vibration mode of the ligand appear at 3067 cm^{-1} in IR. The bands in region 2930–2970 cm^{-1} are assigned to the symmetrical and asymmetrical stretching vibration mode of C-H (CH_2). These assignments agree with the C-H stretching mode in comparable molecules[13].

The bands around 3368 cm^{-1} in IR spectra are assigned stretching of N-H. The C-N-H bending mode is found to contribute at around 1530 and 1260 cm^{-1}, the former is a coupled vibration of ν(C-C) and ν(C=O), while the latter is a coupled vibration of ν(C-C)(ph) and δ(C-C-C)(ph).

The 1727–1746 cm^{-1} band is a coupled vibration having a major contribution from ν(C-O)(COOH). The 1460 cm^{-1} frequency is a coupled vibration of ν(C=O)(COOH) and δ(OCO).

The C=O stretching mode is attribute to the bands of 1660 and 1530 cm^{-1} frequencies. The former is significantly coupled with C-C, while the latter with C-C stretching and C-N-H bending. These assignments agree well with similar assignment made in related compounds[15,16]. The above bands of the ligand are not very much affected by the coordination.

The vibrations including the Pd occur below 430 cm^{-1} and the most bands are attributed to the coupling of several vibration modes. The FIR active bands 430 and 403 cm^{-1} and Raman active band 426 cm^{-1} are coupled vibrations of Pd-S and C-C (ph) stretching vibration mode with C-C bending mode or C-S stretching vibration mode.

The Pd-Cl stretching mode is attribute to the 255 and 272 cm^{-1} frequencies, the former is coupled with C-C (ph) stretching, the latter with C-C (ph) twisting.

The force constants listed in Table 2 are same as or close to the corresponding complexes[11–14]. It shows the reliability of the final force constants. The nature of bands in the metal complex can be further understood from the final constants.

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In spite of large molecular weight and complicate structure of the title compound, the small average deviation of 2.53 cm^{-1} between the calculated and observed frequencies indicates that the using a modified Urey-Bradley force field and introducing appropriate set of internal coordinates and corresponding rotational force constants makes the NCA successful.

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Received August 1, 1999
Accepted June 12, 2001

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