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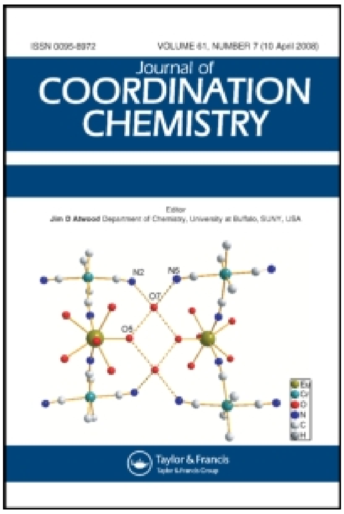

Journal of Coordination Chemistry

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

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To cite this Article Várhelyi, Cs. , Kovács, A. , Gömöry, Á. , Várhelyi, Cs. , Pokol, Gy. , Farkas, Gy. and Sohár, P.(2009) 'Comparative spectral and thermal studies of [Pt(DioxH)$_2$] chelates', Journal of Coordination Chemistry, 62: 15, 2429 — 2437

To link to this Article: DOI: 10.1080/00958970902852926

URL: http://dx.doi.org/10.1080/00958970902852926

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Journal of Coordination Chemistry
Vol. 62, No. 15, 10 August 2009, 2429–2437

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Comparative spectral and thermal studies of [Pt(DioxH)$_2$] chelates

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(*Received 20 October 2008; in final form 11 December 2008*)

Eleven [Pt(DioxH) complexes with various symmetric and asymmetric α-dioximes: R^1–C(=NOH)–C(=NOH)–R^2 ($R^1 = R^2, R^1 \neq R^2, R^1, R^2 =$ H, alkyl-, aryl-, alicyclic, heterocyclic groups) are characterized by IR, NMR, and mass spectrometry. The thermal behaviors of these complexes are studied with thermoanalytical methods (TG, DTA, and DSC). The complexes with serial number: **4**, **5**, **6**, **7**, and **10** are new compounds. The IR and ^{1}H NMR-spectra prove the coplanar structure of the [Pt(DioxH)$_2$] complexes stabilized by two very short O–H$\cdots$O hydrogen bonds. The thermal studies show that the chelates of this type are anhydrous and decompose without well-defined, reproducible melting points. The lack of weight loss and endothermal peaks on the TG and DTA curves, respectively, between 120 and 220°C, proves this phenomenon. The thermal stability of the complexes with symmetrical ligands is higher than with asymmetrical ones. The appearance of the main peaks in the mass spectra (MS) of the complexes shows, generally, an identical decomposition mechanism for all Pt-derivatives studied.

Keywords: Azomethine; Dioxime; Pt-complexes; Thermoanalytical study; Mass spectra

1. Introduction

The first α-dioxime complexes of platinum were obtained by Chugaev [1, 2] using free alkyl- and aryl-dioximes (DioxH$_2$) and platinum(II) compounds. With an excess of DioxH$_2$ the Pt(IV) derivatives ($[PtCl_6]^{2-}$, $[PtBr_6]^{2-}$) are reduced first to form the mentioned complexes [1–5]. Pt(II) also reacts with non-α-substituted monoximes (e.g., acetaldoxime, propion–aldoxime) and appears in coordination compounds of other bi- and polydentate azomethines (hydrazones, semi- and thiosemicarbazones,

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902852926

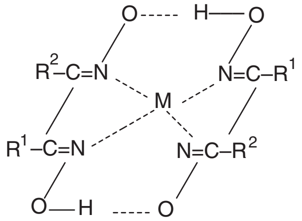


Figure 1. Coplanar structure of the [Pt(DioxH)$_2$] complexes. R^1, R^2 = H, Me, Et, Propyl, Phenyl, Benzyl, Furyl, and alicyclic rings.

Schiff-bases, etc. [6–23]). Ni(II) and Pd(II) also form [M(DioxH)$_2$] type coplanar chelates. The stability of the M–N bonds is influenced by steric factors, bulk of the DioxH ligand, and the O···O distance in the O–H···O intramolecular hydrogen bonds.

X-ray studies prove the coplanar *trans* structure of these compounds (figure 1) [13, 14], as for analogous Ni(II)- and Pd(II)-derivatives.

Some complexes of the type [Pt(DioxH)$_2$] were used for gravimetric and UV–Vis spectrophotometric determination of platinum in apolar solvents, in the presence of Ni and Pd. Only dimethyl-glyoxime and furyl-dioxime derivatives (**2** and **11** in table 1) were used for analytical purposes [24].

Thermal behavior of Pt(II) derivatives gives useful data for determination of the drying temperature range. The bulk of the R^1, R^2 ligands increases the sensitivity of the analytical methods (higher alicyclic dioximes with C$_7$–C$_{12}$, macrocyclic dioximes).

2. Experimental

2.1. *Synthesis of [Pt(DioxH)$_2$] compounds*

About 5 mmol of K$_2$[PtCl$_4$] in 100 mL of 1% HCl solution was treated with an excess of α-dioxime in ethanol (15 mmol of the reagent in 50–100 mL of 90% ethanol). The mixture was refluxed for 3 h forming greenish or brown crystalline product that was filtered, washed with dilute ethanol (20%) and dried at room temperature. The products can be obtained also at room temperature with 10–20 days of reaction time. This time period promotes the growing of crystalline particles.

2.2. *Analysis*

The IR spectra of the complexes were obtained in KBr and polyethylene pellets in the mid-IR (4000–450 cm^{-1}) and far-IR (650–150 cm^{-1}) range, respectively, on a Perkin–Elmer System 2000 FTIR spectrometer operating with a resolution of 4 cm^{-1}. The NMR spectra were recorded in DMSO-d$_6$ in 5 mm tubes at RT on a Bruker DRX 500 spectrometer at 500 MHz using TMS as internal reference. Mass spectrometric (MS) measurements were carried out by a VG ZAB2-SEQ tandem mass spectrometer in electron impact ionization (EI) mode (ionization energy: 70 eV, temperature of the ion source: 200°C). Thermal measurements were performed with a 951 TG and 910 DSC calorimeter (DuPont Instruments) in Ar or N$_2$ at a heating rate of 10 K min^{-1} (sample mass 4–10 mg). Qualitative tests were accomplished by heating 20–30 mg of solid complexes in a test tube in an oil bath at 10°C min^{-1}.

Table 1. [Pt(DioxH)$_2$] type complexes.

					Analysis (%)	
No.	Formula	Mol. Wt. Calcd	Yield (%)	Characterization (microscope)	Calcd	Found
1	[Pt(GlyoxH)$_2$] $C_4H_6N_4O_4Pt$	369.3	40	Greenish-brown prisms	Pt 53.3 N 15.3	53.2 15.1
2	[Pt(Dimethyl-GlyoxH)$_2$] $C_8H_{14}N_4O_4Pt$	425.3	60	Green needles with bronze nuance	Pt 45.9 N 13.2	46.3 13.4
3	[Pt(Me-Et-DioxH)$_2$] $C_{10}H_{18}N_4O_4Pt$	453.1	50	Greenish-brown crops	Pt 43.0 N 12.3	43.4 12.4
4	[Pt(Me-i-Propyl-DioxH)$_2$] $C_{12}H_{22}N_4O_4Pt$	481.1	55	Greenish-brown microcrystals	Pt 40.5 C 31.9 H 4.6 N 11.6	40.7 32.2 4.8 11.8
5	[Pt(Phenyl-GlyoxH)$_2$] $C_{16}H_{14}N_4O_4Pt$	521.1	45	Greenish-brown crops	Pt 37.5 C 36.8 H 2.7 N 10.7	37.8 37.1 2.8 10.5
6	[Pt(Benzyl-Me-GlyoxH)$_2$] $C_{20}H_{22}N_4O_4Pt$	577.5	75	Brown microcrystals	Pt 33.8 C 41.5 H 3.8 N 9.7	4.1 41.7 3.6 9.8
7	[Pt(Cyclopentane-DioxH)$_2$] $C_{10}H_{14}N_4O_4Pt$	449.5	60	Greenish-brown needles	Pt 43.4 C 26.7 H 3.1 N 12.4	43.0 26.6 2.9 12.5
8	[Pt(Cyclohexane- DioxH)$_2$] $C_{12}H_{18}N_4O_4Pt$	477.5	80	Greenish-brown irregular prism	Pt 40.9 N 11.7	41.2 11.5
9	[Pt(Cycloheptane-DioxH)$_2$] $C_{14}H_{22}N_4O_4Pt$	505.6	75	Greenish-brown plates	Pt 38.6 N 11.0	38.3 11.4
10	[Pt(Cyclooctane-DioxH)$_2$] $C_{16}H_{26}N_4O_4Pt$	533.6	80	Brown irregular crystals	Pt 36.6 C 36.0 H 4.9 N 10.5	36.2 35.9 5.1 10.8
11	[Pt(Furyl-DioxH)$_2$] $C_{20}H_{14}N_4O_8Pt$	633.6	70	Brown microcrystals	t 30.8 N 8.8	1.0 8.7

Symbols: GlyoxH$_2$, DioxH$_2$: α-(anti)-dioximes.

3. Results and discussion

In this article 11 [Pt(DioxH)$_2$] complexes (four new compounds) were obtained in weak acidic aqueous solutions with different symmetric and asymmetric aliphatic-, aromatic-, alicyclic-, and heterocyclic α-dioximes. The complexes were studied with IR-, MS, and various thermoanalytical methods. The obtained compounds are listed in table 1. The [Pt(DioxH)$_2$] complexes are very slightly soluble in water and soluble in non-polar organic solvents (e.g., $CHCl_3$, CCl_4, etc.).

3.1. *Infrared spectra*

Selected absorption bands from the IR spectra of the complexes are given in table 2 with assignments based on related transition metal dioximato complexes [16, 25–28]. The most characteristic vibrations of the complexes are those of the hydrogen-bonded oxime moieties and the metal–ligand vibrations. The very strong H$\cdots$O hydrogen

Table 2. Selected FTIR-spectral data of some [Pt(DioxH)$_2$] type complexes.

Vibration	**1**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
$\delta_{O-H\cdots O}$	1720–1780 w	1700–1840 w	1750–1830 w	1740–1820 m	1700–1800 m	1720–1790 w	1740–1820 w	1730–1820 m	1700–1800 w
$\nu_{C=N}$	1518 vs	1524 vs	1528 vs	1530–1540 vs	1560 vs	1550 vs	1547 vs	1541 vs	1530 vs
ν_{NO}	1261 vs	1267 vs	1280 m	1266 vs	1248 vs	1250 vs	1251 vs	1260 vs	1240 vs
ν_{NOH}	1150 m	1103 vs	1187 vs	1156 vs	1120 vs	1150 vs	1145 vs	1093 vs	1120 s
γ_{OH}	825 s	985 vs	827 m	998 m, 956 m	950 vs	945 vs	960 vs, 910 vs	975 m, 920 vs	–
ν_{Pt-N}	525 m	510 vs	609 s	510 s	525 s	526s	527 s	521 vs	512 m
Skeleton	452 m	455 m	444 s	457 s	446 m	450 m	452 m	465 s	440 m
δ_{CNO}	360 vs	371 vs	356 m	364 vs	380 s	385 m	395 s	370 m	390 s
δ_{N-Pt-N}	430 vs, 350 m	419 s, 344 vs	402 s, 302 w	419 s, 303 m	425 s	427 s	431 s, 327 s	417 s, 338 m	440 m, 321 s
γ_{NO}	175 m, 166 m	176 m, 170 m	188 s, 174 m	195 m, 176 m	180 s	178 s	187 s	169 s	194 m, 156 m
Skeleton	124 s	227 s, 202 s	160 s	150 s	230m	240 m	265 m	102 s	–

Notes: vs: very strong, s: strong, m: medium, w: weak.

bonding interaction stabilizes the coplanar geometric structure of complexes of this type and results in considerable change from vibrations of the free ligands. The strong ν_{as}OH and ν_sOH bands of the free dioximes (between 3400 and 3150 cm^{-1}) are absent in spectra of the $[Pt(DioxH)_2]$ type complexes and a wide, weak, or medium band appears in the spectra of the complexes at 1700–1850 cm^{-1} ($\delta_{O-H\cdots O}$), only slightly influenced by the nature of the central metal and ligands.

The $\nu_{C=N}$ appears at 1540–1580 cm^{-1} shifted from 60 to 80 cm^{-1} as compared to those of the free dioximes (1640–1620 cm^{-1}), due to weakening of the CN bond, as a result of the $Pt \rightarrow \pi^*C{=}N$ back-donation in the complexes.

The $\nu_{N-O(H)}$ band at 950–980 cm^{-1} of the free oximes is split and shifted by complex formation, ν_{NO} (1280–1240 cm^{-1}) and $\nu_{N-O(H)}$ (1050–1120 cm^{-1}) depending on the nature of metals, and substituents of the ligands. The split is due to deprotonation of one oxime in the complex and formation of a partial NO double bond. The NO-bond is also influenced by the σ-donor–acceptor $N \rightarrow Pt$ interaction. These significant shifts of $\nu_{C=N}$ and ν_{NO} prove the strong covalent character of the Pt–N bonds.

The high γ_{OH} values between 960 and 1000 cm^{-1} in complexes **4**, **6**, **9**, and **10** may be associated with strain introduced by the large substituents in these ligands.

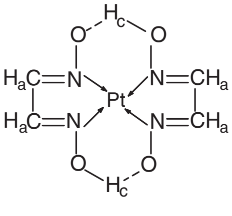
The ν_{Pt-N} vibrations appear in the far-IR region at 510 cm^{-1}, while the δ_{N-Pt-N} vibrations are involved in two intense bands at 420 and 340 cm^{-1} except in **5**, where the band is shifted by 100 cm^{-1} to higher wavenumber. As this is the only complex with an aromatic group attached directly to glyoxime, the extended electron delocalization seems to affect the metal–ligand interaction. The higher wavenumber indicates a strengthening of the Pt–N bonds. Parallel, the δ_{N-Pt-N} vibration appears at slightly lower wavenumbers (402 and 302 cm^{-1}) than those of the aliphatic ligands at 420 and 320 cm^{-1}. The γ_{NO} vibrations give bands at 170 cm^{-1}.

3.2. *NMR spectra*

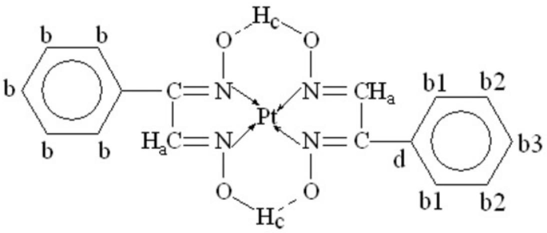
^{1}H- and ^{13}C-NMR measurements were carried out for some $[Pt(DioxH)_2]$ complexes and their free ligands in DMSO-d_6.

The chemical shift for the H_a protons (scheme 1) in the free dioxime is 7.74 ppm and in **1** 7.5 ppm. The H_c proton's chemical shift in the free glyoxime is 11.6 ppm. The chemical shift for C_a in the free dioxime is 145.9 ppm and in the complex 138.2 ppm.

The chemical shift for the H_a protons (scheme 2) in **5** is between 8.94 and 9.15 ppm and H_{b1} at 7.65 ppm in free glyoxime is at 8.24 ppm in the complex, H_{b2} and H_{b3} in the free glyoxime at 7.38 ppm, while 7.6 ppm in the complex, and H_c appears at 11.2 ppm



Scheme 1. $[Pt(GlyoxH)_2]$ (**1**).



Scheme 2. [Pt(Phenyl-glyoxH)$_2$] (**5**).

in the free glyoxime and 12.03 ppm in the complex. The ^{13}C chemical shift in the free dioxime for C_a is 153.3 ppm, C_{b1} 126.0 ppm, C_{b2} 128.8 ppm, C_{b3} 129.1 ppm, and C_d 137.4 ppm.

The proton signal from –OH for free dioximes are at 11–12 ppm, while in the complex more than 12 ppm. This chemical shift of the O–H···O bridge can be explained by a very short O···O distance, and great shielding of the oxygens. Loss of the O–H···O signal shows, in many cases, the asymmetric structure of this bridge, with different O–H, O···H distances.

The NMR study of [M(dimethyl-glyoxime)$_2$], M = Ni, Pd, Pt, shows the stability of the O–H···O bridge decreases in the order Ni < Pd < Pt. This appears as a little shift of the corresponding ppm value (>12 ppm) [29, 30].

3.3. *Thermal decomposition of [Pt(DioxH)$_2$] type chelates*

Thermoanalytical measurements show that the compounds decompose in a temperature range of 130–350°C, influenced by the nature of the chelating agent. These platinum derivatives melt generally at temperatures between 120°C and 300°C and a dark resinous mass is formed followed by evolution of gaseous by-products. In table 3, row 2, the thermal stability range ($\Delta m = 0$) shows the melting points of all the [Pt(DioxH)$_2$] complexes studied take place parallel with beginning of decomposition; the melting points of the complexes are not reproducible.

The lack of well-formed endothermal peaks on the DTA curves, characteristic for endothermal melting, proves that the thermal decomposition of the studied complexes takes place directly, without reproducible melting point. The strong exothermal DTA peaks, in inert gas atmosphere (N_2 or Ar), shows the participation of the oxygen in the oxime, sometimes with explosion, in a very complicated oxidation and other decomposition processes.

The shape of the TG curves shows one, two, and rarely three decomposition stages, influenced by the nature and size of the ligands. Some decompositions take place explosively in a single step with one exotherm bifurcate peak on the DTA curve. These results show a very complicated process. The residue of the pyrolysis at 700–800°C (by heating rate of 10 K min^{-1} by the thermal analysis) is Pt powder (Supplementary material).

Table 3. Thermoanalytical data of some [Pt(DioxH)$_2$] type complexes.

Experimental method	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
TG sample (mg)	8.525	9.5573	11.0494	5.8866	4.7784	5.0223	7.8870	8.2533	9.4480	10.1200	–
Thermal stability											
Δt (°C)	20–230	20–290	20–160	20–125	20–120	20–175	20–260	20–280	20–289	20–300	–
$-\Delta m$ (%)	0	0	0	0	0	0	0	0	0	0	–
1st step											
Δt (°C)	240–260	290–330	165–185	130–212	130–225	177–210	260–290	270–290	290–320	305–320	–
$-\Delta m_1$ (%)	28.2	29.0	14.15	13.17	8.63	8.21	30.0	25.0	22.0	25.0	–
2nd step											
Δt (°C)	270–290	340–390	190–275	220–290	260–315	220–350	300–350	300–360	330–360	330–400	–
$-\Delta m_2$ (%)	10.2	12.0	27.03	12.88	15.01	12.8	18.0	15.0	15.2	9.0	–
3rd step											
Δt (°C)	–	–	–	300–410	320–360	340–380	–	–	–	–	–
$-\Delta m_3$ (%)	–	–	–	6.99	15.38	5.0	–	–	–	–	–
Pt(DioxH) Calcd	64.8	69.67	79.02	41.37	32.63	33.60	–	–	65.20	69.01	–
Residue		43.86	47.57	23.88	17.78	16.97	43.4	40.9	36.47	36.94	–
Pt (%) Calcd	45.0	42	52.0	25.2	–	19.0	46.0	42.8	–	–	–
Pt found	46.2	(700)	(700)	(600)	–	(500)	(600)	(600)	–	–	–
t (°C)	(600)										
DTA peak, t(°C)	237 (exo) 230 (endo) 243 (endo) 307 (endo)	302.7 (exo) bifurcate 182.4 (endo)	182.4 (endo) 271.9 (exo) bifurcate	211.5 (exo) 286.6 (exo) bifurcate 342.8 (exo)	195.6 (exo) 252 (exo) 343.9 (exo)	210 (endo) 275 (exo) 330–340 (exo)	265 (exo)	275 (exo)	280 (exo)	310 (exo)	308 (exo)
DTG peak (t°C)	233.3	300	272	206 212 244 287	193.8 253.3 352.9	215 272.9	260	265	270	289 315	310
DSC t (°C)	233	–	–	267	–	–	–	–	–	315.7	305.6
Q Calcd J g^{-1}	489	–	–	541	–	–	–	–	–	323	511
Kcal mol^{-1}	180.5	–	–	260.3	–	–	–	–	–	143	323.5

The order of thermal stability of the Pt-derivatives on the basis of TG and DTG data is the following:

$$\mathbf{2} > \mathbf{11} > \mathbf{10} > \mathbf{3} > \mathbf{9} > \mathbf{8} > \mathbf{7} > \mathbf{6} > \mathbf{1} > \mathbf{4} > \mathbf{5}$$

with the most stable chelates derivatives of symmetric aliphatic and alicyclic dioximes. The complexes with asymmetric dioximes decompose at lower temperatures.

If we compare with analogous Ni(II) [31] and Pd(II) [32] derivatives with identical ligands, the order of the thermal stability is the following:

$$\mathrm{Ni} > \mathrm{Pd} \approx \mathrm{Pt}\ (\mathbf{1}, \mathbf{2}, \mathbf{6}); \quad \mathrm{Pd} \geq \mathrm{Pt} > \mathrm{Ni}\ (\mathbf{3}, \mathbf{4}, \mathbf{5}, \mathbf{7}, \mathbf{8}, \mathbf{9}, \mathbf{10}, \mathbf{11})$$

with influence of steric factors and of O–H···O bond stability generally Ni > Pd > Pt.

Thermal stabilities of the free α-dioximes are smaller than the $[\mathrm{Pt(DioxH)_2}]$ chelates because of the existence of free >C=N–OH in inter- and intramolecular O–H···O, N–O–H bonds promoting redox and decomposition processes (unpublished results).

3.4. *Mass spectrometric measurements*

The EI mass spectral data of the obtained $[\mathrm{Pt(DioxH)_2}]$ type chelates are provided in "Supplementary material". The molecular ions appear in the MS with high m/z (%) values (80–100%), indicating non-electrolytic character of the studied complexes. The three stable isotopes of platinum ^{194}Pt (32.9%), ^{195}Pt (33.8%), and ^{196}Pt (25%) show in molecular ions and the m/z values of some Pt-nitriles-, Pt-furazanes-, and oxime fragments (2–3 m/z peaks of the fragments).

The following decomposition mechanism can be suggested based on MS values: $[\mathrm{Pt(DioxH)_2}] \rightarrow$ [Pt(DioxH)(furazane)] $\rightarrow$ Pt(DioxH)NO $\rightarrow$ Pt(DioxH) $\rightarrow$ Pt(furazane) $\rightarrow$ PtCN $\rightarrow$ Pt.

4. Conclusions

The complexes were synthesized and characterized by spectral (FTIR, NMR, and MS) and thermal (TG, DTA, and DTG) methods. These measurements demonstrate the structure, thermal stability, and decomposition mechanism of the complexes. We propose a general decomposition mechanism for these very complicated processes (oxidation, reduction, and elimination reactions in various ratios) based on m/z values of the mass spectra using the isotopic effect of Pt.

Acknowledgments

The authors wish to thank for the fellowships provided for Csaba Várhelyi Jr in every year, by Foundation "Domus Hungarica" to Hungary are gratefully acknowledged. Part of the research was supported by the Hungarian Scientific Research Foundation (OTKA No. T038189). The quantum chemical calculations have been performed on the

SUN Fire supercomputer operated by the National Information Infrastructure Development Program of Hungary. A.K. thanks the Bolyai Foundation for support.

References

[1] L.A. Chugaev. *Z. Anorg. Allg. Chem.*, **46**, 144 (1905).
[2] L.A. Chugaev, V.G. Chlopin. *Z. Anorg. Allg. Chem.*, **151**, 253 (1926).
[3] G. Wilkinson, R.D. Gillard, J.A.C. McCleverty. *Comprehensive Coordination Chemistry*, Vol. 4, p. 353, Pergamon Press, Oxford, NY (1987).
[4] U. Belluco. *Organometallic and Coordination Chemistry of Platinum*, Academic Press, NY (1974).
[5] F.R. Hartley. *The Chemistry of Platinum and Palladium*, Wiley J., NY (1973).
[6] E. Cesarotti, A. Pasini, R. Ugo. *J. Chem. Soc., Dalton Trans.*, 2174 (1981).
[7] R.H. Holm, M.J. O'Connor. *Progr. Inorg. Chem.*, **14**, 277 (1971).
[8] T.W. Thomas, A.E. Underhill. *Chem. Soc. Rev.*, **1**, 90 (1972).
[9] A. Chakravorty. *Coord. Chem. Rev.*, **13**, 1 (1974).
[10] G.N. Schrauzer. *Angew. Chem. Int. Ed. Engl.*, **15**, 417 (1975).
[11] Z. Guo, P.J. Sadler. *Adv. Inorg. Chem.*, **49**, 183 (2000).
[12] M.D. Hall, T.W. Hambley. *Coord. Chem. Rev.*, **232**, 49 (2002).
[13] G. Ferraris, D. Viterbo. *Acta Crystallogr., Sect. B*, **25**, 2066 (1969).
[14] L. Maresca, G. Natile, J. Cattalini, F. Gasparrini. *J. Chem. Soc., Dalton Trans.*, 1090 (1976).
[15] M.S. Ma, R.J. Angelici. *Inorg. Chem.*, **19**, 363 (1980).
[16] A. Bigotto, G. Costa, V. Galasso, G. De Alti. *Spectrochim. Acta*, **26A**, 1939 (1970).
[17] V.Y.Yu. Kukushkin, D. Tudela, A.J.L. Pombeiro. *Coord. Chem. Rev.*, **156**, 333 (1996).
[18] V.Y.Yu. Kukushkin, V.K. Belsky, D. Tudela. *Inorg. Chem.*, **35**, 510 (1996).
[19] H. Kantekin, G. Dilber, Y. Goek, U. Ocak, R. Abbasoglu. *Trans. Met. Chem.*, **28**, 51 (2003).
[20] L. Alexandrova, O.G. D'yachenko, G.M. Kazankov, V.A. Polyakov, P.V. Samuleev, E. Sansores, A.D.J. Ryabov. *Amer. Chem. Soc.*, **122**, 5189 (2000).
[21] M.K. Biyala, K. Sharma, M. Swami, N. Fahmi, R.V. Singh. Trans. Met. Chem., 10.1007/s11243-008-9053-3 (2008).
[22] I. Gaubeur, M. Guekezian, L.H.S.A. Terra, M.C.B. Moraes, C.L. Lago, J.R. Matos, M.E.V. Suárez-Iha. *Polyhedron*, **23**, 2095 (2004).
[23] S.M. Sbovata, F. Bettio, Ch. Marzano, A. Tassan, M. Mozzon, R. Bertani, F. Benetollo, R.A. Michelin. *J. Inorg. Biochem.*, **102**, 882 (2008).
[24] V.M. Peshkova, V.M. Savostina, E.K. Ivanova. *Analiticheskie reagenti: Oksimi*, pp. 80–140, Izd. Nauka, Moscva (1977).
[25] J.E. Caton Jr, C.V. Banks. *Inorg. Chem.*, **6**, 1670 (1967).
[26] B. Orel, M. Penko, D. Hadži. *Spectrochim. Acta*, **36A**, 859 (1980).
[27] D.M. Adams, D.C. Stevens. *Inorg. Chem.*, **20**, 525 (1981).
[28] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B: Applications in Coordination, Organometallic and Bioinorganic Chemistry*, p. 38, Wiley J., NY (1997).
[29] P. Sohár. *Mágneses Magrezonancia Spektroszkópia*, Vol. 1, p. 2, Akad. Kiadó, Budapest (Hungary) (1976).
[30] P. Sohár. *Nuclear Magnetic Resonance Spectroscopy*, Vol. 1, pp. 24–42, CRC Press, Boca Raton, FL (1983).
[31] Cs. Várhelyi Jr, Gy. Pokol, Á. Gömöry, A. Gănescu, P. Sohár, Gy. Liptay, Cs. Várhelyi. *J. Therm. Anal. Calorim.*, **83**, 701 (2006).
[32] Cs. Várhelyi Jr, *et al.* Spectral and thermal studies of some palladium (II) complexes of the type [Pd(DioxH)$_2$] with symmetric and asymmetric alpha-dioximes (Unpublished).