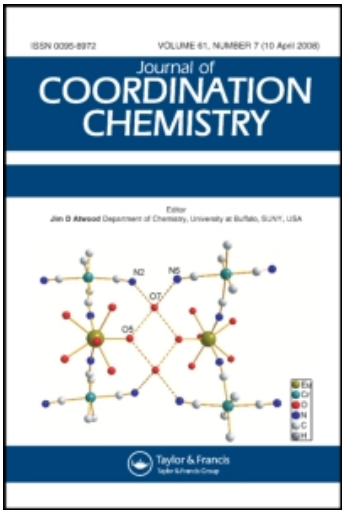


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Characterization of Some Platinum(II) and Palladium(II) Complexes with Thioamide Analogues of Amino Acids

Zhivko Velkov[a]; Radka Pelova[a]; Stoycho Stoev[a]; Evgeny Golovinsky[a]
[a] Department of Chemistry, SIV University of Blagoevgrad, Bulgaria

To cite this Article Velkov, Zhivko , Pelova, Radka , Stoev, Stoycho and Golovinsky, Evgeny(1992) 'Synthesis and Characterization of Some Platinum(II) and Palladium(II) Complexes with Thioamide Analogues of Amino Acids', Journal of Coordination Chemistry, 26: 1, 75 — 78
To link to this Article: DOI: 10.1080/00958979209407914
URL: http://dx.doi.org/10.1080/00958979209407914

J. Coord. Chem. 1992 Vol. 26, pp. 75–78
Reprints available directly from the publisher
Photocopying permitted by license only

NOTE

SYNTHESIS AND CHARACTERIZATION OF SOME PLATINUM(II) AND PALLADIUM(II) COMPLEXES WITH THIOAMIDE ANALOGUES OF AMINO ACIDS

ZHIVKO VELKOV*, RADKA PELOVA, STOYCHO STOEV and EVGENY GOLOVINSKY

Department of Chemistry, SW University of Blagoevgrad, Blagoevgrad 2700, Aleksy Velitchov str. 66, Bulgaria

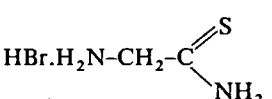
(*Received 14 November 1991*)

Keywords: Thioamide, amino acids, palladium, platinum

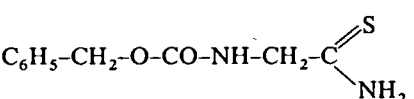
INTRODUCTION

A number of platinum group metal complexes are known to possess antineoplastic activity.[1,2] Significant attention has been paid to complexes of these metals with natural amino acids and their derivatives as potential antitumor agents.[3–8] In this respect complexes of platinum and palladium with thioanalogues of amino acid derivatives could also be of interest.

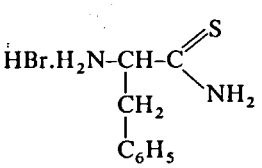
The coordination ability of thioamide analogues of amino acids and peptides toward some transition metals has been investigated.[9,10] However, there are no data in the literature on complex compounds of Pt and Pd with glycinethioamide and phenylalaninethioamide. In this work we report the synthesis and characterization of Pt(II) and Pd(II) complexes with the following thioamides:



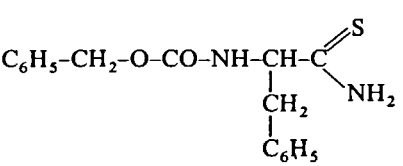
(GTA)



(Z-GTA)



(FATA)



(Z-FATA)

* Author for correspondence.

EXPERIMENTAL

Starting materials

The ligands used were synthesized in a four steps scheme: protection of the amino group,[11] preparation of *N*-protected amide,[12] selective thionation with Lawesson's reagent,[13,14] and deblocking with HBr/CH_3COOH.[15]

K_2PtCl_4, $(NH_4)_2PdCl_2$ and solvents were A.R. grade reagents.

Preparation of the complexes

The complexes were prepared according to the following general procedure: 1 mmol of the corresponding ligand (0.171g GTA; 0.224g Z-GTA; 0.261g FATA; 0.314g Z-FATA) was dissolved in minimum volume (2 to 3 cm^3) of the solvent-water for GTA and FATA, and CH_3OH for the solution of the corresponding ligand. The mixtures were kept overnight at room temperature. The precipitates obtained were filtered, washed with water and methanol and dried in air.

Analyses and physical measurements

Elemental analyses were performed according to standard microanalytical procedures. I.R. spectra (4000 – 150 cm^{-1}) were recorded on a Bruker IFS-113V instrument in CsI disks.

The molar conductivities of 10^{-4} M solutions of the complexes in DMF/H_2O (1:10) were measured at room temperature using a Wheatstone bridge.

The visible spectra of DMF solutions of the complexes were recorded on a Perkin Elmer Lambda 5 spectrophotometer.

RESULTS AND DISCUSSION

The elemental analyses and some physical properties of the complexes obtained are presented in Table I. All complexes are of the type $MLCl_2$. The molar electric conductivity values are typical for nonelectrolytes.

TABLE I
Analytical data and physical properties of the complexes.

Complex	Analysis: calcd. (found), % C	H	N	Metal	λm/ $m\Omega^{-1}mol^{-1}cm^{-2}$	λmax/ nm
$Pt(GTA)Cl_2$	5.83 (5.49)	2.30 (1.60)	5.74 (6.40)	45.07 (44.62)	*a*	314;403
$Pd(GTA)Cl_2$	8.88 (9.30)	2.12 (2.71)	10.86 (10.85)	40.75 (41.08)	*a*	310
$Pt(FATA)Cl_2$	19.03 (18.68)	2.68 (2.33)	4.68 (5.44)	38.82 (37.94)	18.5	396
$Pd(FATA)Cl_2$	23.30 (22.58)	2.89 (2.82)	6.60 (6.58)	25.89 (24.94)	24.60	312
$Pt(Z\text{-}GTA(Cl_2$	25.06 (24.48)	2.71 (2.44)	4.82 (5.70)	40.52 (39.80)	33.10	311
$Pd(Z\text{-}GTA)Cl_2$	29.58 (29.92)	3.47 (2.99)	8.05 (7.00)	25.79 (26.43)	28.70	311
$Pt(Z\text{-}FATA)Cl_2$	32.50 (33.10)	2.18 (2.93)	4.25 (4.82)	33.01 (33.62)	31.50	314
$Pd(Z\text{-}FATA)Cl_2$	38.55 (39.10)	2.85 (3.46)	5.10 (5.70)	21.06 (21.58)	24.40	312

[a] No reliable data due to insufficient solubility.

TABLE II
Characteristic infrared bands (cm^{-1}) of the ligands and the complexes.[a]

Compound	ν(N-H)	νC=S	δ(N-H)+ ν(C-N)	ν(Me-N)	ν(Me-Cl)	ν(Me-S)
GTA	3313;3271;3136	1551	1350	–	–	–
$Pt(GTA)Cl_2$	3165 br	1400	1319 w	550 sh	310 br	230 sh
$Pd(GTA)Cl_2$	3160 br	1408	1315 w	560 sh	315 br	225 sh
FATA	3296;3150	1570	1358			
$Pt(FATA)Cl_2$	3194;3107	1495	1350 w	528	310 br	220 br
$Pd(FATA)Cl_2$	3275;3111	1493	1335 w	552	318 br	225 br
Z-GTA	3392;3155;3047	1541	1356			
$Pt(Z\text{-}GTA)Cl_2$	3327;3064;3034	1516	1248 br	532	309 br	220 br
$Pd(Z\text{-}GTA)Cl_2$	3340;3063;3034	1518	1259 br	563	337 br	215 sh
Z-FATA	3387;3175	1560	1354			
$Pt(Z\text{-}FATA)Cl_2$	3342;3075	1530	1263	548	320 br	225 sh
$Pd(Z\text{-}FATA)Cl_2$	3350;3065	1525	1271	545	330 br	230 sh

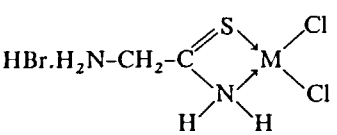
[a] Abbrebiations used: br = broad, w = weak, sh = shoulder.

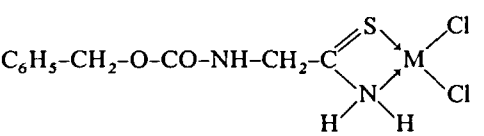
The most characteristic IR bands of the ligands and complexes are summarized in Table II.

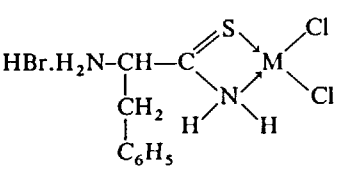
A significant low frequency shift of the N—H stretching bands in the spectra of the complexes as compared to the free ligands is observed. This is characteristic of a coordinated amino group[16] and can be due to participation of the *N*-atom of the thioamide group in coordination. This is also supported by the presence of bands in the range 528–563 cm^{-1} in the spectra of the complexes, which can be assigned to the M—N stretches.[16]

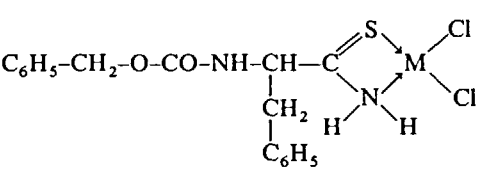
In the spectra of the complexes an appreciable lowering of the C=S stretching frequencies in comparison with the free ligands takes place.[17] An additional indication for such coordination is the presence of weak bands in the region 215–230 cm^{-1} in the spectra of the complexes, which may be due to M—S stretches.[18] The bands registered in the spectra of the complexes in the range 309–337 cm^{-1} are assignable to M—Cl stretches.[16]

On the basis of the results the following structure can be proposed for the complexes discussed:









REFERENCES

1. P. C. Hydes and M. J. H. Russell, *Cancer Metastasis Rev.*, **7**, 67 (1988).
2. I. Haiduc and C. Silvestru, *Coord. Chem. Rev.* **99**, 253 (1990).
3. A. J. Charlson, R. J. Banner, R. P. Gale, N. T. McArdle, K. E. Trainor and E. C. Watton, *J. Clin. Hematol. Oncol.*, **7**, 293 (1977).
4. P. Arrizabalaga, P. Castan and J.-P. Laurent, *Z. Naturforsch. B*, **35**, 1508 (1980).
5. H. Seidenberger, H. Schonenberger, W. Beck, M. Grinth Weller and G. Rudckdeschel, *Arch. Pharm. (Weinheim)*, **317**, 760 (1984).
6. S. Mylonas, A. Valavanidis, V. Voukouvalidis and M. Poulysion, *Inorg. Chim. Acta*, **55**, 125 (1981).
7. K. H. Putharaya, T. S. Srivastava, A. J. Amonkar, M. K. Adwankar and M. P. Chitnis, *J. Inorg. Biochem.*, **25**, 207 (1985).
8. K. H. Putharaya, T. S. Srivastava, A. J. Amonkar, M. K. Adwankar and M. P. Chitnis, *J. Inorg. Biochem.*, **26**, 45 (1986).
9. T. Kowalik, H. Kozlowski, I. Sovago, K. Varnagy, G. Kupryszewski and K. Rolka, *J. Chem. Soc., Dalton Trans.*, 1 (1987).
10. K. Varnagy, H. Kozlowski, I. Sovago, T. Kowalik-Janowska, M. Kruszynski and J. Zboinska, *J. Inorg. Biochem.*, **34**, 83 (1988).
11 M. Bergmann and L. Zervas, *Chem. Berichte*, **65**, 1192 (1932).
12 B. Rzestobarska, M. Makowski and Z. Kybica, *Org. Prep. Proceed. Int.*, **16**, 136 (1984).
13 M. P. Cava and M. I. Levison, *Tetrahedron*, **41**, 5061 (1985).
14. M. Thorsen, B. Yde, U. Pedersen, K. Clausen and S.-O. Lawesson, *Tetrahedron*, **39**, 3429 (1983).
15. W. C. Jones, Jr., J. J. Nestor, Jr. and V. du Vigneaut, *J. Amer. Chem. Soc.*, **95**, 5677 (1973).
16. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1978), Part III.
17. S. Spasov and M. Arnaudov, *Prilozhenie na Spektroskopiata v Organitchnata Chimia* (Nauka i izkoustvo, Sofia, 1978), str. 161.
18. U. I. Haritonov, R. I. Matchhoshvili, A. N. Kravtchenko and R. N. Shtelokov, *Coord. Chim.*, **1**, 323 (1975).