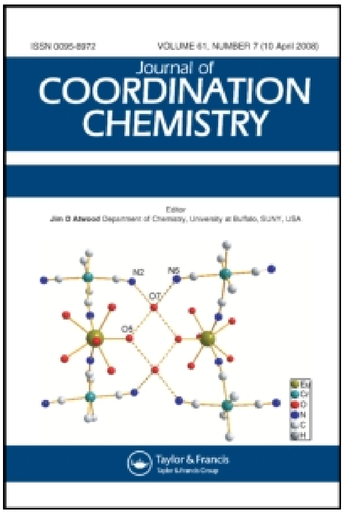
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

VIBRATIONAL SPECTROSCOPIC STUDIES AND NORMAL COORDINATE ANALYSIS OF A GLUTARIMIDATO-PALLADIUM(II) COMPLEX, *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2]$ 4.5H_2O

Barbara Morzyk[a]; Danuta Michalska[b]; Mariusz K. Marchewka[c]
[a] Institute of Chemistry, Pedagogical University, Czestochowa, PL, Poland [b] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw, Wroclaw, PL, Poland [c] Institute of Low Temperature and Structural Research, Polish Academy of Science, Wroclaw, PL, Poland

To cite this Article Morzyk, Barbara , Michalska, Danuta and Marchewka, Mariusz K.(1999) 'VIBRATIONAL SPECTROSCOPIC STUDIES AND NORMAL COORDINATE ANALYSIS OF A GLUTARIMIDATO-PALLADIUM(II) COMPLEX, *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2]$ 4.5H_2O', Journal of Coordination Chemistry, 47: 2, 241 — 250
To link to this Article: DOI: 10.1080/00958979908023057
URL: http://dx.doi.org/10.1080/00958979908023057

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1999, Vol. 47, pp. 241–250
Reprints available directly from the publisher
Photocopying permitted by license only

© 1999 OPA (Overseas Publishers Association) N.V.
Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

VIBRATIONAL SPECTROSCOPIC STUDIES AND NORMAL COORDINATE ANALYSIS OF A GLUTARIMIDATO-PALLADIUM(II) COMPLEX, *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2]\cdot 4.5H_2O$

BARBARA MORZYK[a,†], DANUTA MICHALSKA[b,*]
and MARIUSZ K. MARCHEWKA[c]

[a]*Institute of Chemistry, Pedagogical University, Al. Armii Krajowej 13/15, PL 42-200 Czestochowa, Poland;* [b]*Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, PL 50-370 Wrocław, Poland;* [c]*Institute of Low Temperature and Structural Research, Polish Academy of Science, ul. Okólna 2, PL 50-950 Wrocław, Poland*

(Received 11 March 1998)

FT-Raman and FT-infrared (FT-IR) spectra of the novel glutarimidato-palladium(II) complex, *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2]\cdot 4.5H_2O$, are reported in the range 4000–100 cm^{-1}. Vibrational assignments are given and are supported by normal coordinate calculations based on a general valence force field. A striking feature of the spectra of the anionic Pd(II) complex is a pronounced shift of the C=O stretching bands to lower wavenumbers relative to those in the neutral ligand. It has been concluded that after removal of two protons from the nitrogen atoms of two glutarimide rings and after formation of the palladium(II)–nitrogen bonds in *trans*-$[Pd(glutarimidato)_2Cl_2]^{2-}$, π electrons from the exocyclic carbonyl groups are transferred to the ring, which leads to the accommodation of the negative charge on the oxygen atoms. Thus, in the *N*-deprotonated Pd(II) complex the C=O bond order decreases and the oxygen atoms may bind with additional metal cations.

Keywords: Palladium(II); glutarimide; vibrational spectra; force constants

Downloaded At: 14:49 23 January 2011

---

* Corresponding author.

[†] Holder of a scholarship from the Foundation for Polish Science.

INTRODUCTION

The presence of the glutarimide ring in a variety of compounds with the antiviral and anticancer activity has stimulated our studies on metal complexes with glutarimides.[1–6] For a proper use of vibrational spectra in the structural studies it is essential to have a reliable knowledge of the normal mode of vibration for each Raman line or infrared (IR) band.

In a previous paper[1] a complete vibrational assignment for glutarimide has been reported. Here a detailed analysis of the vibrational spectra of the novel *bis*(glutarimidato)–palladium(II) complex, *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2] \cdot 4.5H_2O$ is presented. This compound is an interesting example of a simultaneous binding of soft and hard metal ions to a ligand containing the imide group. As revealed by the single-crystal X-ray studies of K and Na salts of the anionic complex $[Pd(C_5H_6NO_2)_2Cl_2]^{2-}$, transition metal ions like Pd(II) bind to the deprotonated nitrogen atom of the glutarimide ring, whereas hard metal ions like K^+ or Na^+ bind with the exocyclic carbonyl oxygen atoms.[6] It should be emphasized that a very similar type of bonding has been found in the platinum(II) complex with the 1-methyluracil anion, *trans*-$K_2[PtI_2(1\text{-}MeU)_2] \cdot 6H_2O$.[7] It has also been reported that thymine and uracil nucleobases, when metallated at the deprotonated N3 position, bind additional metal ions through the exocyclic oxygens which leads to the formation of polynuclear complexes.[7–9]

This principle seems to be common for metal complexes with cyclic imides; thus it is of interest to explore the chemistry of these compounds in greater depth. The results obtained from normal coordinate analysis of the anionic unit, *trans*-$[Pd(glutarimidato)_2Cl_2]^{2-}$, provide more information on electronic density distribution and resonance hybrid structures of multinuclear complexes derived from cyclic imides.

EXPERIMENTAL

The synthesis of the crystalline complex *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2] \cdot 4.5H_2O$ was performed according to the reported procedure.[6] Raman spectra were recorded on a Bruker 88 FT-Raman spectrophotometer equipped with a Nd-YAG laser (maximum power 200 mW and resolution 2 cm^{-1}). The infrared spectra were measured on a Bruker ISF-113V FT-IR spectrophotometer in the regions 4000–400 and 500–50 cm^{-1} with resolution of 2 cm^{-1}. IR spectra were recorded in KBr pellets and in nujol mulls on polyethylene plates.

Downloaded At: 14:49 23 January 2011

TABLE I Geometrical parameters of Pd(glutarimidato)$_2$Cl$_2^{2-}$ used in calculations

Bond lengths (Å)		*Bond angles and torsional angles* (deg)[a]	
C2–C1	1.525	N3–C2–C1	119.1
N3–C2	1.360	C4–N3–C2	123.1
C4–N3	1.355	C5–C4–N3	119.6
C5–C4	1.498	C6–C5–C4	117.9
C6–C5	1.487	O13–C2–N3	121.2
O13–C2	1.235	O14–C4–N3	120.8
O14–C4	1.248	Pd15–N3–C2	119.0
C–H	1.00	C6–C5–C4–N3	−23.0
Pd–N3	2.033	H–C–C	109.0
Pd–Cl	2.320		

[a] N–Pd–N Cl–Pd–Cl bonds are linear. The carbonyl groups are coplanar with the C1C2N3-C4C5 plane. C–H bonds are assumed to be in a tetrahedral arrangement.

Downloaded At: 14:49 23 January 2011

CALCULATION PROCEDURE

The bond lengths and angles used in the normal coordinate analysis are listed in Table I. A simplified model (1 : 1 metal : ligand) was applied. This is justified since this model takes into account significant vibrational coupling within the ring of the complex. In order to calculate both the symmetric and antisymmetric metal–ligand vibrations we performed additional calculations on the *trans*-PdN$_2$Cl$_2$ skeleton, which represents the model coordination sphere. A complete set of internal coordinates was applied, analogous to that used in the previous calculation.[1] The potential energy was expressed by a simplified general valence force field (SGVFF).[1,10] The procedure for the adjustment of force constants was the same as that described earlier.[11] Normal coordinate analysis was performed with a modified version of the Schachtschneider programs.[12] The calculated and experimental wavenumbers are in very good agreement (average error is less than 1%).

RESULTS AND DISCUSSION

Figure 1 provides a view of the model of glutarimide and its anionic complex *trans*-[Pd(glutarimidato)$_2$Cl$_2$]$^{2-}$ for which normal coordinate analysis was performed. According to the X-ray data[6] two glutarimide ligands are coordinated with Pd *via* the deprotonated ring nitrogen atoms. The two chloride and two nitrogen atoms form a *trans* square-planar environment around the palladium atom and the Cl–Pd–Cl and N–Pd–N bonds are linear.

Fourier-transform infrared and Raman spectra of crystalline *trans*-K$_2$[Pd(C$_5$H$_6$NO$_2$)$_2$Cl$_2$] · 4.5H$_2$O are shown in Figure 2 and the far infrared

Downloaded At: 14:49 23 January 2011

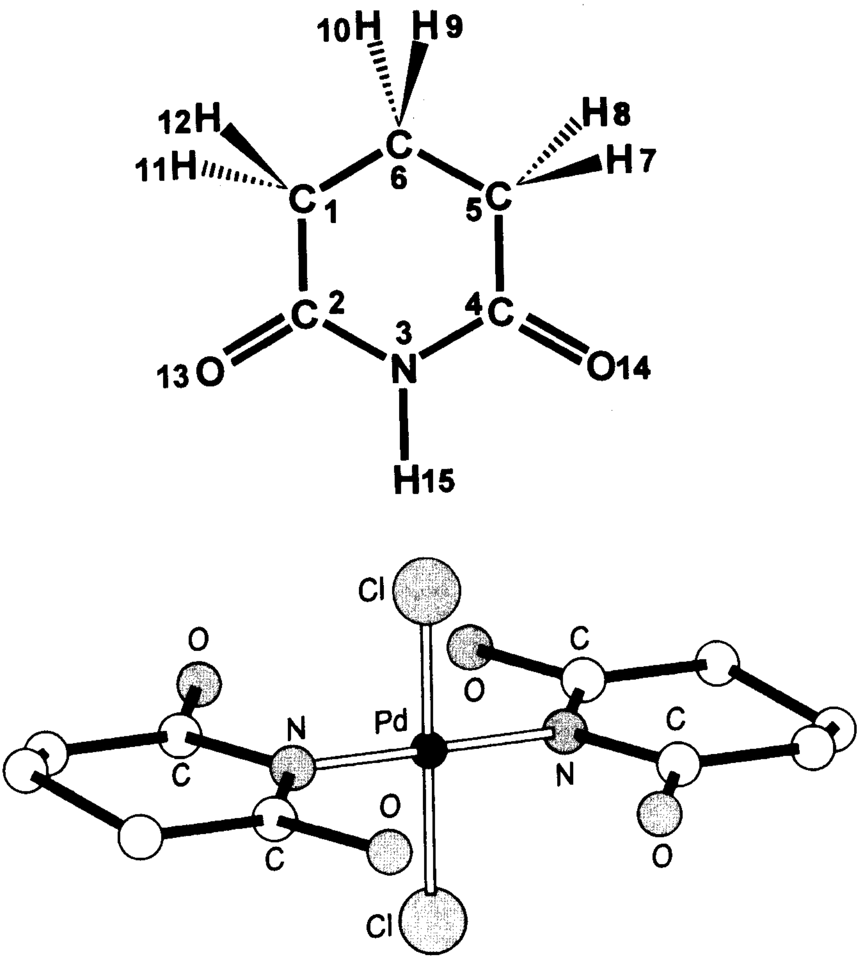


FIGURE 1 Molecular model and atom numbering of glutarimide and of Pd(glutarimidato)$_2$Cl$_2^{2-}$ complex ion.

spectrum is displayed in Figure 3. Experimental and calculated frequencies (selected bands) are shown in Table II. Vibrational assignment given in this table is based on the calculated potential energy distribution (PED) in terms of internal coordinates.

Vibrations of the Glutarimide Ring

Comparison of the infrared and Raman spectra of *trans*-K$_2$ [Pd(C$_5$H$_6$NO$_2$)$_2$Cl$_2$]$\cdot$4.5H$_2$O with those of neutral glutarimide[1] indicates that

TABLE II Observed and calculated wavenumbers (cm^{-1}) and vibrational assignment for *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2] \cdot 4.5H_2O$ (selected bands)^{a}

ν *observed* (cm^{-1})		ν *calculated* (cm^{-1})	*Assignment PED* (%)
IR	*Raman*		
3460 m, br			ν (OH) (H_2O)
	2958 vs	2960	ν CH_2 (C1HH) (C5HH) (99)
	2930 sh	2930	ν CH_2 (C6HH) (92)
	2890 vs	2890	ν CH_2 (C1HH) (C5HH) (94)
2850 w		2850	ν CH_2 (C6HH) (98)
1698^{b} w			(1064 + 629 = 1693 or 1330 + 354 = 1684)
1663 sh	1662 s	1663	ν^{s}(C2–O13) (48) + ν(C4–O14) (34)
1643^{b} m	1637^{b} sh		
1622 sh			δ(HOH)
1586 vs		1587	ν^{as}(C4–O14) (51) + ν(C2–O13) (35)
1462 w	1463 w	1463	CH_2 sciss. (HC6H) (96)
1437 sh		1436	CH2 sciss. (HC1H) (HC5H) (89)
1424 w	1417 m	1418	CH_2 sciss. (HC1H) (HC5H) (83)
1371 s	1374 sh	1371	ν(N–C_c) (27) + ν(C_b–C_c) (25)
1357 s	1363 m	1363	CH_2 def. (56) + ν(C_b–C_c) (12)
1329 m	1330 w	1329	ν(N–C_c) (33) + CH_2 def. (9)
1191 m	1189 w	1190	CH_2 def. (62)
	1064 m	1065	CH_2 def. (63) + ν(C_a–C_b) (17)
974 m	970 w	974	CH_2 def. (54) + ν(C_b–C_c) (19) + ν(C_a–C_b) (11)
787 w	788 m	793	CH_2 def. (22) + ring def. (21)
690 w	692 s	693	Ring def. (62)
629 w		635	Ring def. (18) + γ(C2–O13) (14) + γ(C4–O14) (13)
606 w	603 s	602	ν(C_b–C_c) (19) + δ(C2–O13) (14) + δ(C4–O14) (10)
572 m		569	Ring def. (23) + CH_2 def. (17) + ν^{as}(N3–Pd) (10)
540 br^{c}			H_2O librational modes
		538	ν^{as} (N3–Pd) (38) + δ(C4–O14) (14) + ring def. (10)
	478 m	478^{d}	ν^{s}(N3–Pd) (100)
459 m	458 s	457	Ring def. (59)
	445 sh	445	δ($C_aC_bC_c$) (15) + ν(C_a–C_b) (14) + γ(N3–Pd) (10)
395 br			H_2O librational modes
354 m	349 w	353	δ(C2–O13) (18) + δ(C4–O14) (17) + ν (N–C_c) (28)
296 m		296^{d}	ν^{as}(Pd–Cl)
	283 vs	283^{d}	ν^{s}(Pd–Cl)
258 m		257	γ(C2–O13) (65) + τ(C1 + C2) (17)
	235 m		δ(N–Pd–Cl)
208 m			δ(N–Pd–Cl)
	185 sh	186	τ ring def. (79)
172 sh	170 sh	172	τ(C1–C2) (35) + τ(C4–C5) (33) + γ(N3–Pd) (11)
	125 s	123	δ(N3–Pd) (44) + δ(C2N3C4) (27) + δ(C4–O14) (13)

^{a}Complete data are available as supplementary material; ^{b}combination band or crystal field splitting; ^{c}obscured by H_2O librational modes; ^{d}calculated with the model of coordination sphere.Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad; ν, stretching; ν^{as} and ν^{s} antisymmetric and symmetric stretchings, respectively; δ, in-plane bending; γ, out-of-plane bending; τ, torsion; def., deformation; ν(N–C_c) = ν(N3–C2) + ν(N3–C4); ν(C_a–C_b) = ν(C1–C6) + ν(C6–C5); ν(C_b–C_c) = ν(C1–C2) + ν(C5–C4); δ($C_aC_bC_c$) = δ(C6C1C2) + δ(C6C5C4); ring def., ring deformation (linear combination of internal coordinates in ring).

Downloaded At: 14:49 23 January 2011

all bands assigned to NH vibrations in the ligand disappear in the spectra of the Pd(II) complex, a fact which confirms deprotonation of the nitrogen atom upon complex formation.

The strong band at 1662 cm^{-1} in Raman and the very strong band at 1586 cm^{-1} in the infrared spectrum of the Pd(II) complex (Figure 2) have been assigned to the C=O symmetric and antisymmetric stretching vibrations, respectively. It is interesting to note that in the heteronuclear complex, *bis*[*bis*(1-methylthyminato)*cis*-diammineplatinum(II)]silver(I) nitrate pentahydrate, the corresponding bands occur at very similar wavenumbers, 1665 and 1570 cm^{-1}, respectively.[13] This suggests that electron density distribution and polarity of the C=O bonds in these complexes are similar. The other bands observed in the range 1698–1560 cm^{-1} for Pd(II) complex, may be due to crystal field splitting or they may arise from combination

Downloaded At: 14:49 23 January 2011

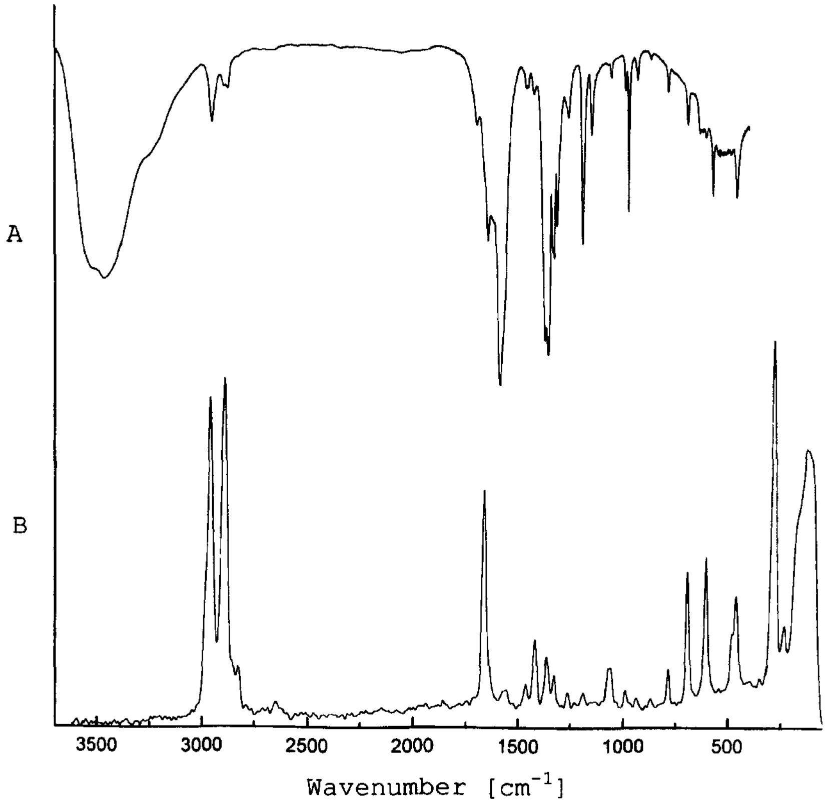


FIGURE 2 A: FT-IR spectra and B: FT-Raman spectra of *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2]\cdot 4.5H_2O$.

tones being enhanced in intensity through Fermi resonance with the C=O stretching fundamentals. Similar effects were noted in the spectra of neutral glutarimide.[1]

It is quite striking that in the *N*-coordinated Pd(II) complex the C=O stretching frequencies are significantly lower than those of neutral glutarimide (which occur at 1722 and 1706 cm^{-1} in the infrared).[1] A plausible explanation of this effect is that after removal of the proton from the nitrogen atom in the glutarimide ring, π electrons from the exocyclic carbonyl groups are transferred to the ring. This leads to accommodation of the negative charge on the oxygen atoms. Thus, the two CO bonds become more ionic. It is interesting that formation of the palladium(II)–nitrogen bond in the anionic complex $[Pd(glutarimidato)_2Cl_2]^{2-}$ does not restore electron density distribution and the negative charge remains on the oxygen atoms. This is reflected in a decrease of C=O stretching frequencies and an increase of C–N stretching frequencies in the Pd(II) complex. For example, the new strong infrared bands at 1371 and 1329 cm^{-1} involve predominant contribution from the C–N stretchings, as shown in Table I. The new distinct Raman lines at 788 and 692 cm^{-1} which appear in the spectrum of the Pd(II) complex have been assigned to deformation modes of the glutarimidate ring. Assignment of the remaining bands is given in Table II.

Downloaded At: 14:49 23 January 2011

Palladium(II)–Nitrogen and Palladium(II)–Chloride Vibrations

The region of the palladium–nitrogen (Pd–N) stretching vibration has been fairly well established.[14] It has been reported for PdL_2Cl_2 complexes[14–16] that the Pd–N stretching frequency ranges from 560 to 430 cm^{-1} depending on the nature of ligand (L). In *trans*-$Pd(NH_3)_2Cl_2$ the antisymmetric ν(Pd–N) mode was assigned to the infrared band at 496 cm^{-1}.[16] Of particular interest is the effect of deprotonation on the metal–nitrogen stretching frequencies. Watt and Knifton[17] showed that deprotonation of the nitrogen atom coordinated to metal ion strengthens the metal–nitrogen bond, reflected in a shift of the corresponding metal–nitrogen stretching vibration towards higher frequencies. It is therefore reasonable to conclude that the antisymmetric Pd(II)–N stretching mode in *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2]\cdot 4.5H_2O$ has a higher frequency than that in *trans*-$Pd(NH_3)_2Cl_2$. However, in the title complex this band is hidden under the very broad band centred at 540 cm^{-1} which arises from the librational modes of lattice water molecules,[14] as shown in Figure 3. Fortunately, the symmetric Pd(II)–N stretching vibration is Raman active and is easily assigned to a distinct new band of medium intensity at 478 cm^{-1} in the Raman spectrum of the complex.

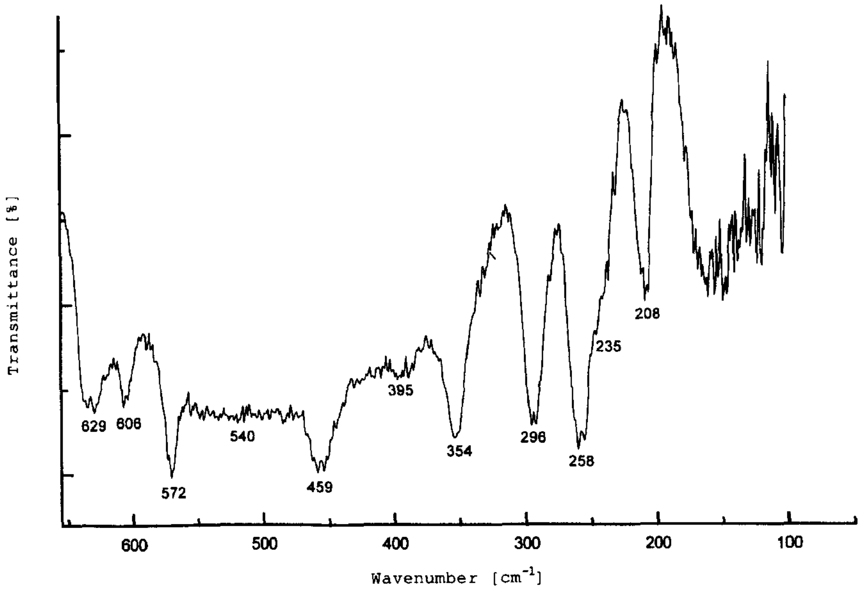


FIGURE 3 Far infrared spectrum of *trans*-$K_2[Pd(C_5H_6NO_2)_2Cl_2] \cdot 4.5H_2O$.

Downloaded At: 14:49 23 January 2011

The Pd–Cl stretching vibrations have been assigned by comparison with the spectra of related molecules.[14–16] Perry *et al.*[15] reported that the Pd–Cl stretching bands were of medium intensity in infrared spectra and ranged from 350 to 285 cm^{-1}. Thus, the infrared band at 296 cm^{-1} (Figure 3) and the very strong Raman band at 283 cm^{-1} in the title complex have been assigned to the antisymmetric and symmetric Pd–Cl stretching vibrations, respectively.

Force Constants

The Pd–N stretching force constant obtained in this work (1.88 mdyn Å^{-1}) is slightly higher than that obtained for tetraammine complexes of palladium(II) (1.71 mdyn Å^{-1})[14] which confirms the strong covalent character of the Pd–N bond in the anionic glutarimidato-Pd(II) complex. On the other hand, the Pd–Cl bonds become quite ionic in this complex, as indicated by much lower value of the Pd–Cl stretching force constant (1.34 mdyn Å^{-1}). The calculated values of the carbonyl stretching force constants *f*(C2–O13) and *f*(C4–O14), 9.83 and 9.63 mdyn Å^{-1}, respectively, are smaller than those in the neutral glutarimide[1] (11.06 and 10.27 mdyn Å^{-1})

which confirms our conclusion that deprotonation of the nitrogen atom reduces the C=O bond order. It should be noted that the $f(CO/CO)$ interaction force constant (0.39 mdyn Å^{-1}) was indispensable for reproducing the frequencies of the antisymmetric and symmetric C=O stretching vibrations of two carbonyl groups in the complex.

The final set of force constants derived in the normal coordinate analysis of Pd(glutarimidato)$_2$Cl$_2^{2-}$ anion is available as supplementary material.

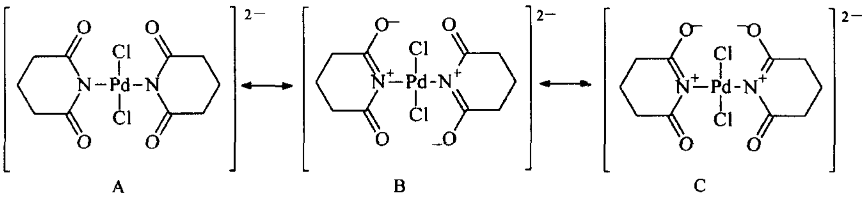
It is concluded that after removal of two protons from two glutarimide rings and after formation of the palladium(II)–nitrogen bonds in *trans*-[Pd(glutarimidato)$_2$Cl$_2$]$^{2-}$, π electrons from the exocyclic carbonyl groups are transferred to the ring which leads to accommodation of the negative charge on the oxygen atoms. Thus, in the anionic complex the C=O bond order decreases and the oxygen atoms may bind with additional metal cations. It follows from the above discussion that the electronic structure of Pd(glutarimidato)$_2$Cl$_2^{2-}$ complex anion may be represented by a resonance hybrid of structures A, B and C (as shown in Scheme 1) with B and C having predominant contribution. It is apparent from the resonance structures B and C that the oxygen atoms may interact with K$^+$ or Na$^+$ cations or possibly other metal cations. This may lead to formation of polynuclear complexes of glutarimide with different metal ions.

It is possible that similar effect occurs for thymine and uracil nucleobases bonded at the N3 position with Pt(II) or Pd(II). This may explain formation of the polynuclear complexes of cyclic imides.

Downloaded At: 14:49 23 January 2011

Supplementary Material

Tables listing all experimental and calculated frequencies and the set of force constants obtained in the normal coordinate analysis of the Pd(II) complex are available from the authors on request.



SCHEME 1 Resonance structures of Pd(glutarimidato)$_2$Cl$_2^{2-}$ complex ion.

References

[1] B. Morzyk, D. Michalska and J. Baran, *J. Coord. Chem.*, **47**, 231 (1999).
[2] B. Morzyk, D. Michalska and W. Wojciechowski, *J. Coord. Chem.*, **34**, 179 (1995).
[3] D. Michaiska, B. Morzyk and W. Wojciechowski, *J. Coord. Chem.*, **38**, 101 (1996).
[4] B. Morzyk, D. Michalska and W. Wojciechowski, *Chem. Papers*, **48**, 84 (1994).
[5] D. Michalska, B. Morzyk and W. Wojciechowski, *Bull. Acad. Pol. Sci. Ser. Chim.*, **42**, 467 (1994).
[6] D. Michalska, B. Morzyk, W. Wojciechowski and T. Glowiak, *Inorg. Chim. Acta*, **248**, 159 (1996).
[7] O. Renn, B. Lippert and I. Mutikainen, *Inorg. Chim. Acta*, **218**, 117 (1994).
[8] B. Lippert, *Prog. Inorg. Chem.*, **37**, 1 (1989).
[9] M. Goodgame and D.A. Jakubovic, *Coord. Chem. Rev.*, **79**, 97 (1987).
[10] S. Krimm, *Spectra and Structure of Polypeptides in Vibrational Spectra and Structure.* Vol. 16, Edited by J.R. Durig (Elsevier, Amsterdam, 1987).
[11] D. Michalska, *Spectrochim. Acta*, **49A**, 303 (1993).
[12] J.H. Schachtschneider, *Vibrational Analysis of Polyatomic Molecules*, Technical Report nos. 231-64 and 57-65, Shell Development Co., Emeryville, California.
[13] B. Lippert and D. Neugebauer, *Inorg. Chim. Acta*, **46**, 171 (1980).
[14] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (J. Wiley & Sons, 1986), Chapter III.
[15] C.H. Perry, D.P. Athans, E.F. Young, J.R. Dung and B.R. Mitchell, *Spectrochim. Acta*, **23A**, 1137 (1967).
[16] J. Hiraishi, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **24A**, 819 (1968).
[17] G.W. Watt and J.F. Knifton, *Inorg. Chem.*, **6**, 1010 (1967).

Downloaded At: 14:49 23 January 2011