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Synthesis and vibrational study of platinum(II) and palladium(II) complexes of glyoxilic acid oxime

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Abstract

New platinum(II) and palladium(II) complexes of glyoxilic acid oxime (gao) have been prepared and characterised by infrared (4000–150 cm⁻¹) and Raman (4000–200 cm⁻¹) spectra. The gao acts as bidentate ligand bonding through the oxime nitrogen and carboxyl oxygen atoms to form neutral bis-chelate square-planar complexes. The lowest energy conformer of the gao ligand (*ectt*) was selected among 16 theoretically possible conformers on the basis of ab initio calculations at HF/3-21G*, HF/6-31G* and HF/6-311** levels of the theory from which structural parameters and conformational stabilities have been obtained. A complete vibrational assignment of the gao was performed for the lowest energy *ectt* conformer on the basis of ab initio optimised parameters and normal coordinate analysis calculations (PED). NCA calculations of the complexes studied were also performed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Infrared and Raman spectra; Platinum(II)- and palladium(II)-complexes; Glyoxilic acid oxime

1. Introduction

Platinum(II) and palladium(II) form stable square-planar complexes with a number of bidentate ligands as amino acids [1–6], mono- and dioximes [7–12]. In these cases, different mixed-ligand complexes in which the ligand acts as unidentate, bidentate, or both, have been prepared and characterised. Glyoxilic acid oxime (gao) has two donor atoms (the carboxyl oxygen

and the oxime nitrogen) and thus it can act as a mono- or bidentate ligand in platinum(II) and palladium(II) complexes. The coordination behaviour of this ligand is not known and Pt(II) and Pd(II) complexes with this ligand were not reported so far.

In this paper, we study two new bis-chelate square-planar complexes of Pt(II) and Pd(II) with gao. The complexes are characterised by elemental analysis, electric conductivity measurements, IR and Raman spectroscopy and normal coordinate analysis. The conformational behaviour and stability of the ligand were studied by ab initio

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calculations at HF/3-21G*, HF/6-31G* and HF/6-311G** level of the theory. The structural parameters obtained from the ab initio calculations were used to perform vibrational assignment of the ligand.

To give a more detailed description of the calculated and the observed vibrational modes, normal coordinate analysis (NCA) calculations of the ligand and the complexes studied were also performed. The theoretical predictions are compared with the experimental results where appropriate.

2. Experimental

2.1. Starting materials

The gao was prepared using the method described in [13]. The product was recrystallized from an ethylacetate– nC_7H_{16} mixture (m.p. 145–150°C). The metal salts (K_2PtCl_4 and K_2PdCl_4) were analytical grade purity products.

2.2. Preparation of the complexes

[Pt(gao)₂]. A concentrated aqueous solution of the gao ligand (0.2 g, 0.25 mmol) was added dropwise to an aqueous solution of K_2PtCl_4 (0.933 g, 0.25 mmol). The complex precipitated from the solution as dark-red crystals after 48 h at room temperature. It was filtered and washed with cold water, $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$ (1:1) mixture, ether and dried under vacuum. Yield: 0.278 g (60%).

[Pd(gao)₂]. The complex was prepared in a similar way. A concentrated aqueous solution of gao ligand (0.273 g, 0.306 mmol) was added dropwise to a stirred solution of K_2PdCl_4 (1 g, 0.306 mmol) in H_2O (6 ml). The mixture was stirred at room temperature for 3–4 h. After 8 h, the yellow precipitate which formed was filtered off, washed with cold H_2O , $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$ (1:1) mixture, ether and dried under vacuum. Yield: 0.277 g (64%).

2.3. Physical measurements and analysis

The melting points of the Pt(gao)₂ and Pd(gao)₂ complexes were measured with Boetius apparatus

and were not corrected. The elemental analysis for C, H, N and M were performed according to standard microanalytical procedures.

Conductivity measurements were carried out using a Conductivity meter type OK-102/1, Radelkis, for 1×10^{-3} mol l⁻¹ solutions in dimethylformamide (DMF).

2.4. Infrared and Raman spectra

The solid state infrared spectra of gao-ligand, Pt(gao)₂ and Pd(gao)₂ were recorded in the 4000–150 cm⁻¹ frequency range (in KBr 4000–400 cm⁻¹ and in CsI in the 400–150 cm⁻¹) by FTIR 113V Bruker spectrometer. The Raman spectra of the compounds mentioned above were measured in the solid state with a SPEX-Ramalog spectrometer (double monochromator with 1152×298 pixels CCD-camera detector) in the 4000–200 cm⁻¹ frequency range. An argon ion laser (514.5 nm) as well as krypton ion laser (647.1 nm) were used for excitation. In all cases, the resolution was 1 cm⁻¹.

3. Computational procedure

3.1. Ab initio calculations

The ab initio calculations on gao were performed by GAUSSIAN 94 program set [14]. Geometry optimisations were performed at the Hartree–Fock level for all possible conformers of the molecule using 3-21G*, 6-31G* and 6-311G** basis sets.

3.2. Normal coordinate analysis

The normal coordinate analysis of the gao was carried out for the lowest energy conformer, *ectt*, using FCR1 and FCR2 programs [15a,15b]. The FCR1 program calculated for the given structure and set of force constants with assumed numerical values the eigenvalues and the normal coordinates. The calculations were performed with ab initio optimised geometry. The force field was defined by the Cartesian components of the internal coordinates of the molecule. The complete set of $3N - 6 = 21$ internal coordinates has been

defined for gao molecule: eight stretching, seven bending and six torsions. The initial force constant values were taken from NCA calculations of similar molecules [2,3]. The force constants were optimised using FCR2 program, which performed a least-squares-fit for the calculated vibrational eigenvalues of the molecule to its experimental frequencies by changing the force constants. The calculated PED values are related to internal force constants.

The initial geometries for NCA calculations of $\text{Pt}(\text{gao})_2$ and $\text{Pd}(\text{gao})_2$ complexes were obtained from molecular mechanics calculations using the standard PCMODEL program, version 4.0 [16]. 44 internal coordinates were included and discussed for $\text{Pt}(\text{gao})_2$ and $\text{Pd}(\text{gao})_2$ complexes. The optimised force constants for the gao molecule were used as initial set force constants for the studied complexes. The M–L force constants were taken from the literature [2,3]. All force constants were optimised using FCR2 program.

4. Results and discussion

4.1. Characterisation of the complexes

The isolated complexes, $\text{Pt}(\text{gao})_2$ and $\text{Pd}(\text{gao})_2$, with their analytical data, melting point and molar electric conductivity values are listed in Table 1. The complexes were analysed for the carbon,

hydrogen, nitrogen and metal content. The values obtained are in agreement with the suggested general formula of bis-chelate square-planar complexes- $\text{M}(\text{gao})_2$, ($\text{M} = \text{Pt}$ and Pd). It should be mentioned that an attempt was made to obtain complexes with a general formula $\text{M}(\text{gao})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) by reacting gao with K_2PtBr_4 and K_2PtI_4 being prepared in situ. In all cases, however, the analysis and the vibrational spectra of complexes obtained showed the general formula of bis-chelate square-planar complexes, $\text{M}(\text{gao})_2$. The absence of Cl, Br and I in the complexes obtained was confirmed by the IR and Raman spectra; no bands due to the M–X vibrations were detected in the far IR and Raman spectra. In addition, identical powder X-ray diagrams have been obtained for all the complexes studied. Thus, we concluded that Cl, Br and I do not participate in the coordination and bis-chelate square-planar complexes were obtained in all cases. Obviously, the coordination ability of the ligand allowed both Cl^- (Br^- or I^-) ligands (if coordinated at the very beginning) to leave the coordination sphere of the metal ion and second gao molecule coordinates forming the second chelate ring.

The palladium complex, $\text{Pd}(\text{gao})_2$, is light yellow crystalline soluble in water and dimethylformamide. The $\text{Pt}(\text{gao})_2$ complex showed, however, dark-red colour. The variation in the colour of many bis-chelate square-planar complexes of ligands that allow a formation of *cis*- and *trans*-iso-

Table 1
Analytical and physical data for the $\text{Pt}(\text{gao})_2$ and $\text{Pd}(\text{gao})_2$ complexes

Complexes	Colour	Melting point (°C)	Analysis (%) ^a				Λ_m^b (cm $\Omega^{-1}\text{mol}^{-1}$) (DMF)
			M	C	H	N	
$\text{Pt}(\text{gao})_2$	Dark-red	> 290	59.86 (52.56)	12.04 (12.94)	1.72 (1.08)	6.8 (7.55)	21.6
$\text{Pt}(\text{gao})_2$ (1.5 H_2O)			(49.00)	(12.06)	(1.77)	(7.03)	
$\text{Pd}(\text{gao})_2$	Light-yellow	295–297	50.49 (49.67)	14.86 (17.0)	1.02 (1.42)	9.69 (9.9)	17.7

^a The calculated values are given in parenthesis.

^b At room temperature in dimethylformamide, $c = 1 \times 10^{-3} \text{ mol l}^{-1}$.

mers was explained by geometrical isomerism. For discrimination of the geometrical isomers a vibrational criterion was developed [2,3,17,18]. This is, however, not the case with the $\text{Pt}(\text{gao})_2$ complex since its IR and Raman spectra (in the high- and mid-frequency region) are identical with those of $\text{Pd}(\text{gao})_2$ and they both are in agreement with *trans*-isomer spectral behaviour (comment will be given also in Section 4.4).

4.2. *Ab initio* calculations on glyoxilic acid oxime

Considering only the planar structures for the molecule, there might be several possible structures arising from rotations around the C–O, C–C, C=N and N–O bonds. The rotation around C=N determines two groups of conformers: *anti*, *e* and *syn*, *z*. Every one of these two groups includes eight conformations arising from rotation around the other three bonds: C–O, C–C and N–O. Thus, for the four torsional angles there are in principle 16 possible planar structures. All these structures were considered in our study. The calculated relative conformational energies, however, are often sensitive to the basis sets used in the calculations [19]. In order to obtain the lowest energy conformer for the *gao* the calculations were done at the Hartree–Fock level using different basis sets: 3-21G*, 6-31G* and 6-311G**. On the basis of all the three basis sets we were able to distinguish among three conformers with significantly lower energy, *ectt*, *ecct* and *ett* (see Fig. 1). All basis sets used in this study gave preference to the *ectt* conformer. The relative energy differences of the studied conformers are very small, 0.75 and 1.25 kcal mol^{−1} for *ecct* and *ett*, respectively. The assignment of the IR and Raman spectra of the *gao* was performed on the basis of normal coordinate analysis using the structural parameters for the lowest energy conformer, *ectt*. In addition, this conformer geometry is interesting since it offers the best possibility for coordination to the metal ions in a bis-chelate square-planar configuration as we suggested for the studied complexes.

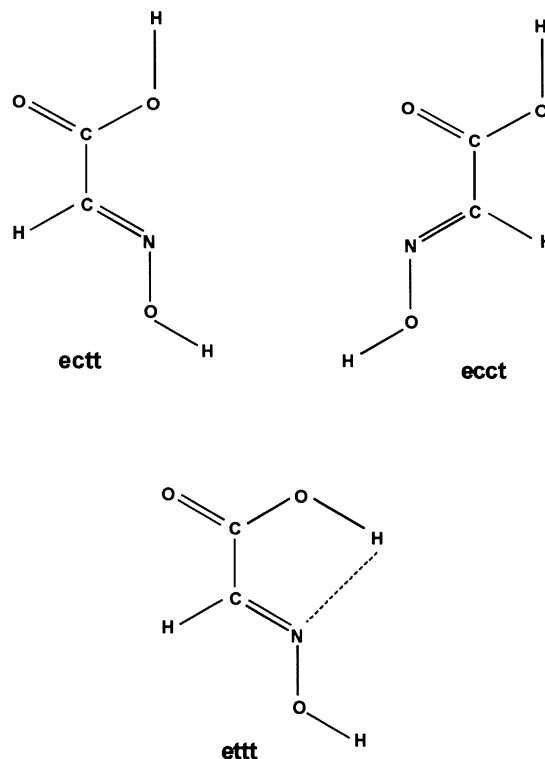


Fig. 1. *ectt*, *ecct* and *ett* conformations of *gao*.

4.3. Vibrational assignment of the ligand. Normal coordinate analysis

The experimental (IR and Raman) and calculated (for *ectt* conformer) frequencies (NCA) of *gao* are given in Table 2. The optimised force constants are summarised in Table 3. Twenty one vibrational modes were calculated and assigned on the basis of the calculated PED values. Several absorptions of the *gao* spectrum are interesting to be considered since they change their positions during the complex formation. These absorptions are discussed below.

The COO stretching vibrations usually give two strong and characteristic absorptions in the IR spectrum and their positions vary in the range 1740–1380 cm^{−1} [2–4,17,20–22]. In *gao* IR and Raman spectra, strong absorptions were obtained at 1713 (1720) and 1450 (1446) cm^{−1} and in agreement with the calculated PED values they were undoubtedly assigned to the asymmetric and

symmetric vibrations of the COOH group. This group is unionised in the ligand since the IR and Raman spectra exhibit a stretching band near 1713 cm^{-1} (the free ionised group has this absorption at lower frequencies, $1630\text{--}1575\text{ cm}^{-1}$). The COO stretching modes are expected to shift to the lower frequencies when the carboxyl group coordinates to the metal ion. These trends will be discussed in Section 4.4.

According to our normal coordinate calculations, the other COO vibrational modes (COO-bend, COO-wag and COO-rock) have

Table 2

Experimental (IR and Raman) and calculated (NCA) frequencies of gao (cm^{-1})

Exp. IR	Exp. R	Calc. (NCA)	Assignment PED (%) ^a
3269s	–	3269	100v(OH _{COOH})
	–	3269	100v(OH _{NOH})
2925w,sh	–	2925	99v(CH)
1713s	1720s	1713	83v(CO)
1621m	1636m	1621	73v(CN)
1450m	1446m	1450	40v(CO) + 31δ(OCO)
	1282s		
1253s	1260s	1253	91δ(NOH)
	1246s		
1023s	1046w	1023	75δ(NCH) + 10δ(CCH)
	955m		
938m	934w	938	60δ(COH) + 24v(CO) + 13δ(OCO)
	927w		
752m	709m	720	32δ(COH) + 22v(CO) + 20δ(OCO)
691s	685m	691	76v(NO) + 7δ(OCO)
535m	536m	534	59v(CC) + 12δ(OCO) + 11δ(CNO)
327w	–	327	75δ(OCC) + 11δ(OCO) + 6δ(CNO)
273s	267w	274	90t(OCCH) + 8t(HCNO)
224w	–	224	79t(OCOH) + 18t(CCOH)
179s	–	179	73δ(CNO) + 14v(CC)
–	–	120	97t(CNOH)
–	–	72	40t(OCCN) + 32t(HCNO)
–	–	67	77δ(CCH) + 15δ(NCH)
–	–	34	44t(CCOH) + 36t(OCCN)
–	–	20	+ 17t(OCOH) + 44t(HCNO) + 44t(OCCN)

^a Only the main contributions are shown: s, strong; m, medium; w, weak; d, doublet; vs, very strong; vw, very weak; v, stretching; δ, bend; t, torsion.

Table 3

Optimised (NCA) force constants for gao (in mdyn Å^{-1} and mdyn Å rad^{-2})^a

Definition	Value
F(CO)	8.42
F(CC)	2.12
F(CN)	9.24
F(NO)	2.25
F(OH _{COOH})	7.05
F(CH)	4.65
F(OH _{NOH})	5.96
F(OCO)	2.46
F(COH)	0.36
F(OCC)	1.05
F(CCH)	0.10
F(CNO)	0.40
F(NOH)	0.73
F(NCH)	0.50
F(OCCH)	0.024
F(CCOH)	0.030
F(OCCN)	0.006
F(OCOH)	0.010
F(HCNO)	0.003
F(CNOH)	0.006

^a $\text{mdyn Å}^{-1} = 100\text{ N m}^{-1}$; $\text{mdyn Å rad}^{-2} = 10^{-18}\text{ N m rad}^{-2}$.

contributions to the bands at 938, 752, and 535 cm^{-1} . This is in agreement with the assignment of these modes in some *trans*-bis-chelate square-planar Pt(II), Pd(II), Ni(II) and Cu(II) complexes, where the COOH group takes part in the coordination to the metal ion [17,18].

In open-chain unsaturated compounds the C=N absorption was observed in the $1690\text{--}1590\text{ cm}^{-1}$ frequency range [23]. According to our PED values, the C=N stretching mode was assigned to the medium band observed at 1621 cm^{-1} in agreement with its assignment in aliphatic oximes (C=N–OH) [24–34]. The band remains a difficult one to identify, however, owing to the considerable changes in intensity which follow changes in its environment. In the Raman spectra, the C=N band is very much stronger than in the infrared and is always easy to identify [23]. In the Pt(II) and Pd(II) complex spectra this absorption was shifted to low frequency since the coordination through the oxime group (NOH) occurs. This shift confirms the assignment of 1621 cm^{-1} band

Table 4

Experimental (IR and R) and calculated (NCA) frequencies of Pt(gao)₂, (cm⁻¹)

Exp. IR	Exp. R	Calc. (NCA)	Assignment ^a (PED, %)
3270m,sh	–	3270	100(OH _{NoH})
		3270	100(OH _{NoH})
3040m	–	3040	99(CH)
		3040	99(CH)
1682s,d	–	1667	48(C=O) + 23(C–O)
1632s		1664	48(C=O) + 19(C–O)
1550m,d	1542w	1552	36(C=N) + 33(C–O)
1523m		1529	36(C=N) + 32(C–O)
1390m,d	1352m,d	1386	21(C–O) + 32(C=N) + 14(C=O)
1380m	1340m	1369	20(C–O) + 36(C=N) + 13(C=O)
1260m,d	1265m,d	254	92(NOH)
1240m	1249s	1246	85(NOH)
1160m,d		1179	89(HCCO)
1140m	1127m	1120	89(HCCO)
950m	–	954	30(NCH) + 10(CNPt) + 8(C=N)
		949	40(NCH) + 14(CC) + 9(CNPt)
888m,d	–	883	36(NO) + 17(C=O) + 15(CC)
861m		862	31(NO) + 17(C=O) + 7(CC)
780m	–	786	28(OCO) + 18(NCH) + 17(Pt–O)
		778	23(OCO) + 14(Pt–O) + 13(OCCN)
740w,d		738	47(OCCN) + 14(NO) + 12(ONCC)
730w		727	53(OCCN) + 12(NO) + 7(NCH)
645m	–	645	42(NCH) + 24(CC) + 10(OCC)
		636	28(NCH) + 26(CC) + 10(OCCN)
530w	–	532	9(Pt–N) + 32(OPtO) + 28(CO–t)
		523	27(Pt–N) + 13(CO–t) + 11(OCC)
470w		482	21(CO–t) + 19(OCC) + 12(Pt–N)
		475	30(CO–t) + 27(Pt–N) + 11(NO)
410w	415w	404	31(Pt–O) + 18(ONCC) + 12(OPtN)
		400	23(Pt–O) + 22(OCC) + 12(CO–t)
370s	–	365	27(CO–t) + 13(OCO) + 11(OPtN)
		362	20(Pt–O) + 19(ONCC) + 15(OCCN)
350s	–	320	29(OCO) + 32(Pt–O) + 10(OPtO)
304m	299w	296	16(CO–t) + 19(ONCC) + 12(OCC)
–	250w	267	21(ONCC) + 15(OPtN) + 11(OPtO)
		244	16(OPtN) + 16(CNPt) + 12(Pt–O)
220m	229w	221	23(CO–t) + 37(CNPt) + 11(ONCC)
175s	–	166	48(CNO) + 11(CNPt) + 12(ONCC)
–	–	144	27(OPtN) + 17(OCC) + 12(ONCC)

Table 4 (Continued)

Exp. IR	Exp. R	Calc. (NCA)	Assignment ^a (PED, %)
–	–	125	58(CNO) + 11(Pt–N) + 11(CNPt)
–	–	107	41(ONCC) + 23(NPtN) + 9(CO–t)
–	–	45	46(NCC) + 17(CNPt) + 13(OPtN)
–	–	12	73(NCC) + 13(CNPt) + 5(OPtN)

^a Only the main contributions are shown: s, strong; m, medium; w, weak; t, torsion; d, doublet.

as C=N stretching mode (see Section 4.4). The strong absorption, observed at 1253 cm⁻¹, was assigned according to the PED values to NOH bending mode.

4.4. IR and Raman spectra of the Pt(gao)₂ and Pd(gao)₂ complexes. Normal coordinate analysis

The optimised force field parameters for the free ligand (Table 3) were used as initial set in the NCA calculations of the studied complexes. Forty four vibrational modes were calculated and assigned on the basis of the calculated PED values.

The results obtained from the calculations of Pt(gao)₂ and Pd(gao)₂ are given in Tables 4 and 5, respectively. As seen from Tables 4 and 5, the observed IR and Raman spectra of the studied Pt(II) and Pd(II) complexes are almost identical and the calculated frequencies and PED values do not differ significantly. As expected, differences were observed in the far IR region due to different metal–ligand vibrations. The optimised force constants for the Pt(gao)₂ and Pd(gao)₂ complexes are given in Table 6. We shall discuss below the group vibrations, which are expected to change their positions upon coordination as well as the calculated force constants for these groups.

The positions of the COO absorptions were used often to decide whether the COOH group is coordinated or not in different Pt(II) complexes [17,18,20]. It was mentioned that when the group is coordinated its absorptions lower up to 100 cm⁻¹ and the lowering is metal sensitive [18]. In

Table 5
Experimental (IR and R) and calculated (NCA) frequencies of
Pd(gao)₂, (cm⁻¹)

Exp. IR	Exp. R	Calc. (NCA)	Assignment ^a (PED, %)
3265m,sh	–	3265	100(OH _{NOH})
		3264	100(OH _{NOH})
3051m	3080m	99	99(CH)
	3054m	3051	99(CH)
	3030m	3051	
1675s,d	1663s,d	1660	42(C=O)+40(C–O)
1635s	1637w	1654	42(C=O)+37(C–O)
1545m	1554s	1562	63(C=N)+14(C–O)
		1529	68(C=N)+12(C–O)
1360m,d	–	1352	31(C–O)+26(C=O)+17(OCO)
1340m	1343m	1343	30(C–O)+26(C=O)+17(OCO)
1265m,d	1263s,d	1262	91(NOH)
1255m	1255s	1259	84(NOH)
1165m,d	–	1186	90(HCCO)
1150m,sh	–	1126	90(HCCO)
955w	970w	961	33(NCH)+18(NO)
		945	59(NCH)+9(CNO)
875m,d	880w	882	42(NO)+28(NCH)+11(CC)
860m		863	48(NO)+10(C=O)+5(CC)
780m	785	784	30(OCO)+25(Pd–O)+15(CO)
		772	29(OCO)+22(Pd–O)+13(CO)
731w,d	732w	736	70(OCCN)+6(HCCO)
720w		728	65(OCCN)+12(ONCC)
600m	629m	613	27(CC)+29(NCH)+10(CNO)
		597	36(CC)+20(NCH)+10(PdO)
520w	517w	519	29(Pd–N)+16(CNO)+14(CC)
		494	32(Pd–N)+21(CNO)
			+17(OCC)
430w	442w	447	31(CO–t)+52(OPdO)
		438	43(CO–t)+14(Pd–O)
			+11(OCC)
400w	400w	403	39(Pd–O)+21(OCC)
		384	30(Pd–O)+18(OCC)
			+23(CO–t)
329s	–	335	31(OCO)+23(Pd–O)
			+10(OPdO)
		326	51(ONCC)+12(NPdN)
			+12(OCCN)
290s	290w	306	19(CO–t)+12(ONCC)
			+15(OCO)
		277	18(OCO)+28(CO–t)
			+11(OCC)
250sh	229w	245	24(CNO)+20(ONCC)
			+10(OPdN)
		215	36(CNPd)+18(Pd–N)
			+14(OPdN)
219s	–	205	29(CO–t)+23(CNPd)
			+19(OPdN)
177s	178w	155	30(CNO)+27(CNPd)
			+10(OPdN)

Table 5 (Continued)

Exp. IR	Exp. R	Calc. (NCA)	Assignment ^a (PED, %)
–	–	136	26(CNO)+16(ONCC)
–	–	117	+15(OPdN)
–	–	94	34(OPdN)+21(CNO)
–	–		+11(PdN)
–	–	42	37(ONCC)+30(NPdN)
–	–		+8(OPdN)
–	–	11	57(NCC)+13(CNPd)
–	–		+13(OPdN)
–	–		70(NCC)+15(CNPd)
–	–		+7(OPdN)

^a Only the main contributions are shown: s, strong; m, medium; w, weak; t, torsion; d, doublet.

general, the coordinated bonds are intermediate between purely ionic and purely covalent [22]. It was reported further that there is a relationship between the covalent character of the metal–carboxylate bond and the positions of the COO absorptions [20–22]. An increase of covalent character leads to more asymmetric structure of the carboxyl group (form I, Fig. 2) and this results in an increase in the frequency separation of the two carboxyl bands (asymmetric and symmetric).

In our Pt(II)- and Pd(II) complex spectra, the higher frequency COO absorptions (asymmetric) were obtained split and shifted to lower frequencies (1682, 1632 cm⁻¹ for Pt(gao)₂ complex and 1675, 1635 cm⁻¹ for Pd(gao)₂) as compared with the position of this absorption in the free ligand spectrum (1713 cm⁻¹). This negative shift confirms the participation of the COOH group in the coordination to the metal ion. The observed splittings confirm the presence of two ligands in the complex molecule. Further, in agreement with [20] since the carbonyl band absorption appears above 1610 cm⁻¹, the M–OOC bonding is expected to be to a great extent covalent and thus a contribution of the form (I) is present. If we accept the conclusion made previously [20], i.e. that the increase in the stability of the chelates is related to the increase in the covalent nature of the metal–ligand bond, it is expected that the covalent character of the M–OOC bond predicts stable bonding in the studied complexes.

Table 6

Optimised force constants for Pt(gao)₂ and Pd(gao)₂ (in mdyn Å⁻¹ and mdyn Å rad⁻²)^a

Definition	Pt(gao) ₂	Pd(gao) ₂
F(C=O)	7.613	7.900
F(C–O)	7.509	7.328
F(CC)	3.801	2.468
F(CN)	7.074	7.713
F(NO)	3.373	3.908
F(CH)	5.032	5.069
F(OH _{NOH})	5.967	5.948
F(OCO)	1.731	1.502
F(OCC)	1.588	1.457
F(CNO)	0.446	0.602
F(NOH)	0.665	0.670
F(NCH)	0.393	0.432
F(OCCH)	0.598	0.604
F(OCCN)	1.002	1.060
F(ONCC)	0.205	0.156
F(NCC)	0.084	0.091
F(M–O)	2.337	2.494
F(M–N)	1.816	1.275
F(CNM)	1.225	0.920
F(CO–t)	0.339	0.291
F(NMN)	1.335	0.726
F(OMO)	3.071	3.006
F(OMN)	3.463	1.464

^a mdyn Å⁻¹ = 100 N⁻¹; mdyn Å rad⁻² = 10⁻¹⁸ N m rad⁻².

Carboxylate groups when coordinated in a complex compound are known to give rise to another peak in the 1450–1390 cm⁻¹ region [20]. According to our PED values, the ligand band at 1450 cm⁻¹ was assigned to the second (symmetric) carboxylate band (Table 2). The symmetric COO absorption was also split and shifted to 1390, 1380 cm⁻¹ (doublet) in Pt(gao)₂ and to 1360, 1340 cm⁻¹ (doublet) in Pd(gao)₂ complex spectra as expected for a coordinated carboxylate group (Tables 4 and 5).

An increase of the covalent character of the M–OOC bond leads to a more asymmetric structure of the carboxyl group and results in an increase in the frequency separation of the carboxyl bands [22]. For the complexes studied, the separation between the two (asymmetric and symmetric) COO absorptions is in agreement

with unidentate coordination of the COO and presence of form I in Fig. 2 [17,22]: 292 (252) and 315 (295) cm⁻¹ for Pt(gao)₂ and Pd(gao)₂, respectively. Obviously, the separations found in the IR and Raman spectra of the studied complexes are of the same order. They are in agreement with the order obtained for different metal ions mentioned in [22] and predict asymmetric structure of the COO⁻ unit and thus covalent character of the metal–oxygen bond in our complexes.

On the other hand, NCA calculations of some bis-chelate square-planar *trans*-bis(glycinato) Pt(II) complexes with coordinated COOH groups predicted equal force constants for the C=O and C–O, F(C=O) = 7.7 and F(C–O) = 7.6 mdyn Å⁻¹, which is in agreement with the presence of the form II in Fig. 2 [4]. Our optimised force constants for Pt(gao)₂ complex are in full agreement with these values: F(C=O) = 7.6 and F(C–O) = 7.5 mdyn Å⁻¹ (see Table 6). The obtained values for the Pd(gao)₂ complex are F(C=O) = 7.9 and F(C–O) = 7.3 mdyn Å⁻¹ and the difference between them, Δ = F(C=O) – F(C–O) = 0.6 mdyn Å⁻¹ is higher compared to the same difference for the Pt(gao)₂ complex Δ = 0.1 mdyn Å⁻¹. The higher Δ = F(C=O) – F(C–O) difference obtained for the Pd(gao)₂ complex is in agreement with the higher frequency difference between the asymmetric and symmetric COO vibrations and predicts slightly higher covalent character of the Pd–carboxylate bond as compared with the Pt–carboxylate bond.

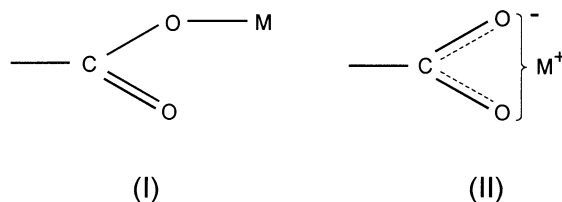


Fig. 2. Asymmetrical and symmetrical coordinated carboxylate group.

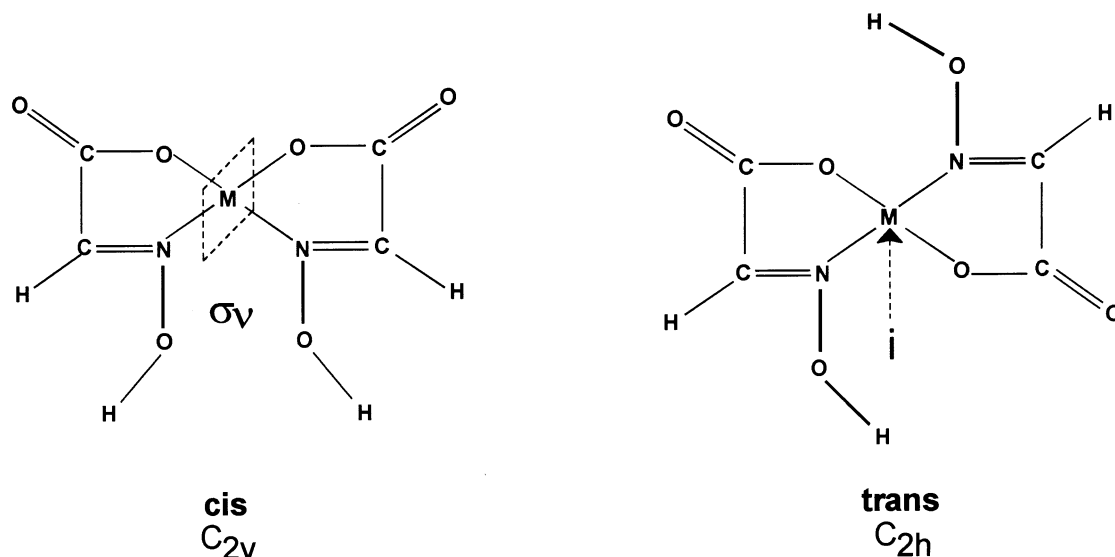


Fig. 3. *Cis*- and *trans*-isomers of $M(\text{gao})_2$ complex ($M = \text{Pt}, \text{Pd}$).

The asymmetric and symmetric stretching bands would be expected to shift in the same direction with a change in the metal [22]. This correlation was also observed in our Pt(II) - and Pd(II) - complex spectra where both components of the COO^- unit for Pd(II) are shifted to lower frequencies, 1675 , 1635 cm^{-1} , respectively (d), 1360 cm^{-1} as compared with those of Pt(II) , 1682 , 1632 cm^{-1} , respectively (d), 1390 cm^{-1} (Tables 4 and 5). Thus, both trends were obtained in our IR and Raman spectra going from Pt(gao)_2 to Pd(gao)_2 complex: (1) both asymmetric and symmetric carboxylate bands shift to lower frequency and at the same time; (2) the separation between them increases. Obviously, the nature of the M-OOC bonding in different metal complexes is always partially ionic and partially covalent and both forms in Fig. 2 should be considered [20,22].

Since in the studied Pt(II) and Pd(II) complexes a coordination through the oxime group (NOH) occurs, the C=N absorption also shifted to lower frequencies compared with the observed ligand frequency ($1621 \rightarrow 1550$, 1523 cm^{-1} for Pt(gao)_2 and $1621 \rightarrow 1545\text{ cm}^{-1}$ for Pd(gao)_2).

The NOH bending mode was observed as a strong band in the ligand spectrum (1253 cm^{-1}).

In the complex spectra, it is a doublet shifted as expected for bending modes to the higher frequencies, 1260 , 1240 cm^{-1} (doublet) for Pt(gao)_2 and 1265 , 1255 cm^{-1} (doublet) for Pd(gao)_2 (Tables 4 and 5). The observed doublets for the COO , NOH and NCH and NO absorptions confirm the presence of two ligands in the complexes studied.

The other skeletal vibrations of the *gao* are slightly shifted to higher frequencies in both complex spectra.

It is known that square-planar bis-chelate complexes of different metal ions can take *cis*- and *trans*-configurations [2,17]. Frequencies, attributed to metal–ligand stretching vibrations were used to develop a vibrational criterion that allows discrimination between the *cis*- and *trans*-configuration of the square-planar bis-chelate complexes [17,18]. As expected from a symmetry consideration, the *cis*-isomer which belongs to the noncentrosymmetric C_s molecular point group and have both asymmetric and symmetric metal–ligand stretching vibrations active, exhibits more bands in the infrared spectra than the *trans*-isomers. The last one belongs to the C_i point group, and only one asymmetric M-ligand stretching vibration is IR active (see Fig. 3). Thus, in the low frequency region, the *cis*-complexes exhibit two

(asymmetric and symmetric) $\nu(\text{M}-\text{N})$ and two $\nu(\text{M}-\text{O})$ stretching modes, while the spectra of *trans*-complexes exhibit only one (asymmetric) for each of these modes [2].

Since the Pt–N (Pd–N) bonds are expected to be less polar than the Pt–O (Pd–O) bonds, it would be expected that the intensities of the Pt–N (Pd–N) stretching bands would be less than that of the Pt–O (Pd–O) stretching bands. In our spectra, both M–N and M–O were detected as very weak bands. According to the PED values, we have assigned the M–N stretching mode to the weak bands at 530–520 cm^{-1} . Similar metal–nitrogen stretching frequencies were reported for bidentate bis(glycino) complexes of Pt(II) and Pd(II) [2]. The metal–nitrogen stretching frequencies in our complexes are higher than those of monodentate amino Pt(II) and Pd(II) complexes reported in [2,35] since the chelation strengthens the coordinate bond and increases the repulsive force between non-bonded atoms.

As seen from Tables 4 and 5, we assigned the Pt–O stretching modes to the weak bands at $\sim 400 \text{ cm}^{-1}$ for both Pt(II)- and Pd(II)-complexes. This is in agreement with the assignment of the M–O stretching modes in bidentate Pt(II)- and Pd(II)-glycino complexes [2]. Both M–N and M–O stretching modes are very weak but not split in two components and thus we suggested *trans*-configuration for the complexes studied. In agreement with [2] we found the Pt–N force constant higher (1.816 $\text{mdyn } \text{\AA}^{-1}$) as compared with Pd–N (1.275 $\text{mdyn } \text{\AA}^{-1}$) and thus the Pt–N covalent character is expected to be higher as compared with the Pd–N. A reverse order, however, was obtained for the M–O force constants; slightly higher is the Pd–O force constant. Thus, the higher covalent character of the Pd–O bond, predicted from the calculated C=O and C–O force constants, is in agreement with the higher Pd–O force constant.

The M–X (X=Cl, Br, I) bands were not detected at their usual positions in the IR and Raman spectra and this confirmed the absence of halogen atoms in the coordination sphere of Pt- and Pd-gao complexes.

5. Conclusions

The vibrational study of $\text{Pt}(\text{gao})_2$ and $\text{Pd}(\text{gao})_2$ complexes have shown identical spectral features in the high- and mid-frequency regions and thus the same structure. The coordination of the COOH and the NOH groups to the Pt(II) and Pd(II) metal ions was confirmed by the significant shift of the vibrational modes of these two groups going from the ligand- to the complex spectra. The observed splitting of the asymmetric and symmetric COO^- unit vibrations is in agreement with asymmetric coordination and covalent character of the metal–carboxylic bond. The calculated force constants of C=O, C–O and Pd–O bonds predicted slightly higher stability and covalent character for the Pd–O bond compared with the Pt–O bond. The Pt–N bond is expected to be more covalent (higher force constant, $F(\text{Pt}-\text{N}) = 1.816 \text{ mdyn } \text{\AA}^{-1}$) than the Pd–N ($F(\text{Pd}-\text{N}) = 1.275 \text{ mdyn } \text{\AA}^{-1}$). The assignment of the bands done on the basis of NCA calculations of the free ligand and the $\text{Pt}(\text{gao})_2$ and $\text{Pd}(\text{gao})_2$ complexes confirmed the presence of two ligands (doublets appeared for several absorptions).

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