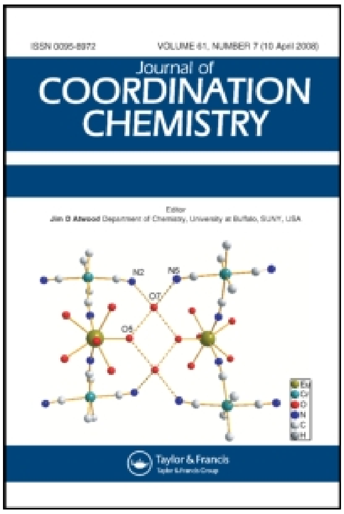

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# A NOVEL SERIES OF PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH 1,4-BENZODIAZEPINES AS LIGANDS

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# A NOVEL SERIES OF PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH 1,4-BENZODIAZEPINES AS LIGANDS

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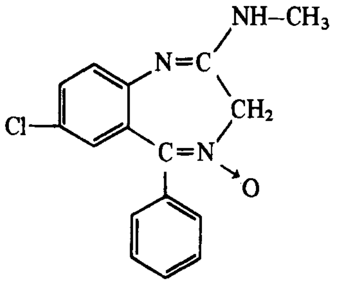
The complexing behaviour towards palladium(II) and platinum(II) halides of some 1,4-benzodiazepines is reported. The ligands used in this study are 7-chloro-2-methylamino-5-phenyl-3H-1,4-benzodiazepin-4-oxide, 1,3-dihydro-7-nitro-5-phenyl-2H-1,4-benzodiazepin-2-one and 7-chloro-1-methyl-5-phenyl-3H-1,4-benzodiazepin-2-one. The complexes have been studied by means of magnetic susceptibility measurements, infrared and far infrared spectra, electronic spectra and conductivity measurements. The most convincing structural evidence for these complexes is a square planar stereochemistry with bridging ligands joining two metal ions and terminal halides in the 1:1 complexes and terminal ligands and terminal halides in the 1:2 derivatives. Assignments for the metal-ligand and metal-halide bands have also been made.

## INTRODUCTION

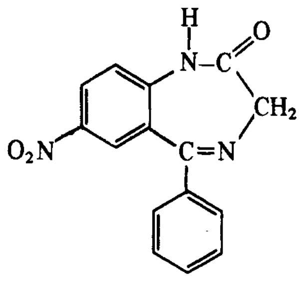
Studies have recently been made on the complex formation of 1,4-benzodiazepines as ligands[1-3] in order to study their behaviour towards metal ions in the coordination. Although the benzodiazepines have wide application in the pharmaceutical industry and in some cases have carcinostatic activity,[4-6] relatively little is known on their behaviour as ligands. Some papers appeared some years ago dealing with the coordinating behaviour of 1,5-benzodiazepines.[7-9]

The most important factor in stimulating our interest in the study of the coordination properties of 1,4-benzodiazepines as ligands towards palladium(II) and platinum(II) has been the fact that the complexes of group VIII metals have been reported to have considerable antibacterial power; in addition platinum complexes induce lysis in lysogenic bacteria.[10-13] We hope that the study of the stereochemistries and the chemical reactivity of their coordination compounds will help to determine what relationship exists between chemical structure and biological activity of these drugs. Furthermore it is well known that the metal complexes of ligands which have biological activity are more active than the free ligands.[14,15]

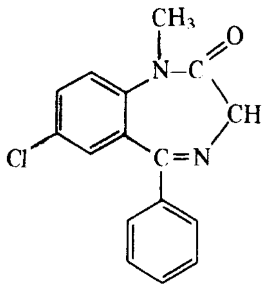
We report in this study the preparation and characterization of palladium(II) and platinum(II) halide complexes with 7-chloro-2-methylamino-5-phenyl-3H-1,4-benzodiazepin-4-oxide



1,3-dihydro-7-nitro-5-phenyl-2H-1,4-benzodiazepin-2-one



and 7-chloro-1-methyl-5-phenyl-3H-1,4-benzodiazepin-2-one.



These three ligands, commercially known as Librium, Mogadon and Diazepam or Valium, are hereafter abbreviated Lib, Mog and Val respectively.

The ligand Lib on exposure to daylight undergoes a photoisomerization resulting in a rearrangement to a oxaziridine that is reconverted quantitatively into the nitrone form on heating or on treatment with an excess of 0.1N hydrochloric acid at room temperature. The ultraviolet absorption spectrum of a dilute isopropyl alcohol solution of the nitrone form shows two maxima at 245 and 265 nm, while the oxaziridine shows in its spectrum a single peak of lower intensity at 278 nm.[16]

## RESULTS AND DISCUSSION

The complexes obtained, of the type $[\mathrm{MLigX_2}]$ or $[\mathrm{MLig_2X_2}]$, are reported in Table I together with their analytical data and other physical properties. They have been studied by means of magnetic susceptibility measurements, electronic spectroscopy, infrared and far infrared spectra and conductivity measurements. The most important i.r. data in the range 4000–100 $\mathrm{cm^{-1}}$ are listed in Table II, while electronic spectra are shown in Table III. The compounds are microcrystalline or powder-like, diamagnetic, soluble in methanol, acetone, benzene and N,N′-dimethylformamide. The molar conductances suggest that the complexes are not conducting in N,N′-dimethylformamide ($\Lambda_M$ lying below 50 $\mathrm{ohm^{-1}\,cm^2\,mole^{-1}}$; the $\Lambda_M$ values even for 1:1 electrolytes should be 70–90 $\mathrm{ohm^{-1}\,cm^2\,mole^{-1}}$ in this solvent).[17]

All the typical bands of the ligands appear in the i.r. spectra of the complexes, furthermore the ligands can be recovered by chemical decomposition of the compounds.

### *Infrared Spectral Studies*

The spectra of the ligands Lib and Mog show a noticeable difference in the position of $\nu$(NH)

TABLE I
Analytical data and other physical properties

| Compounds | Colour | Found % C | H | N | Required % C | H | N | Melting point °C |
|---|---|---|---|---|---|---|---|---|
| $[\mathrm{PdLib_2Cl_2}]$ | brown | 49.0 | 3.3 | 11.0 | 49.5 | 3.6 | 10.8 | 216–218 |
| $[\mathrm{PdLibBr_2}]\cdot 2\mathrm{H_2O}$ | hazel-brown | 31.6 | 2.9 | 6.5 | 31.9 | 3.0 | 7.0 | 224–226 |
| $[\mathrm{PtLib_2Cl_2}]$ | brown | 44.3 | 2.9 | 9.4 | 44.4 | 3.3 | 9.7 | 245–247 |
| $[\mathrm{PtLibBr_2}]$ | brown | 29.3 | 1.8 | 6.2 | 29.4 | 2.2 | 6.4 | 206–208 |
| $[\mathrm{PdMogCl_2}]$ | dark brown | 39.8 | 2.4 | 9.1 | 39.3 | 2.4 | 9.2 | 198–200 |
| $[\mathrm{PdMogBr_2}]\cdot 2\mathrm{H_2O}$ | dark brown | 31.2 | 2.4 | 7.2 | 30.9 | 2.6 | 7.2 | >340 |
| $[\mathrm{PdMog_2I_2}]\cdot \mathrm{H_2O}$ | dark brown | 38.3 | 2.7 | 8.3 | 38.3 | 2.6 | 8.9 | >340 |
| $[\mathrm{PtMog_2Cl_2}]$ | brown | 43.5 | 2.4 | 9.7 | 43.5 | 2.7 | 10.1 | 221–223 |
| $[\mathrm{PtMogBr_2}]$ | brown | 28.1 | 1.6 | 6.7 | 28.3 | 1.7 | 6.6 | 212–214 |
| $[\mathrm{PtMogI_2}]$ | dark brown | 25.3 | 1.5 | 5.9 | 24.7 | 1.5 | 5.8 | 187–189 |
| $[\mathrm{PdValCl_2}]$ | pale yellow | 41.7 | 3.1 | 6.0 | 41.6 | 2.8 | 6.1 | 256–258 |
| $[\mathrm{PdValBr_2}]$ | yellow-brown | 34.5 | 2.4 | 5.0 | 34.9 | 2.4 | 5.1 | 323–325 |
| $[\mathrm{PtValCl_2}]$ | peach | 35.0 | 2.4 | 5.0 | 34.9 | 2.4 | 5.1 | 133–135 |
| $[\mathrm{PtValBr_2}]$ | yellow | 30.1 | 2.1 | 4.2 | 30.0 | 2.0 | 4.4 | 137–139 |

TABLE II
Most important i.r. bands (4000–100 cm$^{-1}$)

| Compounds | | $\nu$(NH) | $\nu$(C=O) | $\nu$(C=N) | $\nu$(M–X) | $\nu$(M–L) | Other bands |
|---|---|---|---|---|---|---|---|
| Lib | solid | 3210s | 1625vs | 1285ms | – | – | 430vs, 395m, 376m, 352m, 317m, 296m, 258ms, 236s, 211w, 206w, 180s, 156sh |
| | CHCl$_3$ sol. | 3480s | 1630vs | – | – | – | |
| [PdLib$_2$Cl$_2$] | | 3100m | 1620s | 1290m | 331ms | 250ms | 437m, 400mw, 378m, 348m, 318m, 298m, 263m, 241m, 212w, 208w, 170ms, 153sh |
| [PdLibBr$_2$]·2H$_2$O | | 3090m | 1680ms, 1620s | 1291m | 277ms, 265m | 248s, 220ms | 438m, 400w, 378m, 348m, 319m, 297m, 254m, 240ms, 210w, 205sh, 170ms, 154w |
| [PtLib$_2$Cl$_2$] | | 3070ms | 1620s | 1290m | 321vs | 216ms | 433m, 400sh, 372m, 350m, 314ms, 296m, 262m, 242m, 210w, 204m, 166m, 152w |
| [PtLibBr$_2$] | | 3080m | 1675ms, 1621s | 1285m | 236m, 228m | 220ms, 188m | 435m, 401m, 375m, 350m, 320m, 298m, 262m, 240ms, 208mw, 204sh, 170ms, 153sh |
| | | $\nu$(NH) | $\nu$(C=O) | $\nu$(C=N) | $\nu$(M–X) | $\nu$(M–L) | |
| Mog | solid | 3190s | 1695vs | 1615vs | – | – | 442ms, 413m, 386s, 318s, 213w, 206w, 158m |
| | CHCl$_3$ sol. | 3400s | 1700vs | 1620vs | – | – | |
| [PdMogCl$_2$] | | 3100ms | 1702vs | 1620vs | 330vs, 313ms | 245ms, 219ms | 455m, 420m, 385ms, 322s, 211w, 200w, 154m |
| [PdMogBr$_2$]·2H$_2$O | | 3120ms | 1710vs | 1620vs | 276ms, 264m | 246vs, 220ms | 440m, 420m, 390ms, 316ms, 212mw, 203mw, 156m |

TABLE II – *continued*

| Compounds | $\nu$(NH) | $\nu$(C=O) | $\nu$(C=N) | $\nu$(M–X) | $\nu$(M–L) | Other bands |
|---|---|---|---|---|---|---|
| $[PdMog_2I_2]\cdot H_2O$ | 3090m | 1698ms | 1630s | 196m | 243ms | 445m, 415w, 380mw, 323m, 215w, 207w, 164m |
| $[PtMog_2Cl_2]$ | 3100ms | 1702vs | 1623vs | 320vs | 223ms | 452m, 421m, 385m, 316m, 214w, 206w, 166m |
| $[PtMogBr_2]$ | 3090ms | 1710vs | 1620vs | 239vs, 229ms | 223ms, 197m | 451m, 420m, 383m, 317m, 210w, 204w, 165m |
| $[PtMogI_2]$ | 3095m | 1700s | 1620s | 184m, 172m | 216ms, 199m | 455m, 420m, 390sh, 318m, 212w, 207w, 166m |
|  | $\nu$(C=O) | $\nu$(C=N) | $\delta_{sym}(N-CH_3)$ | $\nu$(M–X) | $\nu$(M–L) |  |
| Val solid | 1680vs | 1608vs | 1425s | – | – | 428m, 380m, 342m, 333m, 298m, 265mw, 236w, 199mw |
| Val $CHCl_3$ sol. | 1685vs | 1620vs | 1428vs | – | – |  |
| $[PdValCl_2]$ | 1697vs | 1610ms | 1433m | 328s, 312m | 248ms, 219s | 437m, 390m, 340m, 320mw, 301m, 262mw, 240w, 202mw |
| $[PdValBr_2]$ | 1695vs | 1610ms | 1430m | 281m, 269m | 245vs, 222m | 435m, 390m, 345m, 315sh, 300w, 264mw, 231w, 204mw |
| $[PtValCl_2]$ | 1694vs | 1610s | 1430ms | 320vs, 291m | 224m, 190ms | 440m, 375m, 351m, 330m, 299m, 267m, 235mw, 202mw |
| $[PtValBr_2]$ | 1693vs | 1605m | 1430m | 243s, 229m | 222ms, 207m | 437m, 388m, 345m, 318mw, 295m, 263mw, 237w, 198mw |

TABLE III
Electronic spectra and ligand field parameters (cm$^{-1}$)

| Compounds | ${}^1A_{1g} \rightarrow {}^1B_{1g}$ | C.T. | $\Delta_1$ |
|---|---|---|---|
| $[PdLib_2Cl_2]$ | 22075 | 28990 | 24175 |
| $[PdLibBr_2] \cdot 2H_2O$ | 21185 | 28820 | 23285 |
| $[PdMogCl_2]$ | 20620 | 29240 | 22720 |
| $[PdMogBr_2] \cdot 2H_2O$ | 20325 | 29850 | 22425 |
| $[PdMog_2I_2] \cdot H_2O$ | 20000 | 28170 | 22100 |
| $[PdValCl_2]$ | 21140 | 29410 | 23240 |
| $[PdValBr_2]$ | 21050 | 28250 | 23150 |
| $[PtLib_2Cl_2]$ | 25000 | 30300 | 27100 |
| $[PtLibBr_2]$ | 24810 | 29590 | 26910 |
| $[PtMog_2Cl_2]$ | 25315 | 32050 | 27415 |
| $[PtMogBr_2]$ | 25190 | 31445 | 27290 |
| $[PtMogI_2]$ | 24690 | 31050 | 26790 |
| $[PtValCl_2]$ | 26180 | 29850 | 28280 |
| $[PtValBr_2]$ | 25910 | – | 28010 |

stretching frequency in the solid state and in chloroform solution, clearly indicating the presence of intermolecular or intramolecular hydrogen bonding. The ν(NH) in the complexes is shifted towards lower wavenumbers by about 395 cm$^{-1}$ in the Lib-derivatives and by about 300 cm$^{-1}$ in the Mog-derivatives using as reference the value of ν(NH) for the free ligands in chloroform solution. The hydrogen bonding disappears after dissolution in chloroform and after complexation.

According to previously reported data[1, 18, 19] a sharp NH band in the metal complexes is indicative of absence of hydrogen bonding and a comparison of these values with the ν(NH) solution frequency of the free ligand can be used to suggest a coordination through the nitrogen atom. In the complexes here reported sharp bands are present in the range 3100–3070 cm$^{-1}$ and 3120–3090 cm$^{-1}$ for the complexes of Lib and Mog respectively and a comparison with the ν(NH) value of the free ligands in chloroform solution would indicate a M–N coordination.

The exact assignments of the other peaks are quite difficult because the vibrations of the ligands conjugate each other and only with difficulty they can be separated into group vibrations. The band at 1630 cm$^{-1}$ in the free ligand Lib chloroform solution, attributed to the prevailing contribution of ν(C=N),[20, 21] is split towards lower and higher energies in the $[MLibX_2]$ complexes, while undergoes a red shift in the $[MLib_2X_2]$ derivatives. The medium band at 1285 cm$^{-1}$, attributed to the N→O stretching,[22, 23] appears unchanged at the same wavenumber in the spectra of the metal derivatives.

Passing to the Mog derivatives, Table II, the band of the free ligand attributed to the prevailing contribution of ν(C=N) remains unchanged at the same wavenumber in the $[MMogX_2]$-type complexes, while it shows blue shifts in the $[MMog_2X_2]$-type derivatives. The vibrational mode due to the ν(C=O) appears at the same value as in the free ligand or shows very small positive shifts.

As for the Val derivatives, the medium-strong band attributable to the group (aromatic)-N-$CH_3$ lies at 2910 cm$^{-1}$ in the free ligand chloroform solution and at 2850 cm$^{-1}$ in the solid free ligand, but disappears in the spectra of all the studied complexes; the deforming $\delta_{sym}$ (N–$CH_3$) present at some 1425 cm$^{-1}$ in the free ligand, Table II, undergoes blue shifts on complexation.[21, 24] The band at 1620 cm$^{-1}$ in the free ligand Val chloroform solution, attributed to the prevailing ν(C=N) vibrational mode,[20, 21] undergoes red shifts, while the band attributed to the vibrational mode ν(C=O) shows in the complexes small positive shifts.

The spectra of the complexes of Lib and Val show the band characteristic of the grouping Ph–Cl at the same wavenumber, 1090 cm$^{-1}$, as in the free ligands; similarly the spectra of the Mog-derivatives show the bands due to the symmetric and antisymmetric stretching modes of the nitro-group unchanged after coordination at 1340–1345 cm$^{-1}$ and at 1535–1540 cm$^{-1}$.[25]

The medium-strong absorption bands present in the ranges 3480–3450 cm$^{-1}$, ν(OH), and 1640–1625 cm$^{-1}$, δ (HOH), in the palladium bromoderivatives of Lib and Mog and in the palladium iododerivative of Mog, clearly confirm the presence of water of crystallization. Since vibrational modes such as wagging, twisting and rocking activated by coordination to the metal have not been found in the expected ranges,[26] it appears that coordinated water is not present.

With regard to metal-anion stretching modes, Table II, we propose a *trans* square planar $D_{2h}$ stereochemistry for the complexes of the type $[MLig_2X_2]$, while the spectra of $[MLigX_2]$-type derivatives show metal-halogen stretching frequencies whose position and multiplicity are indicative of *cis* square planar $C_{2v}$ symmetry with terminal halides.[27, 28] We have never observed the vibrational modes typical of ν(M–X) for bridging halides.

New halogen independent bands are present in the 250–219 cm$^{-1}$ region and in the range 223–188 cm$^{-1}$ in the palladium and platinum derivatives respectively, absent in the spectra of the starting materials used in this study, and they can be assigned to metal-ligand vibrations involving the nitrogen atoms of the ligands, in very good agreement with published data,[27,28] Table II. No bands are present in the range where $\nu$(M–O) usually lies for these metals.

These far infrared results are in accord with the observed behaviour of the vibrational modes of the ligands in the 4000–1000 $cm^{-1}$ region above discussed, suggesting that the amino group of the ligands Lib and Mog and the nitrogen in 1-position of the Val are responsible for the coordination in the 1:2 derivatives; in addition in the 1:1 complexes the nitrogen atom in 1-position in the case of Lib and in 4-position in the case of Mog and Val are involved in the coordination to the metals. Thus the ligands show a bridging behaviour between two metal ions.

### *Electronic Spectral Studies*

The electronic spectra, Table III, are indicative of square planar geometries.[29,30] The band in the 26180–20000 $cm^{-1}$ region may be assigned to the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition. In the u.v. region there is a strong absorption between 32050–28170 $cm^{-1}$ which may be due to a charge-transfer band.

By assuming a value of $F_2 = 10F_4 = 600$ $cm^{-1}$ for the Slater-Condon interelectronic repulsion paramaters both for palladium and platinum,[31] it is possible to derive from the first spin allowed d–d transition the values of $\Delta_1$, Table III. The splitting parameter increases in the expected order Pt > Pd.

## CONCLUSIONS

The infrared data, magnetic and spectral properties of these complexes confirm their square planar stereochemistry with respect to the metal(II) ions.

The calculated orbital parameter $\Delta_1$ from the $x^2-y^2 \rightarrow xy$ in plane transition places these ligands in the spectrochemical series of nitrogen donors according to the infrared results. A comparison of the $\Delta_1$ parameter values for Lib, Mog and Val derivatives shows for the palladium(II) complexes a decrease of the values on passing from Lib to Val derivatives, the $\Delta_1$ values for the Mog derivatives being lower than both those of the Lib and Val complexes. The values of the platinum(II) complexes decrease in the order $\Delta_1(\text{Val}) > \Delta_1(\text{Mog}) > \Delta_1(\text{Lib})$.

## EXPERIMENTAL

The ligands Lib, Mog and Val, kindly supplied by Roche, were in high purity grade and were used without further purification.

### *Preparation of the Complexes*

The complexes were obtained by adding an ethanolic solution of the ligand to an aqueous solution of $K_2MX_4$ (M = Pd, Pt; X = Cl, Br) or of $K_2MCl_4$ (M = Pd, Pt) in presence of KI in the case of the iodo-derivatives; the solution was refluxed and vigorously stirred for about five minutes. The complexes were purified by means of repeated washing with water, ethanol and diethyl ether and dried over $P_4O_{10}$. We obtained only the complexes in the molar ratio reported in Table I, regardless of the presence of excess ligand.

### *Conductivity Measurements*

These measurements were carried out with a WTW LBR type conductivity bridge for freshly prepared $10^{-3}$ M solutions in N,N′-dimethylformamide at 25°C.

### *Magnetic Susceptibility Measurements*

These measurements were carried out by Gouy's method. Molecular susceptibilities were corrected for diamagnetism of the component atoms by use of the Pascal's constants.

### *Infrared Spectra*

The i.r. spectra were recorded in the range 4000–100 $cm^{-1}$ with Perkin-Elmer 457 and 225 and Hitachi Perkin-Elmer FIS3 spectrophotometers. The spectra in the range 4000–400 $cm^{-1}$ were measured for KBr discs. Far i.r. spectra were recorded as Nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing dry nitrogen.

### *Ultraviolet-visible Spectra*

The electronic spectra of the solid compounds were recorded with a Shimadzu MPS-50L spectrophotometer. Samples were prepared by grinding the complexes on a filter paper as support according to the method of Venanzi and coworkers.[32]

### *Analyses*

Carbon, nitrogen and hydrogen were determined using a Perkin–Elmer 240 elemental analyzer.

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