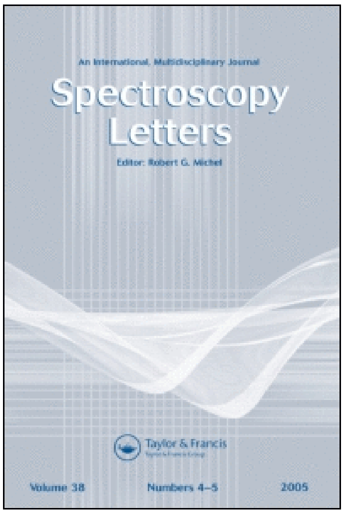

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Vibrational Spectra and Normal Coordinate Analysis for (*S*-Glutathionato) (2,2':6',2'-Terpyridine) Platinum(Ii) Chloride, [Pt(Trpy)Gs]Cl

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VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS FOR (*S*-GLUTATHIONATO) (2,2':6',2"-TERPYRIDINE) PLATINUM(II) CHLORIDE, [PT(TRPY)GS]CL

KEY WORDS: IR spectra, normal coordinate analysis, vibrational assignment

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ABSTRACT

The normal coordinate analysis of [Pt(trpy)GS]Cl (where trpy=2,2':6',2"terpyridine, GS= Glutathionato) has been carried out by using Urey-Bradley force field. According to the molecular structure, 222 internal coordinates were established and 162 theoretical vibrational frequencies agree well with the observed values with the average difference 3.44 cm^{-1} and the maximum deviation 15.1 cm^{-1}.

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INTRODUCTION

Study of platinum (II) complexes with biological important molecules is of considerable interest because of its carcinostatic effect and toxic side-effect [1-4]. Platinum (II) is a 'soft' metal that will be suitable for formation of stable complexes with sulfur-containing amino acids, peptides and proteins. The general idea accepted is that the nephrotoxicity caused by Pt (II) complexes is associated with interaction of it with sulfur-containing peptides and proteins. The interaction of glutathione(GSH) with Pt (II) complexes is of interest, because GSH is the most abundant non-protein thiol in cell. Recently, [Pt(trpy)GS]Cl (trpy=terpyridine) was synthesized and its conformation was studied by COSEY and NOSEY ^{1}H NMR spectra. In this article, we carried out the vibration study for this complex. The normal coordinate analysis (NCA) was made by using a modified Urey-Bradldey force field for the first time, inspite of its large number of atoms and low symmetry. The calculations were refined on the basis of the IR, Raman and FIR spectra.

EXPERIMENTAL

The title compounds [Pt(trpy)GS]Cl was synthesized as described in reference[5]. Its molecular mass was measured by an LCQ electrospray mass spectrometer (ESMS, Finnigan) to be 733 with isotopic peeks separated by 1.0m/z unit; calculated value for $[Pt(trpy)GS]^+$ is 733. Infrared and far-infrared spectra were obtained on Nicolet Fourier transform IR 170-SX spectrometer at room temperature. The KBr pellet technique was used for IR in the 400 ~ 4000 cm^{-1} region as shown in FIG.1, and Nujol mulls technique with polyethylene plates was used for FIR in the 100 ~ 500 cm^{-1} region, as shown in FIG.2. The FIG.3 shows the Raman spectroscopy in the region 400 ~ 4000 cm^{-1}, which was measured on Spex Raman spectrometer model 1403. The excitation line of the Ar^+ laser is 4880Å with an output power of 100mw. The sample was pressed as a disk in a stainless steel cell.

NORMAL COORDINATE ANALYSIS

Since the single crystal of [Pt(trpy)GS]Cl has not been obtained yet, we optimized the conformation of $[Pt(trpy)GS]^+$ by MM$^+$ program of molecular mechanics force field in Hyperchem.

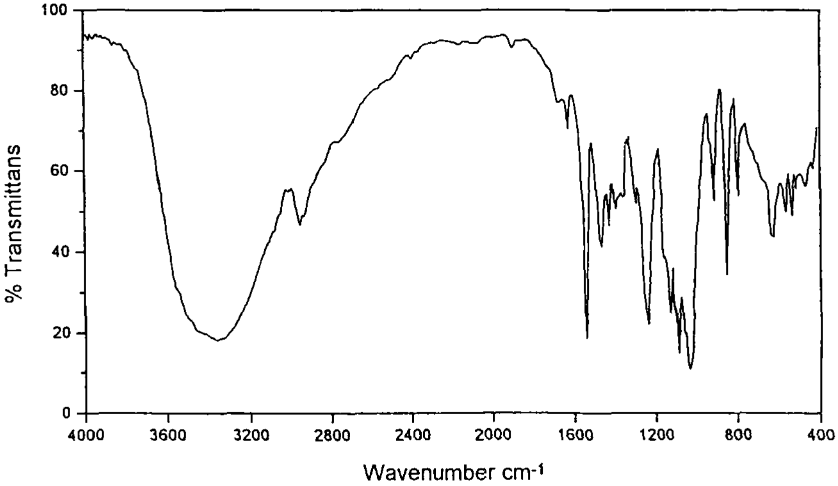

FIG. 1. The IR spectrum of [Pt(trpy)GS]Cl.

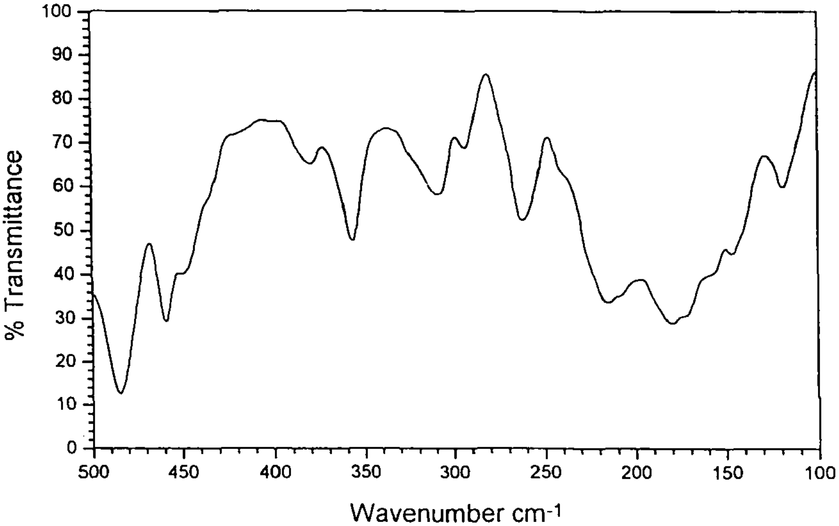

FIG. 2. The far-IR spectrum of [Pt(trpy)GS]Cl.

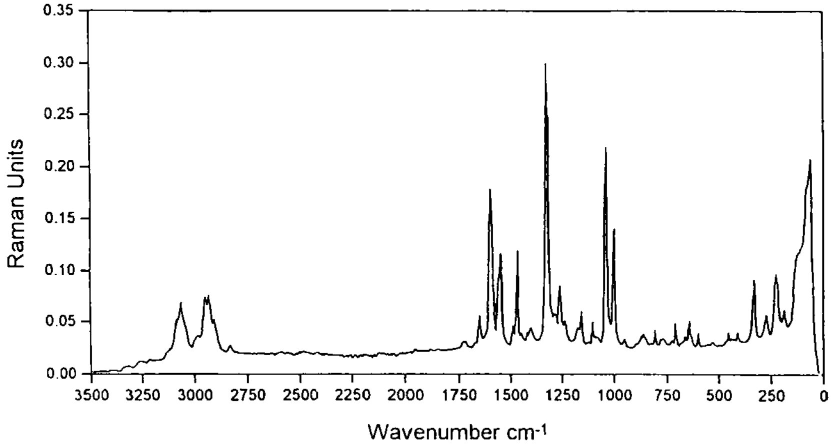

FIG. 3. The Raman spectrum of [Pt(trpy)GS]Cl.

The initial structural parameters of GS fragment were set up using data-base in Hyperchem. The structure parameters of Pt(trpy) fragment were taken from $[\{Pt(trpy)\}_2Can](ClO_4)_3{\cdot}5.5H_2O$[6], and were fixed during optimizing. The optimized bond lengths and bond angles are given in TABLE1. The FIG.4 shows the molecular structure of the title complex. As shown in FIG.4, the molecular has C_1 point group symmetry. The Pt (II) is coordinated by sulphur atom and trpy nearly in a plane. The GS fragment erects up the plane. There is hydrogen bond between the hydrogen atom on N_5 and atom O_6 as well as O_2, the distance are 3.13Å and 2.57Å; The angles of $N_5 — H \cdots O_2$ and $N_5 — H \cdots O_6$ are 160.6° and 101.2° respectively. The optimized molecular conformation is very similar to that obtained by ^1H NMR [5].

The calculation was performed on EC–486 PC using CART, GMAT and FPERT programs provided by National Research Council of Canada[7]. 222 internal coordinates were used as shown in Fig.5, 69 of which were attributed to stretching (ν), 121 to bending (δ), 20 to wagging out of plane (ω) and 12 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[7]. A modified Urey–Bradley force field was used in the calculation.

TABLE 1. Structural Parameters for [Pt(trpy)GS]$^+$

Atoms	Distance (Å)	Atoms	Angle (deg)	Atoms	Angle (deg)
$Pt - N_1$	2.129	$N_1 - Pt - N_2$	79.0	$C_6 - N_2 - C_{10}$	125.5
$Pt - N_2$	1.964	$N_2 - Pt - N_3$	84.0	$C_7 - C_8 - C_9$	120.0
$Pt - S$	2.320	$N_1 - Pt - S$	100.9	$C_7 - C_6 - N_2$	123.5
$N_1 - C_1$	1.296	$N_3 - Pt - S$	96.2	$C_9 - C_{10} - N_2$	110.4
$C_1 - C_2$	1.351	$C_1 - N_1 - Pt$	128.8	$C_{16} - S - Pt$	95.6
$C_2 - C_3$	1.445	$C_{15} - N_3 - Pt$	127.8	$C_{17} - C_{16} - S$	113.7
$C_3 - C_4$	1.383	$N_1 - C_1 - C_2$	123.2	$C_{16} - C_{17} - N_4$	111.7
$C_4 - C_5$	1.379	$N_3 - C_{15} - C_{14}$	121.1	$N_4 - C_{17} - C_{23}$	110.6
$C_5 - N_1$	1.382	$C_1 - C_2 - C_3$	120.7	$C_{16} - C_{17} - C_{23}$	109.0
$C_5 - C_6$	1.487	$C_{15} - C_{14} - C_{13}$	120.2	$C_{17} - C_{23} - O_4$	117.6
$C_6 - N_2$	1.293	$C_2 - C_3 - C_4$	113.9	$C_{17} - C_{23} - N_6$	121.3
$C_6 - C_7$	1.132	$C_{14} - C_{13} - C_{12}$	119.1	$N_6 - C_{23} - O_4$	120.1
$C_7 - C_8$	1.347	$C_3 - C_4 - C_5$	122.3	$C_{23} - N_6 - C_{24}$	123.0
$S - C_{16}$	1.795	$C_{13} - C_{12} - C_{11}$	121.0	$N_6 - C_{24} - C_{25}$	110.3
$C_{16} - C_{17}$	1.552	$C_4 - C_5 - N_1$	119.4	$C_{24} - C_{25} - O_5$	119.0
$C_{17} - N_4$	1.458	$C_{15} - N_3 - Pt$	119.0	$C_{24} - C_{25} - O_6$	119.1
$N_4 - C_{18}$	1.417	$C_1 - N_1 - C_5$	118.4	$O_5 - C_{25} - O_6$	118.1
$C_{18} - O_3$	1.394	$C_{15} - N_3 - C_{11}$	119.2	$C_{17} - N_4 - C_{18}$	121.5
$C_{18} - C_{19}$	1.509	$C_4 - C_5 - C_6$	125.6	$N_4 - C_{18} - O_3$	120.6
$C_{19} - C_{20}$	2.163	$C_{12} - C_{11} - C_{10}$	124.9	$N_4 - C_{18} - C_{19}$	120.1
$C_{20} - C_{21}$	1.564	$C_5 - N_1 - Pt$	112.0	$C_{19} - C_{18} - O_3$	119.2
$C_{21} - N_5$	1.518	$C_{11} - N_3 - Pt$	112.9	$C_{18} - C_{19} - C_{20}$	112.3
$C_{21} - C_{22}$	1.525	$N_1 - C_5 - C_6$	112.7	$C_{19} - C_{20} - C_{21}$	114.2
$C_{22} - O_1$	1.394	$N_3 - C_{11} - C_{10}$	115.7	$C_{20} - C_{21} - N_5$	111.4
$C_{22} - O_2$	1.393	$C_5 - C_6 - C_7$	115.0	$C_{20} - C_{21} - C_{22}$	109.9
$C_{17} - C_{23}$	1.515	$C_{11} - C_{10} - C_9$	136.6	$C_{22} - C_{21} - N_5$	113.2
$C_{23} - O_4$	1.394	$C_5 - C_6 - N_2$	116.2	$C_{21} - C_{22} - O_1$	119.4
$C_{23} - N_6$	1.419	$C_{11} - C_{10} - N_2$	112.3	$C_{21} - C_{22} - O_2$	119.3
$N_6 - C_{24}$	1.455	$C_6 - N_2 - Pt$	119.1	$O_1 - C_{22} - O_2$	116.7
$C_{24} - C_{25}$	1.505	$C_{10} - N_2 - Pt$	115.0		
$C_{25} - O_5$	1.392	$C_6 - C_7 - C_8$	118.3		
$C_{25} - O_6$	1.393	$C_{10} - C_9 - C_8$	118.7		

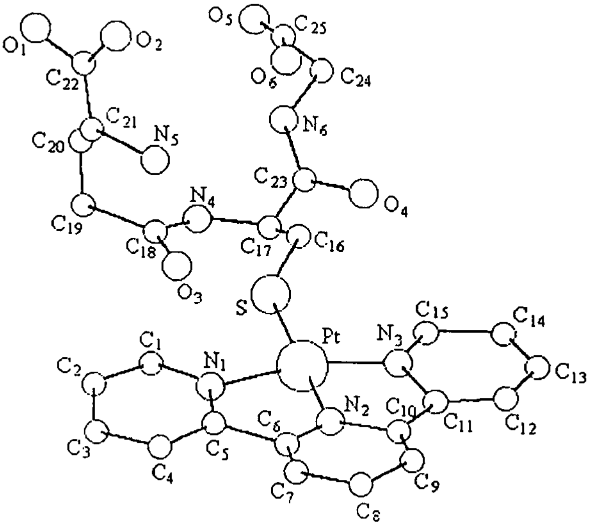

FIG. 4. The molecular structure of [Pt(trpy)GS]Cl.

The initial values of the force constants were collected and transferred from related molecular[10, 12, 13], and refined in accordance with the position of bonds in the IR, Raman and FIR spectra. The final values of force constants are shown in TABLE 3. The observed and the calculated frequencies together with the percentages of potential energy distribution (PED) are presented in TABLE 3. The assignment of frequencies in TABLE 3 considers predominant contribution of the internal coordinates. The calculated fundamentals agree well with the observed ones. The average deviation of the calculated frequencies from the observed ones is about 3.44 cm^{-1}, and the maximum deviation is 15.1 cm^{-1}

DISCUSSION

As shown in TABLE 3, the frequencies above 2800cm^{-1} are dominated by a single vibratinal mode (its contribution to PED is higher than 90%), while the frequencies in the region 2800~600cm^{-1} are attributed to coupling of several vibrational modes.

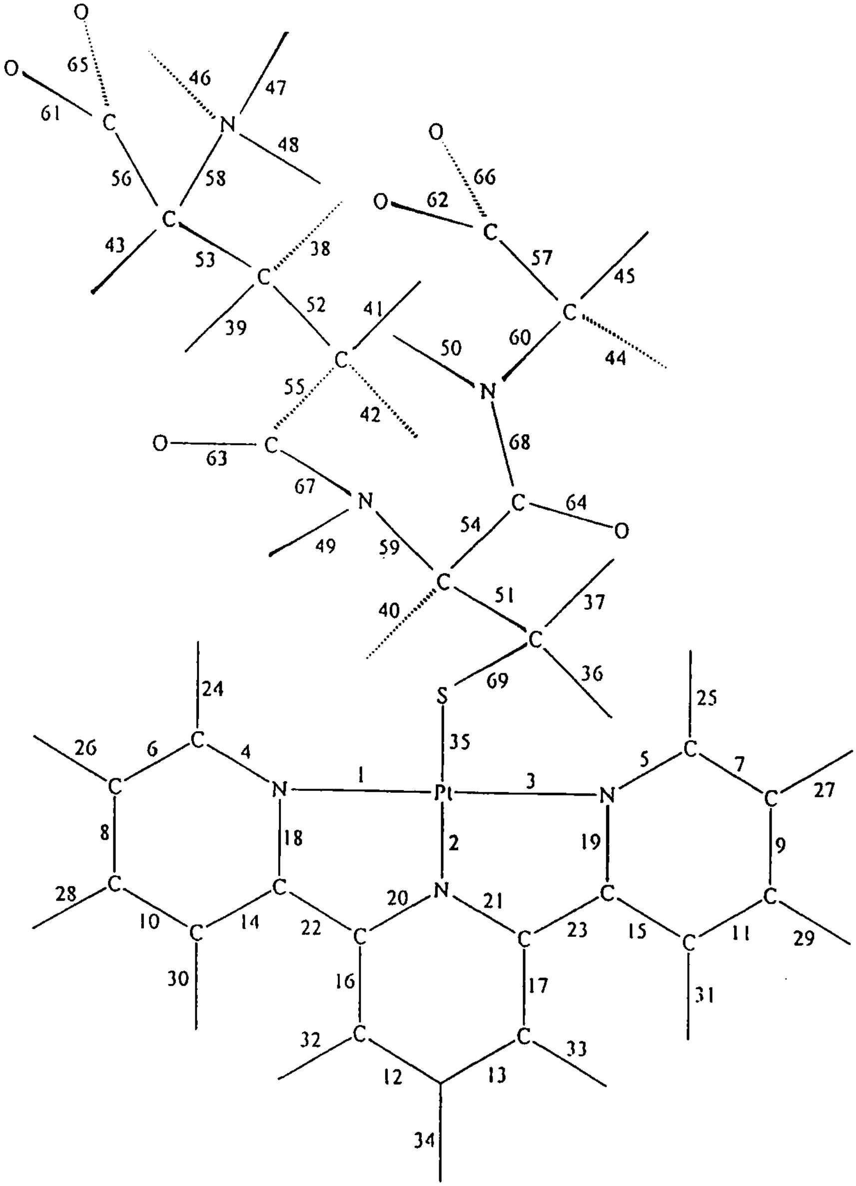

FIG. 5. Numerical identification of internal coordinates for [Pt(trpy)GS]$^{+}$.

(continued)

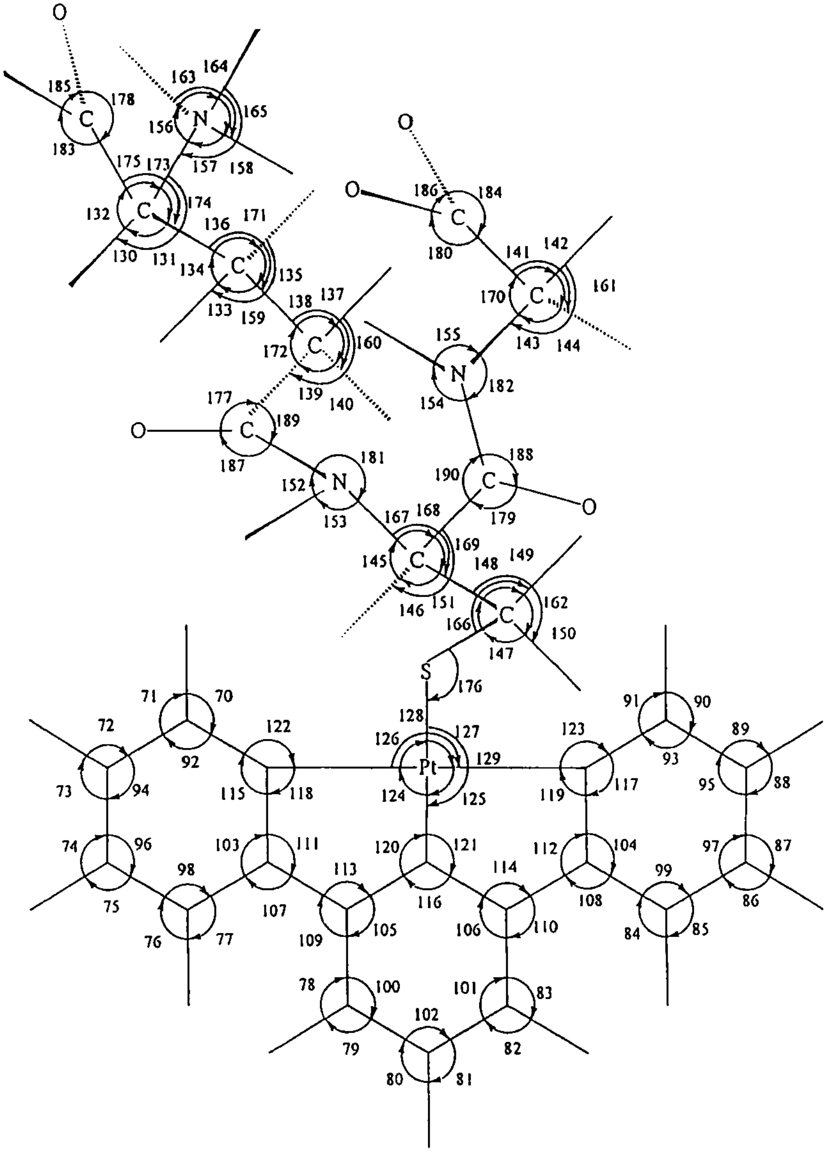

FIG. 5. (continued)

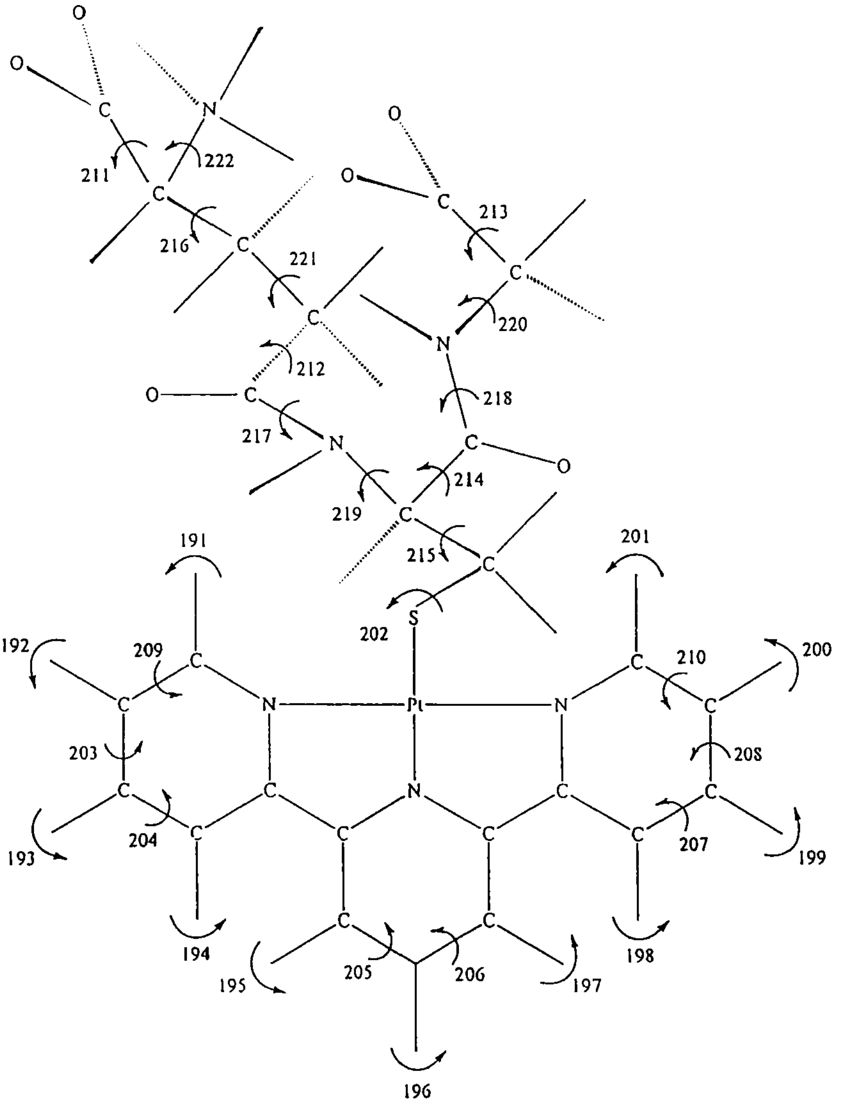

FIG. 5. (continued)

(continued)

TABLE 2. Force Constants for $[Pt(trpy)GS]^+$

Symbol*	Coordinates involved	Value	Symbol	Coordinates involved	Value
K_1	$Pt-N$	1.971	H_{26}	$\angle CNC$ (trpy)	0.990
K_2	N_1-C_1, N_3-C_{15}	6.073	H_{27}	$\angle PtN_1C_5$, $\angle PtN_3C_{11}$	0.851
K_3	C_1-C_2, $C_{15}-C_{14}$	6.062	H_{28}	$\angle PtN_2C_6$, $\angle PtN_2C_{10}$	0.394
K_4	C_2-C_3, $C_{14}-C_{13}$, C_3-C_4,	6.041	H_{29}	$\angle PtN_1C_1$, $\angle PtN_3C_{15}$	0.297
	$C_{13}-C_{12}$, C_7-C_8, C_9-C_8		H_{30}	$\angle N_1PtN_2$, $\angle N_3PtN_2$	0.202
K_5	C_4-C_5, C_6-C_7,	6.023	H_{31}	$\angle N_1PtS$, $\angle N_3PtS$	0.152
	$C_{10}-C_9$, $C_{11}-C_{12}$		H_{32}	$\angle N_2PtS$	0.051
K_6	N_1-C_5, N_3-C_{11},	6.171	H_{33}	$\angle N_3PtS$	0.051
	N_2-C_{20}, N_2-C_{21}		H_{34}	$\angle CCH$, $\angle NCH$, $\angle SCH$ (GS)	0.443
K_7	C_5-C_6, $C_{10}-C_{11}$	6.011	H_{35}	$\angle CNH$ (GS)	0.335
K_8	$C-H$ (trpy)	5.106	H_{36}	$\angle HCH$ (GS)	0.532
K_9	$Pt-S$	1.811	H_{37}	$\angle HNH$ (GS)	0.601
K_{10}	$C_{16}-H$, $C_{20}-H$	4.648	H_{38}	$\angle CCC$, $\angle NCC$, $\angle SCC$ (GS)	0.302
K_{11}	$C-H$ (GS)	4.705	H_{39}	$\angle CSPt$	0.467
K_{12}	$N-H$ (GS)	6.014		$\angle C_{19}C_{18}O_3$, $\angle C_{17}C_{23}O_4$,	
K_{13}	$C_{16}-C_{17}$, $C_{19}-C_{20}$, $C_{20}-C_{21}$	3.853	H_{40}	$\angle C_{21}C_{22}O_2$, $\angle C_{24}C_{25}O_5$	1.242
K_{14}	$C_{17}-C_{23}$, $C_{18}-C_{19}$,	3.627	H_{41}	$\angle CNC$ (GS)	1.090
	$C_{21}-C_{22}$, $C_{24}-C_{25}$		H_{42}	$\angle C_{21}C_{22}O_1$, $\angle C_{24}C_{25}O_6$	1.091
K_{15}	$C_{21}-N_5$, $C_{17}-N_4$, $C_{24}-N_6$	4.525	H_{43}	$\angle OCO$ (GS)	1.281
K_{16}	$C_{22}-O_2$, $C_{25}-O_5$	7.644	H_{44}	$\angle NCO$ (GS)	1.670
K_{17}	$C_{18}-O_3$, $C_{23}-O_4$	7.302	H_{45}	$\angle C_{19}C_{18}N_4$, $\angle C_{17}C_{23}N_6$	1.102
K_{18}	$C_{22}-O_1$, $C_{25}-O_6$	7.111	W_{46}	$\angle H{-}CC{-}C$, $\angle H{-}CC{-}N$ (trpy)	0.308
K_{19}	$C_{18}-N_4$, $C_{23}-N_6$	4.219	W_{47}	$\angle S{-}PtN_2{-}N_1$	0.112
K_{20}	$C_{16}-S$	2.850	T_{48}	$\angle CC{-}C{-}C$ (trpy)	0.161
H_{21}	$\angle CCH$ (trpy)	0.451	T_{49}	$\angle NC{-}C{-}C$ (trpy)	0.472
H_{22}	$\angle C_2C_1N_1$, $\angle C_{14}C_{15}C_{13}$, $\angle C_1C_2C_3$	1.062	T_{50}	$\angle C_{20}C_{21}{-}C_{22}{-}O_1$, $\angle C_{20}C_{19}{-}C_{18}{-}O_3$	0.109
	$\angle C_{15}C_{14}C_{13}$, $\angle C_2C_3C_4$, $\angle C_3C_4C_5$			$\angle C_{16}C_{17}{-}C_{23}{-}O_4$, $\angle N_6C_{24}{-}C_{25}{-}O_5$	
	$\angle C_6C_7C_8$, $\angle C_7C_8C_9$, $\angle C_8C_9C_{10}$		T_{51}	$\angle C_{23}C_{17}{-}C_{16}{-}S$, $\angle C_{19}C_{20}{-}C_{21}{-}C_{22}$	0.191
	$\angle C_{11}C_{12}C_{13}$, $\angle C_{12}C_{13}C_{14}$		T_{52}	$\angle O_3C_{18}{-}N_4{-}C_{17}$, $\angle O_4C_{23}{-}N_6{-}C_{24}$	0.132
H_{23}	$\angle N_1C_5C_4$, $\angle N_3C_{11}C_{12}$, $\angle N_2C_6C_7$	1.159	T_{53}	$\angle C_{18}N_4{-}C_{17}{-}C_{16}$, $\angle C_{23}N_6{-}C_{24}{-}C_{25}$	0.121
	$\angle N_2C_{10}C_9$		T_{54}	$\angle C_{18}C_{19}{-}C_{20}{-}C_{21}$	0.120
H_{24}	$\angle C_4C_5C_6$, $\angle C_{12}C_{11}C_{10}$, $\angle C_5C_6C_7$	1.632	T_{55}	$\angle C_{20}C_{21}{-}N_5{-}H$	0.091
	$\angle C_9C_{10}C_{11}$				
H_{25}	$\angle N_1C_5C_6$, $\angle N_2C_6C_5$, $\angle N_2C_{10}C_{11}$	1.552			
	$\angle N_3C_{11}C_{10}$				

* 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).

The broad bands around 3300cm^{-1} in IR spectra are assigned to the stretching vibrational modes of NH_3^+ and NH groups of GS. The Aromatic C–H stretching vibrational modes of trpy appear at 3060cm^{-1} in Raman spectroscopy, which are 3~14cm^{-1} higher than free trpy[19]. The bands in region 2890~2970cm^{-1} are assigned to stretching vibrational modes of CH_2 and CH group of GS. The bands in the region 500~1650cm^{-1} are assigned to the scissoring, wagging, twisting and rocking vibrational modes of NH_3^+, CH_2 group of GS, stretching, rocking and wagging vibration of COO^- group, C–C, C–N and C–S stretching, trpy ring stretching and the coupling of these vibrational modes respectively. The above results are consistent with the empirical assignments of these vibrational modes in the spectra of trpy complexes[6, 10,18,19], GSH[9] and some amino acid complexes[12, 13, 20].

The vibrations including the Pt (II) occur below 700cm^{-1} and the most bands are attributed to the coupling of several vibrational modes. On the basis of predominant potential energy distribution, the FIR active band 357cm^{-1} and Raman active band 353cm^{-1} are assigned to Pt–S stretching vibrational mode, which is same as or very close to $[Pt(trpy)(SCH_2CH_2OH)]NO_3$ (357cm^{-1}) and $[Pt(trpy)(SCH_2CH_3)]PF_6$ (355 cm^{-1})[18].

R. J. Mureinik and M.Bidani assigned the 460cm^{-1} band to Pt–N stretching vibrational modes and 520cm^{-1} band to N–Pt–N asymmetric stretching vibrational modes[14]. In our research, the FIR active band at 459.5cm^{-1} is assigned to the coupling of Pt–N stretching and trpy ring stretching and bending modes. But the percentage of Pt–N stretching modes in 459.5cm^{-1} is very small. Its contribution to the PED is only 3.6%, while the trpy ring stretching and bending vibrational modes to PED are 12.0% and 20.9%.

We have tried to adjust the Pt–N force constants to reproduce the 520cm^{-1} band, but it reaches an unreasonable high value because of its low contribution to PED. The Pt–N stretching mode may be around 220±10cm^{-1} according to its predominate contribution to PED, and this is consistent with the assignment of Pt–N stretching mode in Pt $(amp)Cl_2$. (where amp=2–aminomethylpyridine)[15]

The force constants listed in TABLE 2 are same as or close to those for the corresponding complexes of $Ru(trpy)_2$[10], L-asparagine[20], glutamic acid[12], and acetamide[13], these results show the

TABLE 3. Calculated and Observed Wavenumber and Percent PED for [Pt(trpy)GS]$^+$

IR (cm^{-1}) obs.	Raman (cm^{-1}) obs.	Calculated (cm^{-1})	Potential energy distribution (%)	Band assignment
		3368.2	$99.8K_{12}$	ν(NH)
3319.2		3315.4	$99.5K_{12}$	ν(NH)
		3302.0	$99.5K_{12}$	$\nu_a(NH_3^+)$
3297.8		3301.9	$99.5K_{12}$	$\nu_a(NH_3^+)$
		3209.2	$99.9K_{12}$	$\nu_s(NH_3^+)$
		3070.6	$98.5K_8$	ν(CH) (trpy)
		3068.9	$98.7K_8$	ν(CH) (trpy)
		3068.3	$98.8K_8$	ν(CH) (trpy)
		3067.8	$98.7K_8$	ν(CH) (trpy)
		3067.1	$98.8K_8$	ν(CH) (trpy)
		3066.9	$98.8K_8$	ν(CH) (trpy)
	3065.8	3066.0	$98.9K_8$	ν(CH) (trpy)
		3065.3	$99.0K_8$	ν(CH) (trpy)
		3065.2	$99.0K_8$	ν(CH) (trpy)
		3064.3	$99.1K_8$	ν(CH) (trpy)
		3064.0	$99.1K_8$	ν(CH) (trpy)
		2973.9	$99.4K_{11}$	ν(CH) (GS)
		2972.4	$99.1K_{11}$	ν(CH) (GS)
	2950.8	2952.3	$97.3K_{10}$	ν(CH) (GS)
		2937.6	$98.9K_{11}$	ν(CH) (GS)
	2932.8	2935.7	$97.6K_{11}$	ν(CH) (GS)
2912.1		2917.0	$99.0K_{10}$	ν(CH) (GS)
	2908.7	2901.9	$98.4K_{11}$	ν(CH) (GS)
2893.1		2901.5	$99.4K_{11}$	ν(CH) (GS)
		2884.6	$98.4K_{10}$	ν(CH) (GS)
		1857.2	$8.8K_5 + 19.9K_6 + 19.9K_7 + 9.6H_{24}$	ν(CC) (trpy)
		1841.2	$35.7K_{10} + 33.8K_{13} + 21.3H_{35}$	$\nu(CH_2)$, $\delta(CH_2)$, ν(CC) (GS)
		1812.1	$24.1K_5 + 30.7K_7 + 9.0H_{21}$	ν(CC) (trpy)
		1791.1	$29.6K_5 + 23.0K_6 + 12.5H_{24} + 14.6H_{25}$	ν(CC) (trpy)
		1739.1	$21.5K_5 + 28.6K_6 + 15.5H_{24}$	ν(CC) (trpy)
		1687.5	$37.7K_4 + 12.6K_5 + 20.3H_{21}$	ν(CC), δ(CCC) (trpy)
		1669.7	$30.4K_3 + 36.6K_4 + 18.9H_{21}$	ν(CC), δ(CH) (trpy)
		1668.6	$29.4K_3 + 36.5K_4 + 17.8H_{21}$	ν(CC), δ(CH) (trpy)
	1658.7	1663.8	$93.8H_{38}$	$\delta_a(NH_3^+)$
1649.5		1646.4	$95.2H_{38}$	$\delta_a(NH_3^+)$

TABLE 3. (Continued)

IR (cm^{-1}) obs.	Raman (cm^{-1}) obs.	Calculated (cm^{-1})	Potential energy distribution (%)	Band assignment
		1639.3	$13.0K_2 + 23.2K_4 + 24.8H_{21}$	ν(CC), δ(CH) (trpy)
		1621.0	$48.8K_{16} + 36.6K_{18}$	ν(COO$^-$)
	1606.7	1607.9	$48.3K_{16} + 36.0K_{18}$	ν(COO$^-$)
1600.0		1596.6	$16.1K_4 + 21.6K_5 + 41.1K_6$	ν(CC), (trpy)
		1574.3	$10.3K_{14} + 58.4K_{12} + 8.7H_{46}$	ν(CC), ν(NH) (GS)
		1564.6	$61.6K_{17}$	ν(C=O)
	1557.5	1559.5	$9.1K_2 + 26.2K_4 + 10.1K_7$	ν(CC)
		1537.4	$14.4K_4 + 12.8K_5 + 24.0K_6 + 17.6H_{21}$	ν(CC), δ(CH) (trpy)
1513.4		1510.8	$20.5K_4 + 46.9H_{21}$	ν(CC), δ(CH) (trpy)
	1479.3	1464.2	$19.3K_{14} + 19.9K_{15} + 15.9K_{19}$	ν(CC), ν(CN) (GS)
		1452.5	$14.7K_4 + 10.8K_5 + 10.2K_6 + 50.1H_{21}$	ν(CC), δ(CH) (trpy)
		1448.8	$32.3K_{14} + 14.7K_{16} + 20.8K_{18}$	ν(CC), ν(C=O) (GS)
1440.1		1436.6	$14.4K_{14} + 10.2K_{15} + 26.4K_{19} + 13.5H_{37}$	ν(CC), ν(CN), δ(CH$_2$) (GS)
		1433.7	$13.7K_{14} + 49.8H_{37}$	ν(CC), δ(CH$_2$) (GS)
		1420.9	$10.1K_6 + 55.7H_{21}$	ν(CC), δ(CH) (trpy)
	1413.5	1413.9	$10.9K_{13} + 15.3H_{35} + 68.5H_{37}$	δ(CH$_2$) (GS)
		1407.8	$9.3K_6 + 8.6K_5 + 56.7H_{21}$	ν(CC), δ(CH) (trpy)
1401.2		1396.8	$10.2K_{13} + 14.5H_{35} + 64.3H_{37}$	δ(CH$_2$) (GS)
		1374.4	$13.9K_{14} + 14.6K_{19} + 29.4H_{37}$	ν(CC), ν(CN), δ(CH$_2$) (GS)
1371.5		1370.5	$19.4H_{35} + 67.6H_{37}$	δ(CH$_2$) (GS)
		1349.2	$23.9K_{13} + 11.2K_{15} + 26.6H_{35} + 23.0H_{37}$	ν(CC), ν(CN), δ(CH$_2$) (GS)
1335.7	1335.6	1336.2	$9.6K_4 + 9.0K_6 + 51.8H_{21}$	δ(CH) (trpy)
1309.2		1315.9	$89.7W_{47}$	ω (CH) (trpy)
		1294.6	$11.8K_7 + 67.9H_{21}$	ν(CC), δ(CH) (trpy)
1272.1	1277.0	1278.5	$29.5K_{15} + 24.8H_{35} + 10.2H_{36}$	ν(CC), ν(CN), δ(CH$_2$) (GS)
		1227.6	$13.6K_{14} + 15.4K_{15} + 36.6H_{35}$	ν(CC), ν(CN), δ(CH$_2$) (GS)
		1217.5	$10.3K_2 + 52.2H_{21}$	δ(CH) (trpy)
1212.5		1217.0	$11.8K_{14} + 14.1K_{15} + 40.7H_{35}$	ν(CC), ν(CN), δ(CH$_2$) (GS)
		1214.4	$58.6W_{47} + 11.2T_{49} + 20.0T_{50}$	ω (CH), τ(CC) (trpy)
		1199.3	$13.0K_2 + 55.7H_{21}$	ω (CH) (trpy)
	1174.9	1179.6	$61.3W_{47} + 27.5T_{50}$	ω (CH), τ(CC) (trpy)
		1154.1	$27.8H_{35} + 20.8H_{36} + 30.9H_{38}$	δ(CH$_2$), δ(NH$_3^+$) (GS)
1137.1		1139.1	$56.9H_{35}$	δ(CH$_2$), (GS)
		1130.0	$42.9H_{35} + 40.4H_{36}$	δ(CH$_2$), (GS)
	1121.6	1125.6	$39.4H_{21} + 19.2H_{22} + 10.5H_{23}$	δ(CH), δ(CCC) (trpy)

(continued)

TABLE 3. (Continued)

IR (cm^{-1}) obs.	Raman (cm^{-1}) obs.	Calculated (cm^{-1})	Potential energy distribution (%)	Band assignment
		1117.4	$67.8H_{21}$	δ (CH) (trpy)
		1106.0	$13.2K_4 + 71.7H_{21}$	ν (CC), δ (CH) (trpy)
1099.7		1103.4	$11.7K_4 + 60.5H_{21} + 11.4H_{22}$	δ (CC), δ (CH) (trpy)
		1089.2	$33.0H_{35} + 44.1H_{36}$	δ (CH_2) (GS)
		1079.9	$14.6K_4 + 47.2H_{21} + 16.1H_{22}$	δ (CCC), δ (CH) (trpy)
1065.9		1070.1	$46.9H_{35} + 32.4H_{36}$	δ (CH_2) (GS)
	1057.8	1063.2	$78.5H_{35}$	δ (CH_2) (GS)
		1042.0	$11.4K_3 + 19.4K_4 + 51.5H_{21}$	ν (CC), δ (CH) (trpy)
		1040.0	$10.9K_3 + 15.6K_4 + 47.0H_{21}$	ν (CC), δ (CH) (trpy)
		1035.8	$11.5K_5 + 9.8K_6 + 22.6H_{21} + 19.4H_{22}$	ν (CC), δ (CH) (trpy)
		1032.7	$86.3H_{35}$	δ (CH_2) (GS)
1015.1	1020.2	1022.9	$12.9K_5 + 12.4K_6 + 27.8H_{21} + 10.5H_{22}$	ν (CC), δ (CH) (trpy)
		1008.2	$23.4K_4 + 42.8H_{21}$	ν (CC), δ (CH) (trpy)
		1007.4	$95.7H_{35}$	δ (CH_2) (GS)
		996.2	$84.5H_{35}$	δ (CH_2) (GS)
		993.8	$92.6H_{35}$	δ (CH_2) (GS)
	970.6	970.4	$35.6K_4 + 10.3K_5 + 9.2K_6$	ν (CC) (trpy)
		962.3	$25.4K_{15} + 47.2H_{35}$	δ (CH_2), ν (CC) (GS)
		958.4	$90.3W_{47}$	ω (CH) (trpy)
		948.9	$24.0K_3 + 35.0K_4 + 18.4H_{21}$	ν (CC), δ (CH) (trpy)
		942.2	$21.8K_{15} + 60.9H_{35} + 9.8H_{36}$	δ (CH_2), ν (CC) (GS)
		932.8	$32.3K_{15} + 41.4H_{35}$	δ (CH_2), ν (CC) (GS)
		926.8	$82.7W_{47}$	ω (CH) (trpy)
		923.8	$14.9K_3 + 30.9K_4 + 24.8W_{47}$	ν (CC), ω (CH) (trpy)
894.7		892.3	$10.9K_4 + 62.5W_{47}$	ν (CC), ω (CH) (trpy)
	883.3	884.7	$27.7K_{13} + 51.0H_{35} + 9.0H_{36}$	δ (CH_2), ν (CC) (GS)
		855.9	$38.5K_{13} + 48.9H_{35}$	δ (CH_2), ν (CC) (GS)
	825.8	828.9	$9.3K_4 + 17.3K_5 + 17.9K_6 + 16.7H_{22}$	ν (CC), δ (CH) (trpy)
		821.7	$11.4K_{19} + 36.2H_{35} + 10.2H_{42}$	ν (CC), δ (CCC) (GS)
		815.7	$99.0W_{47}$	ω (CH) (trpy)
		812.9	$15.1K_{14} + 27.3H_{35} + 14.7H_{36}$	δ (CH_2), ν (CC) (GS)
		807.4	$91.7W_{47}$	ω (CH) (trpy)
778.4		776.5	$10.7K_{14} + 17.7K_{17} + 19.5K_{19} + 11.0H_{35} + 11.9H_{42}$	ν (CC), δ (CCC), ν (CN), δ (CCN) (GS)
		763.3	$38.8K_{14} + 17.8K_{16} + 17.2K_{18} + 11.7H_{35}$	ν (CC), ν (CO), δ (CCC), δ (C=O) (GS)

TABLE 3. (Continued)

IR (cm^{-1}) obs.	Raman (cm^{-1}) obs.	Calculated (cm^{-1})	Potential energy distribution (%)	Band assignment
		757.3	$13.9K_{14} + 53.4H_{36}$	ν(CC), δ(CH$_2$) (GS)
		747.7	$13.5K_{20} + 69.0H_{35}$	δ(CH$_2$) (GS)
		740.7	$97.4W_{47}$	ω(CH) (trpy)
		738.1	$98.7W_{47}$	ω(CH) (trpy)
	727.8	721.9	$19.5K_5 + 43.7H_{22}$	ν(CC), δ(CCC) (trpy)
		716.0	$53.2H_{35} + 15.6H_{36}$	δ(CH$_2$) (GS)
		701.5	$10.5K_1 + 37.5H_{22} + 9.1H_{24}$	δ(CC) (trpy)
		691.6	$9.1K_{14} + 17.6K_{19} + 38.6H_{35}$	ν(CC), ν(CN), δ(CH$_2$) (GS)
		686.7	$57.6K_{20} + 27.0H_{35}$	ν(CS), δ(CH$_2$) (GS)
		675.7	$40.1H_{22}$	δ(CCC) (trpy)
		675.1	$47.4H_{35} + 36.9H_{36}$	δ(CH$_2$) (GS)
660.7	658.4	658.3	$10.0H_{21} + 47.3H_{22}$	δ(CCC) (trpy)
		654.6	$15.0K_{13} + 12.6H_{35} + 45.9H_{36}$	ν(CC), δ(CH$_2$) (GS)
		639.9	$11.3K_6 + 10.4H_{21} + 49.0H_{22}$	ν(CC), δ(CCC) (trpy)
608.4		604.1	$18.2K_{14} + 15.3H_{35} + 19.8H_{45}$	ν(CC), δ(CH$_2$),δ(CCN) (GS)
		556.4	$18.6K_5 + 21.1H_{24} + 22.1H_{25}$	ν(CC), δ(CCC) (trpy)
548.2		548.1	$24.1K_{14} + 29.1H_{35}$	ν(CC), δ(CH$_2$) (GS)
		539.8	$11.9K_{14} + 15.9H_{35} + 13.2H_{41} + 10.5H_{44}$ $+12.1H_{45} + 12.0H_{46}$	ν(CC), δ(CH$_2$), δ(COO$^-$) (GS)
		533.7	$14.7K_{14} + 10.7H_{41} + 11.0H_{43} + 43.3H_{44}$	ν(CC), δ(COO$^-$) (GS)
517.7		532.0	$10.0K_{14} + 11.7H_{35} + 9.9H_{41} + 35.1H_{44}$	ν(CC), δ(COO$^-$) (GS)
484.8		480.5	$34.9W_{47} + 14.1T_{49} + 43.3T_{50}$	δ(CH), ω(CC) (trpy)
		466.7	$32.1W_{47} + 13.6T_{49} + 44.8T_{50}$	δ(CH), ω(CC) (trpy)
459.5		457.7	$3.6K_1 + 12.0K_5 + 20.9H_{25}$	ν(PtN), δ(CCC) (trpy)
449.4		454.5	$22.3H_{35} + 30.9H_{41} + 12.3H_{46}$	δ(CH$_2$), δ(COO$^-$) (GS)
	432.1	442.6	$28.3H_{35} + 30.5H_{41} + 28.1H_{43}$	δ(CH$_2$), δ(COO$^-$) (GS)
		435.7	$35.8H_{41} + 36.5H_{43}$	δ(COO$^-$)
		408.4	$10.6W_{47} + 67.1T_{49}$	ω(CC) (trpy)
380.0		378.6	$14.8H_{35} + 16.4H_{39} + 15.5H_{41} + 19.6H_{46}$	δ(CH$_2$), δ(CCC), δ(CCN) (GS)
357.3	353.1	359.8	$6.7K_1 + 37.5K_9 + 9.6H_{23} + 9.7T_{49}$	ν(PtN), δ(CCC) (trpy)
		355.3	$6.3K_1 + 12.7K_7 + 24.6K_9 + 14.0H_{23}$	ν(CC), δ(CCC) (trpy)
		336.9	$8.5K_1 + 8.2K_7 + 19.3H_{24} + 11.9T_{49}$	ν(CC), δ(CCC), ω(CC) (trpy)
		331.2	$20.9H_{35} + 29.0H_{39}$	δ(CH$_2$), δ(CCC), δ(CCN) (GS)
		324.5	$26.9H_{35} + 24.5H_{39}$	δ(CH$_2$), δ(CCC), δ(CCN) (GS)
		319.3	$43.2W_{48} + 33.7T_{49}$	ω (PtS), δ(CCC) (trpy)

(continued)

TABLE 3. (Continued)

IR (cm^{-1}) obs.	Raman (cm^{-1}) obs.	Calculated (cm^{-1})	Potential energy distribution (%)	Band assignment
		308.4	$15.0H_{35} + 31.9H_{39} + 12.7T_{53}$	$\delta(CH_2)$, $\delta(CCC)$ (GS)
309.6		297.3	$8.9K_1 + 25.8H_{24} + 10.0W_{48} + 16.9T_{49}$	$\delta(CCC)$ (GS)
294.1	295.3	285.4	$22.5H_{35} + 20.1H_{39}$	$\delta(CH_2)$, $\delta(CCC)$ (GS)
		279.2	$11.1H_{39} + 19.7H_{42}$	$\delta(CCC)$, $\delta(CNC)$ (GS)
		276.9	$47.9T_{49} + 10.2\ T_{50}$	$\delta(CCC)$ (trpy)
		271.5	$12.7H_{43} + 12.0H_{44} + 23.4T_{51} + 16.7T_{56}$	$\delta(COO^-)$, $\tau(NH_3^+)$, $\tau(COO^-)$
		267.0	$10.9H_{39} + 13.1T_{51}$	$\delta(CCC)$, $\tau(COO^-)$ (GS)
		266.2	$15.1H_{26} + 12.1H_{28} + 12.7H_{29}$	$\delta(CCC)$ (trpy)
262.9		254.9	$22.2W_{48} + 41.6T_{49} + 11.5T_{50}$	$\omega(CC)$, $\tau(CC)$ (trpy)
	248.3	238.3	$11.0H_{39} + 15.6T_{51}$	$\delta(CH_2)$, $\tau(COO^-)$ (GS)
		224.5	$50.1K_1 + 9.6H_{27}$	$\nu(PtN)$, $\delta(CCC)$ (trpy)
		222.6	$22.5K_1$	$\nu(PtN)$
		219.6	$13.5K_1 + 15.3H_{39} + 8.1T_{56}$	$\delta(CCC)$, $\tau(NH_3^+)$ (GS)
217.4		215.3	$17.5H_{39} + 12.4T_{51} + 14.8T_{56}$	$\delta(COO^-)$, $\tau(NH_3^+)$, $\tau(COO^-)$
	212.4	210.5	$10.6H_{39} + 17.3T_{51} + 19.7T_{53} + 21.8T_{54}$	$\delta(COO^-)$, $\tau(COO^-)$, $\tau(CONH)$
182.1		184.8	$9.5H_{35} + 8.9H_{36} + 16.5H_{39} + 14.4H_{40} + 14.4T_{52} + 14.5T_{54}$	$\delta(CCC)$, $\tau(CC)$ (trpy)
		171.5	$13.3H_{23} + 20.3H_{24} + 36.1T_{49}$	$\delta(CCC)$, $\tau(CC)$ (trpy)
		163.0	$67.5H_{39}$	$\delta(CCC)$ (GS)
		148.8	$26.4H_{23} + 15.3H_{24} + 27.9T_{49}$	$\delta(CC)$, $\tau(CC)$ (trpy)
148.8		140.9	$16.5H_{35} + 34.7H_{39}$	$\delta(CH_2)$, $\delta(CCC)$ (GS)
		128.1	$16.2K_1 + 9.9H_{39} + 11.2T_{55}$	$\tau(CC)$ (GS)
		120.5	$21.4K_1 + 10.0T_{55}$	$\nu(PtN)$, $\tau(CC)$ (GS)
121.0		111.0	$35.2H_{36} + 23.7H_{39} + 19.0T_{51}$	$\delta(CC)$, $\tau(CC)$ (GS)
		109.4	$24.9H_{36} + 46.1H_{39}$	$\delta(NH)$, $\delta(CCC)$ (GS)

reliability of the final force constants. The nature of bands in the metal complex can be further understood from the final constants.

In spite of large molecular weight and complicated structure of the title compound, the small average deviation of 3.44cm^{-1} between the calculated and observed frequences indicates that the optimized structure is appropriate, using a modified Urey-Bradley force field and introducing an appropriate set of internal coordinates and corresponding rational force constants make the normal coordinate analysis successful.

REFERENCES

[1] B. Rosenberg, L. van Camp, J. E. Ytroska, V. E. Manson, *Nature*, 1969; 22: 385.

[2] L. M. Edwin, J. Reedijk, *Inorg. Chem.*, 1991; 30: 2648.

[3] K. S. Wyatt, K. N. Harrison, C. M. Jensen, *Inorg. Chem.*, 1992; 31: 3867.

[4] N. Hadjiliadis, N. Ferderigos, J-L. Butour, H. Marzarguil, G. Gasmi, J-P. Laussac, *Inorg. Chem.*, 1994; 33: 5057.

[5] N. Juranic, V. Likic, N. M. Kostic and S. Macura , *Inorg. Chem.*, 1995; 34: 938.

[6] E. M. A. Ratilla, B. K. Michael, M. S. Moxness and N. M. Kostic, *Inorg. Chem.*, 1990; 29: 918.

[7] H. Fuhrer, W. B. Kartha, P. J. Krueger, H. H. Mantsch and R. N. Jones, *Chem. Rev.*, 1972; 72: 439.

[8] B. Durham and S. R. Wilson, *J. Amer. Chem. Soc.*, 1980; 102: 600.

[9] L. Zhu and N. M. Kostic, *Inorg. Chem.*, 1992; 31: 3994.

[10] P. W. Hansen and P. W. Jensen, *Spectrochim. Acta.*, 1994; 50A: 169.

[11] C. V. Weill and J. Corset, *Spectrochim. Acta.*, 1995; 51A: 2347.

[12] F. J. Ramfrez and J. T. L. Navarrete, *Spectrochim. Acta.*, 1995; 51A: 293.

[13] Y. Hase, *Spectrochim. Acta.*, 1995; 51A: 2561.

[14] R. J. Mureinik and M. Bidani, *Inorg. Nucl. Chem. Lett.*, 1977; 12: 625.

[15] M. L. Niven and G. C. Percy, *Spectroscopy letters*, 1977; 7: 519.

[16] C. D. Li and L. J. Jiang, *Spectrochim. Acta*, 1993; 49A: 339.

[17] L. J. Jiang and C. D. Li, *Spectroscopy letters*, 1994; 10: 1309.

[18] K. W. Jennrttr and J. T. Gill, *J. Amer. Chem. Soc.*, 1976; 98: 6159.

[19] A. Sarkar and S. Chakravorti, *Spectroscopy letters*, 1994; 3: 305.

[20] J. Casado, J. T. L. Navarrete and F. J. Ramirez, *Spectrochim. Acta*, 1995; 51A: 2347.

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